For the ratio $dJ_{\text{meas}}/J_{\text{meas}}$ we insert the planimetering values. The characteristic temperature ($\Theta = 543\,^\circ\text{K}$) of chromium at 310°K was obtained from the work of Wilson *et al.* (1966).

The following results were obtained from the calculations:

$$\Delta\Theta_{(550)} = 8{\cdot}0 \pm 1{\cdot}0\,^\circ\text{K}$$
$$\Delta\Theta_{(712)A} = 7{\cdot}3 \pm 0{\cdot}8\,^\circ\text{K}$$
$$\Delta\Theta_{(712)B} = 8{\cdot}2 \pm 0{\cdot}6\,^\circ\text{K}$$

The statistical error quoted was determined from the variation of the experimental values of

$$\frac{dJ_{\text{meas}}}{J_{\text{meas}}}\,.$$

These results are summarized as

$$\Delta\Theta = 7{\cdot}9 \pm 0{\cdot}8\,^\circ\text{K}$$

This result is about 2·8 times larger than the one calculated from the discontinuity of the elastic constants (Wilson *et al.*, 1966).

I should like to thank Professor K. D. Alexopoulos for his encouragement of this work and for his helpful advice.

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Electron Population Analysis of Accurate Diffraction Data. I. Formalisms and Restrictions

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A two-dimensional polynomial method is described which allows rapid evaluation of bond-scattering factors in a structure factor least-squares program. Correlation effects between electron population parameters are analyzed. It is concluded that simultaneous refinement of $2s^2$ and three $2p^2$ one-center populations is not possible. Similarly, for the y axis being along a bond AB, the distributions $p_x(A)p_z(B)$ and $p_z(A)p_x(B)$ are identical and only the sum of the corresponding population parameters can be refined. A variety of models is discussed, in which the number of parameters is reduced by selective elimination. In the *two-center model* all terms but those describing 'long' bonds are included. In the *symmetry-restricted two-center model* all bonds are required to have *mm* symmetry, while in the *one-center model* all two-center terms are neglected. Finally, a full table of symmetry restrictions on population parameters and a brief discussion of thermal motion treatment are given.

Introduction

With the improvement in experimental accuracy made possible by diffractometers the information contained in diffraction data has increased considerably.

One of the potentially important extensions of X-ray crystallography is the study of electron distribution in crystals. For molecular crystals the interest is focused on the redistribution of the electron upon the formation of a molecule, or, in other words, upon the study of the covalent bond. In the last few years evidence has accumulated which shows that X-ray diffraction data can be used for such a purpose. In particular, it has been realized that the amazing, and continuing, success of the spherical atom model is due to a refinement of electron density features through adjustment of anisotropic temperature parameters and atomic positions. This can be illustrated through a combination of X-ray and neutron diffraction data (Coppens 1967; Coppens, Sabine, Delaplane & Ibers, 1969; Coppens & Vos, 1971) or by the use of high-order X-ray thermal parameters (Stewart & Jensen, 1969; Verschoor, 1967).

If the X-ray data contain such information on covalent bonding, the need arises for a quantitative description of the effects, suitable for comparison with the results of theoretical calculations.

Expressions for the scattering by non-spherical atoms and density concentrated in a bond, were first derived in a series of articles by McWeeny (1953, 1954). At that time diffraction data were not yet sufficiently accurate for such a treatment, which explains the limited use that has been made of the formalisms. The expressions used in the present study were developed more recently by Stewart (1969) and are compatible with McWeeny's formulae.

In both treatments, the evaluation of the X-ray scattering is facilitated considerably by expressing the atomic orbitals φ as expansions of p Gaussian terms of the form

$$\varphi_{1s,2s}=N_{1s,2s}\sum_p c_p\alpha_p^{3/4}\exp(-\alpha_p r^2);$$
$$\varphi_{2p}=N_{2p}\sum_p c_p\alpha_p^{5/4}(\mathbf{r}\,.\,\boldsymbol{\delta})\exp(-\alpha_p r^2)\qquad(1)$$

in which $\boldsymbol{\delta}$ is a unit vector along the p-orbital axis, $\mathbf{r}$ is a radial vector, and the coefficients N normalize the orbitals. While McWeeny included only three terms in the summation, Stewart derived coefficients and orbital exponents for larger expansions fitted to Hartree–Fock and Slater type orbitals.

Stewart (1969) also proposed that the expression for the molecular X-ray scattering be generalized by the use of a molecular orbital formalism. If the molecular orbitals ψ_i are written as linear combinations of atomic orbitals (LCAO)

$$\psi_i=\sum_\mu c_{i\mu}\varphi_\mu$$

the one-electron density function ϱ is given by a sum over orbital products, each multiplied by a population parameter $P_{\mu\nu}$:

As the X-ray scattering corresponding to the density distribution $\varphi_\mu\varphi_\nu$ can be calculated, the parameters $P_{\mu\nu}$ can be adjusted in a least-squares refinement minimizing the discrepancies between the observations and the calculated values. The $P_{\mu\nu}$'s are not occupancy factors in the conventional sense, because the number of electrons associated with each $P_{\mu\nu}$ depends on the overlap integral $S_{\mu\nu}$:

$$\text{Number of electrons}=\int P_{\mu\nu}\varphi_\mu\varphi_\nu\mathrm{d}\tau=P_{\mu\nu}S_{\mu\nu}\,.\qquad(3)$$

In this article further expressions are developed to make the application of (2) practical in structure analysis, and limitations imposed by the nature of the experimental data and crystallographic and chemical symmetry are discussed. Application of the formalisms to the diffraction data on cyanuric acid and oxalic acid dihydrate will be described in following articles (Coppens, Pautler & Griffin, 1971; Coppens, Jones & Pautler, 1971).Some preliminary results have been reported (Coppens, Csonka & Willoughby, 1970).

Evaluation of the scattering expressions

The scattering of an orbital product $\varphi_\mu\varphi_\nu$ at rest is defined by its Fourier transform:

$$<\varphi_\mu|f|\varphi_\nu>=\int\varphi_\mu\varphi_\nu\exp\{i\mathbf{S}\,.\,\mathbf{r}\}\mathrm{d}\tau\qquad(4)$$

in which $|S|=4\pi\sin\theta/\lambda$.

As an example we take the $\varphi_{2p}\varphi_{2s}$ orbital product. The expression for the X-ray scattering phased to the midpoint of the bond is:

$$\langle 2p_x(A)|f|2s(B)\rangle=\boldsymbol{\delta}_x\,.\,\mathbf{R}\textstyle\sum_2+i\boldsymbol{\delta}_x\,.\,\mathbf{S}\sum_3\qquad(5)$$

(Stewart, 1969), were $\mathbf{R}$ is the vector between nuclei A and B, $\boldsymbol{\delta}_x$ is a unit vector along the x axis, and where

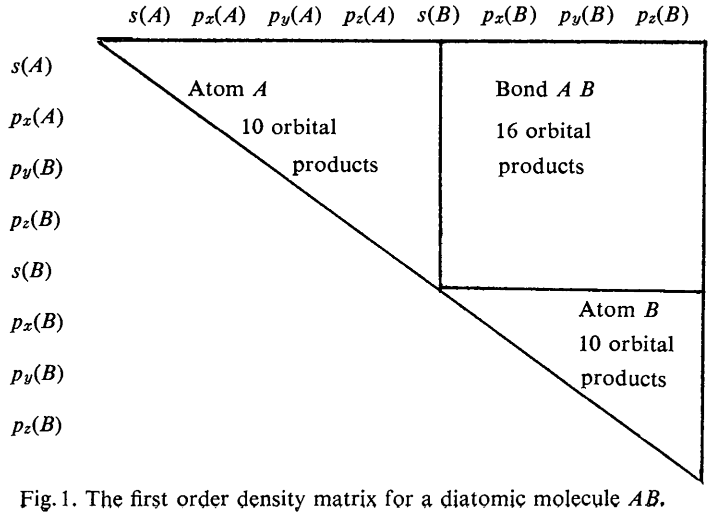


Fig. 1. The first order density matrix for a diatomic molecule *AB*.

$$\varrho=2\sum_i\sum_\mu\sum_\nu c_{i\mu}c_{i\nu}\varphi_\mu\varphi_\nu\equiv\sum_\mu\sum_\nu P_{\mu\nu}\varphi_\mu\varphi_\nu\,. \tag{2}$$

$$\sum_2=\sum_{p,q}2^{5/2}F_{p,q}(\mathbf{S},\mathbf{R})\,\frac{\alpha_p^{1/2}\alpha_q}{\alpha_p+\alpha_q} \tag{6}$$

and

$$\sum_3=\sum_{p,q}2^{3/2}F_{p,q}(\mathbf{S},\mathbf{R})\,\frac{\alpha_p^{1/2}}{\alpha_p+\alpha_q}\,. \tag{7}$$

$F_{p,q}$ is defined by:

$$F_{p,q}=\frac{c_pc_q}{(\alpha_p+\alpha_q)^{3/2}}\,\alpha_p^{3/4}\alpha_q^{3/4}\exp\left[-\mathrm{S}^2/4(\alpha_p+\alpha_q)\right]$$
$$\times\exp\left[\frac{-\alpha_p\alpha_q}{\alpha_p+\alpha_q}\,R^2\right]\times\exp\left[-ig_{pq}\mathbf{S}\,.\,\mathbf{R}\right] \tag{8}$$

in which $g_{pq}=(\alpha_p-\alpha_q)/(\alpha_p+\alpha_q)$ and $\alpha_{p,q}$ and $c_{p,q}$ are defined by (1).

The description of the scattering of all possible products of *s* and *p* orbitals requires ten summations $\sum_i$, which all contain the terms $F_{p,q}$, but differ in the exponents of the factor

$$\frac{\alpha_p^n\alpha_q^m}{(\alpha_p+\alpha_q)^r}\,.$$

For products between orbitals on the same center, the internuclear distance R is zero and the summations $\sum_i$ are only dependent on the magnitude of S.

By tabulating $\sum_i$ as a function of $|S|$, the scattering by the one-center orbital products can be evaluated for each reflection in a relatively short time with expressions similar to (5). Evaluation of the scattering of the two-center orbital products is more complex because the sums are not only functions of $|S|$, but contain the dot products $\mathbf{S}\,.\,\mathbf{R}$ which cannot be factored out. The summations therefore, have to be evaluated in every cycle of the least-squares refinement, for each reflection and each two-center product in each of the bonds.

To avoid the time-consuming direct evaluation, we use a two-dimensional polynomial approximation, in which the sums $\sum_i$ are expresssed as polynomials of $\sin\theta/\lambda$ and the cosine of ψ, the angle between S and R.

Every summation $\sum_i$ can be written as

$$\sum_i=\sum_{p,q}f(c_p,c_q,\alpha_p,\alpha_q,|\mathbf{S}|,|\mathbf{R}|)\cos\left(g_{pq}|\mathbf{S}|\,|\mathbf{R}|\cos\psi\right)$$
$$+i\sum_{pq}f'(c_p,c_q,\alpha_p,\alpha_q,|\mathbf{S}|,|\mathbf{R}|)\sin\left(g_{pq}|\mathbf{S}|\,|\mathbf{R}|\cos\psi\right) \tag{9}$$

in which f and f' indicate functions defined by expressions like (6) and (7). Since the real and imaginary part are respectively symmetric and anti-symmetric with respect to $\psi=0°$, the polynomial contains even and odd powers of $\cos\psi$ for the real and imaginary parts respectively:

$$\sum_i=(A_{0i}+A_{2i}\cos^2\psi+A_{4i}\cos^4\psi+A_{6i}\cos^6\psi+\ldots)$$
$$+i(A_{1i}\cos\psi+A_{3i}\cos^3\psi+A_{5i}\cos^5\psi+A_{7i}$$
$$\times\cos^7\psi+\ldots)\,. \tag{10}$$

Each of the coefficients A_{ji} depends on the functions f and f' and therefore on $|S|$ and $|R|$. It follows that for a bond of length R between orbitals defined by sets of c_p, α_p and c_q, α_q the A_{ij} can be approximated by a polynomial in S or $\sin\theta/\lambda$:

$$A_{ji}(\sin\theta/\lambda)=C_{ji0}+C_{ji1}(\sin\theta/\lambda)+\ldots C_{ji6}(\sin\theta/\lambda)^6$$
$$+\ldots \tag{11}$$

Thus, the coefficients C_{jik} can be obtained from a two-dimensional (in ψ and $|S|$) least-squares fit to the numerical results of (6) and (7) and analogous expressions. The evaluation of the Fourier transform of the orbital products in the structure factor least-squares program from the C_{jik} is relatively fast.

A satisfactory accuracy is obtained with the inclusion of four terms in both the real and imaginary parts of (10) and seven terms in (11). Some figures of merit are given in Table 1. The maximum deviation between the direct and the polynomial evaluation in any of the sums describing the scattering in a C–O bond of 1·22 Å length is 0·002 electrons, which is an order of magnitude smaller than the standard deviations of the population parameters obtained in the application of the expressions.

Table 1. *'Goodness of polynomial fit' to bond scattering factors*

$$R=\frac{\sum(f_{\text{direct}}-f_{\text{polynomial}})^{\dagger}}{\sum f_{\text{direct}}}$$

C=O bond, length = 1·22 Å

$\sum_i$	Real part	Imaginary part
$i=1$	0·007	0·01
2	0·005	0·01
3	0·006	0·07
4	0·005	0·001
5	0·005	0·008
6	0·004	0·008
7	0·003	0·003
8	0·004	0·02
9	0·004	0·005
10	0·004	0·007

Maximum deviation: 0·002 electrons

† f_{direct} and $f_{\text{polynomial}}$ are the scattering factors obtained with expressions like (5) and with (10), (11).

Since the bond scattering factors are to be employed only after a conventional refinement procedure has been completed, the bond-lengths are practically fixed and the coefficient C_{jik} have only to be evaluated once for each bond in a molecule.

For each bond 56 values of C_{jik} are tabulated for each of the ten summations $\sum_i$, a total of 560 entries for each *type* of bond in the crystal. Scattering is then evaluated with (5) and similar expressions.

The savings in computer time are considerable. In a typical test-case, a saving of a factor 5 in computing time was achieved with a five-term Gaussian expansion.

The generalized structure factor

For a crystal structure with j atoms, each with k orbital products, and s asymmetric units per unit cell, the contribution of the atoms to the structure factor is:

$$F_{hkl}(\text{atoms}) = \sum_j \sum_s \sum_k a_{jk} f_{jks} T_{js} \exp(i\mathbf{S} \,.\, \mathbf{r}_{js}) \quad (12)$$

in which a_{jk} are the one-center population coefficients, f_{jks} the corresponding scattering factors; T_{js} are the temperature factors and the vectors $\mathbf{r}_{js}$ define the atomic positions.

Similarly for m bonds, each described by l orbital products, between atoms j and i the contribution is

$$F_{hkl}(\text{bonds}) = \sum_m \sum_s \sum_l b_{jil}\, g_{jils}\, T_{jis} \exp(i\mathbf{S} \,.\, \mathbf{r}_{jis}) \quad (13)$$

in which b_{jil} are the two-center population coefficients, g_{jils} are the corresponding scattering factors; T_{jis} are the bond temperature factors and the vector $\mathbf{r}_{jis}$ defines the midpoint of the bond between atoms j and i.

If

$f_{jks} = f'_{jks} + if''_{jks}$

and

$g_{jils} = g'_{jils} + ig''_{jils}$

and

$F_{hkl} = F_{hkl}(\text{atoms}) + F_{hkl}(\text{bonds}) = A_{hkl} + iB_{hkl}$

we have, assuming that T_{js} and T_{jis} are real (see Dawson (1967*a*) for the limitations of this assumption):

$$\begin{aligned} A_{hkl} = {} & \sum_j \sum_s \sum_k a_{jk}\, T_{js}[f'_{jks} \cos(\mathbf{S} \,.\, \mathbf{r}_{js}) - f''_{jks} \\ & \times \sin(\mathbf{S} \,.\, \mathbf{r}_{js})] + \sum_m \sum_s \sum_l b_{jil}\, T_{jis}[g'_{jils} \cos(\mathbf{S} \,.\, \mathbf{r}_{jis}) \\ & - g''_{jils} \sin(\mathbf{S} \,.\, \mathbf{r}_{jis})] \\ B_{hkl} = {} & \sum_j \sum_s \sum_k a_{jk}\, T_{js}\, [f''_{jks} \cos(\mathbf{S} \,.\, \mathbf{r}_{js}) + f'_{jks} \\ & \times \sin(\mathbf{S} \,.\, \mathbf{r}_{js})] + \sum_m \sum_s \sum_l b_{jil}\, T_{jis}[g''_{jils} \cos(\mathbf{S} \,.\, \mathbf{r}_{jis}) \\ & + g'_{jils} \sin(\mathbf{S} \,.\, \mathbf{r}_{jis})]\,. \end{aligned} \quad (14)$$

The expressions for the derivatives required in the least-squares refinement can be easily derived from (14) when it is kept in mind that $\mathbf{r}_{jis} = (\mathbf{r}_{js} + \mathbf{r}_{is})/2$ and that the bond temperature factor T_{jis} may be a function of T_{js} and T_{is} (see below).

Basis functions

The selection of the type of orbital is of considerable importance. Clearly, the electron density parameters will be a function of the basis set. Apart from considerations of comparing the experimental parameters with theoretical results, the main criterion is whether the summation $\sum_\mu \sum_\nu P_{\mu\nu}\varphi_\mu\varphi_\nu$ can, with properly adjusted $P_{\mu\nu}$'s, adequately represent the molecular electron density.

Since conventional X-ray form factors are based on Hartree–Fock isolated-atom densities (with the notable exception of hydrogen), the use of a Hartree–Fock basis set is a logical starting point.

But, it is well known that exponents of Slater-type atomic orbitals $\varphi = Nce^{-\zeta r}$ which lead to the lowest *molecular* energy differ significantly from the isolated-atom values (Ransil, 1960; Hehre, Stewart & Pople, 1969). In the exponent optimization by Hehre, Stewart & Pople (1969) (HSP) the 1*s* orbitals of the non-hydrogen atoms are taken according to Clementi & Raimondi (1963) for isolated atoms, while the hydrogen 1*s* and the first row atom 2*s* orbital exponents are varied to give a minimum energy for each of a number of small, neutral, molecules.

Average values of the results are tabulated by Hehre, Stewart & Pople (1969) as 'standard molecular orbital exponents' which will be referred to here as the HSP set.

In comparison with the Slater values the HSP exponents are considerably larger for the carbon 2*s* and somewhat smaller for oxygen 2*s* orbital (Table 2). As described in a following article (Coppens, Pautler & Griffin, 1971) such a difference significantly affects the net atomic charges obtained from the diffraction data.

Table 2. *Standard molecular orbitals exponents according to Hehre, Stewart & Pople (HSP)* (1970) *and Slater atomic values for* H, C, N, O

	HSP		Slater	
	1*s*	2*s*, 2*p*	1*s*	2*s*, 2*p*
H	1·24	—	1·20*	—
C	5·67	1·72	5·70	1·625
N	6·67	1·95	6·70	1·95
O	7·66	2·25	7·70	2·275

* The standard exponent is 1·00, but differs too much from the molecular value to be of practical use when dealing with molecules.

Correlation between parameters

The population parameters $P_{\mu\nu}$ may correlate strongly with the conventional least-squares parameters. As the anisotropic thermal parameters represent a smearing function multiplying the molecule-at-rest density, accumulation of electron density in bonds or in lone-pair regions can be simulated by an apparent increase in the thermal parameters (Coppens, 1968).

In the present study this correlation problem is circumvented by use of neutron diffraction values for thermal and position parameters.

The remaining variables are the scale factor and the electron population parameters, the latter constrained by the requirement that the total number of electrons remain constant in the refinement (see Hamilton (1963) for the expression used to achieve this constraint). Two types of population parameters $P_{\mu\nu}$ can be distinguished:

(*a*) the parameters multiplying products $\varphi_\mu\varphi_\nu$ of orbitals centered on the same atom. These one-center population parameters occupy blocks centered on the diagonal of the first-order density matrix (Fig. 1). Since the basis set contains four valence orbitals for all non-hydrogen atoms ($2s$, p_x, p_y, p_z) the dimensions of the block are 4×4 (the $1s^2$ population of the first-row atoms is kept frozen at the full shell values, *i.e.* $P_{1s^2}=2$).

It is interesting to note that some of the products are between mutually orthogonal orbitals. In other words, the number of electrons represented by such a term integrates to zero according to expression (3). Its contribution to the charge density consists of a shift of electrons. For example, the product $\varphi_s\varphi_{p_y}$ has the same sign as y, and a positive coefficient P has the effect of shifting density from negative to positive y values.

(*b*) the coefficients of products between orbitals centered on different atoms. They again correspond to 4×4 blocks of the density matrix, but these blocks are not centered on the diagonal (Fig. 1).

Because φ_μ and φ_ν commute in the orbital product $\varphi_\mu\varphi_\nu$, the first-order density matrix is a symmetric matrix *i.e.* $P_{\mu\nu}=P_{\nu\mu}$ and expression (2) can be rewritten as

$$\varrho=\sum_{\mu}\sum_{\nu\geq\mu} P'_{\mu\nu}\varphi_\mu\varphi_\nu \tag{15}$$

where

$$P'_{\mu\nu}=2P_{\mu\nu} \text{ for } \mu\neq\nu.$$

We shall use $P_{\mu\nu}$ as defined by (15) and omit the dash from the symbol. It follows from (15) that each atom is described by ten independent coefficients.

For the two-center product on atoms A and B, $\varphi_\mu(A)\ \varphi_\nu(B)$ is generally not equivalent to $\varphi_\nu(A)\ \varphi_\mu(B)$. The one exception to this rule is discussed in the following argument.

The orbital product between a p-orbital on atom A with its axis parallel to $\boldsymbol{\delta}_i$ and an orbital p_B on atom B with its axis parallel to $\boldsymbol{\delta}_j$ is according to (1):

$$\begin{aligned}\varphi_{iA}\varphi_{jB}&=(\mathbf{r}_A\,.\,\boldsymbol{\delta}_i)\,(\mathbf{r}_B\,.\,\boldsymbol{\delta}_j)\sum_p c_p\alpha_p^{5/4}\exp\left(-\alpha_p r_A^2\right)\\&\times\sum_q c_q\alpha_q^{5/4}\exp\left(-\alpha_q r_B^2\right)=(\mathbf{r}_A\,.\,\boldsymbol{\delta}_i)\,(\mathbf{r}_B\,.\,\boldsymbol{\delta}_j)\\&\times\sum_p\sum_q c_pc_q\alpha_p^{5/4}\,\alpha_q^{5/4}\exp-\left(\alpha_p r_A^2+\alpha_q r_B^2\right)\end{aligned} \tag{16}$$

in which the maximum values of p and q are each equal to the number of terms in the Gaussian expansion and R_A and R_B correspond to the distance from nucleus A and nucleus B respectively.

Suppose the y axis is parallel to the bond AB; then

Table 3. *Correlation matrix for carbon monoxide bond density terms*

Bond length 1·293 Å; $(\sin\theta/\lambda)_{max}=0\cdot5$ Å^{-1}; y axis along bond; x and z perpendicular to the bond. Only valence orbitals are included. First symbol refers to orbital on C, second to orbital on O. Hartree–Fock basis set.

	ss	*p*													

	ss	p_xs	p_ys	p_zs	sp_x	sp_y	sp_z	p_xp_x	p_xp_y	p_xp_z	p_yp_x	p_yp_y	p_yp_z	p_zp_y	p_zp_z
ss	1·0	0·430	*−0·998*	0·430	−0·365	*0·991*	−0·365	−0·868	0·284	−0·169	0·149	*−0·951*	0·149	0·284	−0·868
p_xs		1·0	−0·434	−0·137	−0·536	0·429	−0·073	−0·319	0·838	−0·125	−0·003	−0·411	0·176	−0·190	−0·301
p_ys			1·0	−0·434	0·366	*−0·992*	0·366	0·849	−0·287	0·202	−0·148	*0·957*	−0·148	−0·287	0·849
p_zs				1·0	−0·073	0·429	−0·536	−0·301	−0·190	−0·125	0·176	−0·411	−0·003	0·838	−0·319
sp_x					1·0	−0·382	−0·127	0·224	−0·035	0·123	−0·831	0·366	0·196	−0·180	0·239
sp_y						1·0	−0·382	−0·825	0·279	−0·228	0·170	*−0·976*	0·170	0·279	−0·825
sp_z							1·0	0·239	−0·180	0·123	0·196	0·366	−0·831	−0·035	0·224
p_xp_x								1·0	−0·273	−0·098	−0·079	0·780	−0·071	−0·191	0·855
p_xp_y									1·0	−0·093	−0·456	−0·288	0·334	−0·330	−0·191
p_xp_z										1·0	−0·080	0·264	−0·080	−0·093	−0·098
p_yp_x											1·0	−0·180	−0·347	0·334	−0·071
p_yp_y												1·0	−0·180	−0·288	0·780
p_yp_z													1·0	−0·456	−0·079
p_zp_y														1·0	−0·273
p_zp_z															1·0

$$\varphi_{xA}\,\varphi_{zB}=(\mathbf{r}_A\,.\,\boldsymbol{\delta}_x)\,(\mathbf{r}_B\,.\,\boldsymbol{\delta}_z)\sum_p\sum_q c_p\,c_q \times\exp-(\alpha_p r_A^2+\alpha_q r_B^2) \quad (17)$$

and

$$\varphi_{zA}\,\varphi_{xB}=(\mathbf{r}_A\,.\,\boldsymbol{\delta}_z)\,(\mathbf{r}_B\,.\,\boldsymbol{\delta}_x)\sum_p\sum_q c_p\,c_q \times\exp-(\alpha_p r_A^2+\alpha_q r_B^2) \quad (18)$$

since the x and z directions are perpendicular to the bond $(\mathbf{r}_A\,.\,\boldsymbol{\delta}_z)=(\mathbf{r}_B\,.\,\boldsymbol{\delta}_z)$ and $(\mathbf{r}_B\,.\,\boldsymbol{\delta}_x)=(\mathbf{r}_A\,.\,\boldsymbol{\delta}_x)$. Thus, the two expressions (17) and (18) are equivalent and represent an identical distribution of electrons in space. Though it may be possible to *calculate* the two corresponding population coefficients, only their sum can be obtained experimentally by analysis of X-ray scattering.

It follows that the number of parameters to be determined for each bond is fifteen (four in a bond involving a hydrogen atom).

The equivalence of (17) and (18) is most easily exploited by selection of bond-localized coordinate systems with one axis parallel to the bond described. The reference axis for the one-center products, on the other hand, can be selected the same for all atoms. If desired, the two sets can be transformed to a single reference system by means of similarity transformations of the type:

$$(P_{\mu\nu})_{\text{new}}\equiv AP_{\mu\nu}(A^{-1}) \quad (19)$$

in which A is the transformation matrix to a molecular coordinate system, defined by $\varphi_{\text{new}}=\mathbf{A}\boldsymbol{\varphi}$.

Thus, the number of population parameters in the all-valence electron model is ten for each atom and fifteen for each bond. This number is further reduced when atoms or bonds lie on special positions, or when the electron density is constrained to obey molecular, but non-crystallographic, symmetry. Such symmetry restrictions will be discussed in the next section.

The first refinements with the one-center model on α-oxalic acid dihydrate, indicated a large correlation between the coefficients of $2s2s$ and p_xp_x, p_yp_y and p_zp_z. The sum of the last three-distributions is spherically symmetric like the $2s^2$ density, but the latter has a radial node unlike the spherical sums of the p^2 products. However, as was first pointed out by Stewart (1969), the thermal averaging of the densities in the crystal makes the $2s^2$ virtually indistinguishable from the sum of the p^2 products, as far as X-ray scattering is concerned.

One may therefore, fix the $2s^2$ population at some reasonable value and provide a full description of the atomic asphericity by refining on the remaining nine one-center parameters. With this restriction, no correlation coefficients larger than 0·5 between one-center parameters were encountered.

It can be shown that this procedure is equivalent to refinement on the occupancy of a spherical component of the atomic density, modified by terms describing excess density in variable directions.

In order to assess the magnitude of correlation between two-center parameters a model calculation was performed on a C–O molecule with bond length 1·293 Å, lying along the y axis in a primitive unit cell, and having an isotropic temperature parameter $B=$ 1·0 Å^2.

All one-center populations were set to zero and a set of structure factors was calculated with Hartree–Fock orbitals and unit occupancy of each of the two-center terms only. Reflections were limited to $(\sin\theta/\lambda)_{\max}=$ 0·5 Å^{-1}, because two-center scattering factors are small beyond this limit.

The correlation coefficients obtained in a single cycle of the linear least-squares refinement are given in Table 3. Because the least-squares is linear in the population coefficients, the correlation parameters are independent of the starting values for the parameters. But, as they are calculated from the inverse least-squares matrix, they are dependent on the number and the selection of parameters. In other words, a correlation coefficient r_{ij} between parameters i and j does not depend solely on parameters i and j.

The coefficients in Table 3 are therefore only to be taken as indications; but the general trends observable have been corroborated by later studies with experimental data.

In Table 3 the very large correlations with absolute value $>0·9$ have been underlined. Typically, correlation

Table 4. *Symmetry restrictions on $P_{\mu\nu}$*

– indicates element must be zero. The main symmetry element is taken to be parallel to the z axis. This symbol n represents an integer ≥ 3.

$\mu\nu$	$C_s\,(=m)$	C_i	C_2	C_{2h}	C_{2v}	D_2, D_{2h}	C_{nv}	D_n, D_{nh}, D_{nd}, S_4	T_d, O_h
ss	+	+	+	+	+	+	+	+	+
spx	+	−	−	−	−	−	−	−	−
spy	+	−	−	−	−	−	−	−	−
spz	−	−	+	−	+	−	+	−	−
pxpx	+	+	+	+	+	+	$xx=yy$	$xx=yy$	$xx=yy=zz$
pypy	+	+	+	+	+	+			
pzpz	+	+	+	+	+	+	+	+	
pxpy	+	+	+	+	−	−	−	−	−
pxpz	−	+	−	−	−	−	−	−	−
pypz	−	+	−	−	−	−	−	−	−

is large between terms such as $2s2s$, p_y2s, $2sp_y$, p_yp_y all of which represent components of the electron density cylindrically symmetric with respect to the bond. This redundance in the description of the σ-bond can be reduced by eliminating one or more of the components. A choice consistent with the treatment of the one-center terms is the elimination of the $2s2s$ population coefficient.

It is worth noting that rather large correlations with $0{\cdot}9 > r_{ij} > 0{\cdot}8$ also occur between some of the σ terms and the π-terms, such as p_ys and p_zp_z, and between some of the 'mixed' terms, such as sp_z and p_yp_z.

In the actual refinement of cyanuric acid incorporating both one-center and two-center terms some of the largest correlations occurred between one-center and two-center terms. Such correlations can be reduced by applying symmetry restrictions to the individual bonds (see below). These restrictions lead to a drastic reduction in the number of parameters at the expense of a very small increase in R value. Experimental correlation coefficients obtained with various models will be discussed in detail in later articles.

Symmetry restrictions

(*a*) *One-center products*

Restrictions on the values of the one-center parameters occur when atoms occupy special positions. In addition, it may be desirable to constrain the electron density to conform to non-crystallographic molecular symmetry, such as the mirror plane through all the atoms of an aromatic molecule.

The conditions arising from these situations can be best derived using the concepts of group theory. For the coefficient of an orbital product to be different from zero, it has to belong to the totally symmetric (A_1) representation of the point group describing the site symmetry. Since p_x, p_y and p_z transform like x, y and z while s is fully symmetric; the orbital products sp_i and p_ip_j transform as i and ij respectively.

The transformation properties of these products are given in point-group character tables (see for example, Cotton, 1963). For example, for an atom lying on a mirror plane perpendicular to z, the site symmetry is C_s or m and we find that xx, yy, zz and xy belong to the fully symmetric representation A_1, while xz and yz are antisymmetric with respect to the mirror plane. It follows that the population parameters $P(p_xp_z)$ and $P(p_yp_z)$ are zero.

For point groups with degenerate representations, two of the population coefficients may be related. For example, in point group C_{3v}, $xx+yy$ and zz belong to the fully symmetric representation A_1, implying that $P(p_xp_x)=P(p_yp_y)$, while $P(p_zp_z)$ is the only other population parameter which can be different from zero. Similarly, for an atom on a tetrahedral site $P(p_xp_x)=P(p_yp_y)=P(p_zp_z)$; all other P's being zero.

This implies that the model discussed here cannot describe antisymmetric features for sites of high symmetry when only *one-center* terms are included. In this respect, it differs fundamentally from the description of the electron density in diamond, given by Dawson (1967*b*), in terms of one-center Kubic Harmonics; or from a related formalism proposed by Kurki-Suonio (1968).

The last two models can be expected to be more suitable for crystals composed of monatomic ions or single atoms, while the valence-orbital model is more appropriate for molecular crystals. It is the introduction of two-center terms which gives the latter model the required flexibility. A summary of the symmetry restrictions is given in Table 4.

(*b*) *Two-center products*

We distinguish two cases:

Case 1. A rotation axis parallel to bond AB, or a mirror plane parallel to the bond, lead to restrictions identical to those derived for the one-center terms and summarized in Table 3. For example, if the bond axis is parallel to z and a twofold axis coincides with the bond, the populations of products sp_x, sp_y, p_xp_z and p_yp_z must be zero.

These restrictions apply equally to $s(A)p_i(B)$, $p_i(A)s(B)$ and $p_i(A)p_j(B)$ $(i,j=x,y,z)$. Such a situation occurs in cyanuric acid in which a C=O and an N–H bond lie along the crystallographic twofold axis. (Verschoor & Keulen, 1971).

Case 2. A twofold symmetry axis perpendicular to the bond, a mirror plane perpendicular to the bond or a center of symmetry at the midpoint of the bond are symmetry elements which relate the atoms A and B. These atoms therefore, must be identical. It follows that the populations of $\varphi_i(A)\varphi_j(B)$ and $\varphi_j(A)\varphi_i(B)$ $(\varphi_{i,j}=2s, 2p_x, 2p_y, 2p_z)$ are equal, but all population coefficients can differ from zero.

No symmetry restrictions apply to the $2s(A)2s(B)$ orbital product.

Different models

A full description of the electron density with the valence-orbital products would include the 'long bonds' between atoms which are not bonded in the conventional sense. However, the number of parameters in such a model is prohibitive, while electron density difference maps on a variety of molecules have clearly shown that the density associated with these 'long bonds' is negligible. Moreover, there is little sense in trying to allow for intramolecular long bonds, while at the same time neglecting intermolecular distances of the same length.

In a more realistic model only short bonds are included. Assuming that P_{2s2s} and $P_{2s(A)2s(B)}$ are kept constant, this leads to the following number of parameters:

$$n_p = n_1 \,.\, 9 + n_{\rm H} \,.\, 1 + n_B \,.\, 14 + n_{B{\rm H}} \,.\, 4 \qquad (20)$$

in which n_1, $n_{\rm H}$, n_B, $n_{B{\rm H}}$ are the number of non-hydrogen atoms, the number of hydrogen atoms, the numbers of bonds not involving hydrogen and the number of bonds involving hydrogen atoms respectively. A further reduction in the number of parameters can be achieved by taking into account non-crystallographic symmetry of the molecule (though at the expense of a useful check on the internal consistency of the results), or by assuming symmetry of the bonds. A reasonable assumption in an aromatic molecule is that the bonds have *mm* symmetry, one of the mirror planes coinciding with the molecular plane. In a fully saturated compound or substituent, assumption of cylindrical bond-symmetry will lead to a further decrease in the number of independent parameters.

The reduction of complexity is illustrated in Table 5 for the molecule of *p*-benzoquinone.

The problem of correlation between one-center and two-center terms is eliminated in the *one-center model* in which all two-center terms are neglected. It cannot be expected that this model will allow a faithful representation of the electron density, especially for a site of high symmetry (see above). But it leads to a further reduction in the number of parameters and gives results which are comparable with theoretical calculations with the INDO method (intermediate neglect of differential overlap; Pople, Beveridge & Dobosh, 1967), in which interactions involving two-center densities are similarly neglected.

Finally, the smallest number of population parameters is required in the recently proposed *L*-shell projection method (Stewart, 1970); in which one occupancy factor is applied to the whole spherically-averaged valence shell. This useful model can be applied with very small modifications of existing least-squares programs and leads to net atomic charges in good agreement with theoretical calculations (Stewart, 1970). However, it does not allow for the asymmetric features which are evident in many difference maps.

The selection of model has to depend on the quality and completeness of the data set. Application of the more sophisticated models to data of mediocre accuracy should be avoided.

Treatment of thermal motion

It remains to consider the treatment of molecular vibrations and librations. Thermal motion is strongly correlated with details in the atomic charge distribution; and it has been shown through comparison of X-ray and neutron diffraction results that the use of spherical form factors in X-ray crystallography leads to systematic errors in the temperature parameters. Conversely, simultaneous refinement of population and temperature parameters will lead to large correlations, as confirmed by computations on oxalic acid (Coppens, unpublished).

Thermal parameters, which are completely or to a considerable extent unaffected by bonding, can be obtained by neutron diffraction or from the refinement of high-order X-ray data. The neutron diffraction technique is preferable if systematic errors which may arise from differences in sample quality and thermal diffuse scattering can be eliminated or assessed. The disadvantage of the use of high-order X-ray data is that asphericities expressed by the one-center population terms do persist to large values of $\sin\theta/\lambda$ (Coppens, 1969). High order X-ray thermal parameters are therefore not entirely free of bonding effects.

Thermal parameters less susceptible to bonding effects can be obtained by a rigid-body motion refinement. It is important to realize that such a treatment neglects the effect of internal modes; a more serious drawback the lower the temperature of data collection (Coppens & Vos, 1971).

Perhaps the most promising approach is the mechanistic treatment of thermal motion followed by Maslen (1970), in which temperature factors are derived for each of the molecular modes, rather than for individual atoms.

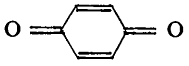
Even if the atomic motions have been determined independently, the choice of the bond temperature factors T_{jis} in (13) is not obvious. In principle, the electron density distribution is to be convoluted with the thermal motion at each point in the molecule:

$$f(\mathrm{S})=\int \varrho(\mathbf{r}) \exp\{i\mathrm{S}\,.\,\mathbf{r}\}\, P(\mathbf{r})\,\mathrm{d}\tau \qquad (21)$$

in which $P(\mathbf{r})$ is the thermal smearing function at point ($\mathbf{r}$). Such a convolution can only be performed if the nature of the molecular modes is known.

In the absence of such information, one may assign to the two-center densities the thermal motion of the *midpoint* of the bond in which the density is centered,

Table 5. *Benzoquinone*



Number of parameters for various models	One-center	Two-center	Total
1. All terms excluding long bonds	76	128	204
2. As 1, assuming mirror plane through all atoms	52	84	136
3. As 2, also assuming *mm* symmetry of bonds	52	48	100
4. *mmm* symmetry	15	22	37
4. One-center model	76	—	76
5. As 4, assuming mirror plane through all atoms	52	—	52
6. *mmm* symmetry	15	—	15
7. *L*-shell projection (Stewart, 1970)	12	—	12

and assume this motion to be equal to the average mean-square displacement of the adjacent atoms *A* and *B*. This leads to $T_{jis}=(T_{js}+T_{is})/2$ and implies that no phase relationship exists between the displacements of atoms *A* and *B*. As the thermal motion is generally an average over many external and internal modes, this assumption is not unreasonable.

The assignment of the single parameter T_{jis} to the whole overlap density implies that the thermal motion varies little in the region of the bond, *i.e.* that $T_{js}\sim T_{is}$. A better approximation to (21) is to be used if this condition is not fulfilled.

Conclusion

We have outlined formalisms and practical considerations pertinent to the population refinement of X-ray diffraction data. This refinement can produce detailed information on the molecular charge-distribution. But, because large correlations exist between its elements, the first-order density matrix cannot be fully determined experimentally, even when 'long bonds' are neglected. The treatment of thermal motion is approximate, and further studies on the effect of thermal averaging are desirable.

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Structure Factor Amplitudes from Thermal Diffuse Scattering Measurements

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A method is proposed, for certain single crystals, of estimating the structure factor amplitudes corresponding to Bragg reflexions with strong to medium integrated intensities from measurements of the thermal diffuse X-ray scattering in regions of reciprocal space close to the appropriate lattice points. The values obtained conventionally from integrated Bragg intensities are often subject to considerable error due to extinction effects. The thermal diffuse scattering, being incoherently scattered and of a relatively weak intensity, would appear to be less likely to be affected by primary and secondary extinction. The structure factor amplitudes (or correction factors for those found from Bragg measurements) are obtained from the observed scattering data by a least-squares refinement method. Procedures are suggested for use where measurements are made on (i) a relative scale, (ii) an absolute scale, with respect to the direct beam intensity. The method is illustrated by application to some single-crystal data.

Introduction

In recent years, considerable progress has been achieved in providing estimates of extinction effects in the determination of structure factor amplitudes from integrated Bragg intensities, by both experimental (Chandrasekhar, Ramaseshan & Singh, 1969) and theoretical (Zachariasen, 1967, 1968*a*,*b*,*c*,*d*, 1969; Coppens &