direction (a principle axis of the crystalline electric field) corresponds in our case with the line joining the two copper ions in a molecule. This line makes an angle of 34·6° with the $a\,c$ plane, and its projection on to the $a\,c$ plane an angle of 32·5° with the c axis. The corresponding values given by Bleaney & Bowers for their z direction are 33° and 33°.

The authors further discuss the question as to whether the interaction between the copper ions is of a direct nature (Cu–Cu distance 2 Å), or of Kramers's super-exchange type acting through intermediate oxygen atoms (Cu–Cu distance 4 Å). Whereas they seem to favour the latter type of interaction, the the structure described in this paper undoubtedly indicates direct interaction between the copper ions (Cu–Cu distance 2·64 Å).

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Vibrational Modifications of the Electron Distribution in Molecular Crystals. I. The Density in a Vibrating Carbon Atom

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The electron density derived from measurements of the Laue scattering of X-rays by a crystal is shown to be the density in the stationary crystal averaged over all possible displaced configurations of the atomic nuclei in thermal equilibrium together at the temperature of the experiment. The calculation of the mean electron distribution falls into two parts: in general the mean density in an atom is a function of the tensor formed by the mean square amplitudes and mean products of amplitudes of the atomic motion; for a particular crystal this tensor has to be calculated from the force constants and geometry.

In the present paper the mean density in a carbon atom is computed as a function of the r.m.s. amplitude of isotropic thermal motion. It is found that quite a small amplitude suffices to reduce the peak density considerably below the value in a stationary atom; on the other hand, the bridge density in a bond between two atoms is increased. At the amplitudes which occur in many molecular crystals at ordinary temperatures the distribution in an atom is nearly gaussian.

In Part II these results will be applied to the interpretation of some experimental distributions.

1. Introduction

Recently theoretical calculations of the electron distributions in some conjugated organic molecules have been made according to several different approximations: Klement (1951) has treated naphthalene by the valence-bond technique; March (1952) has applied both the molecular-orbital and the Thomas–Fermi methods to benzene. On the other hand, detailed electron-density contour maps derived from X-ray diffraction measurements on crystals of naphthalene and anthracene have been published by Robertson *et al.* (Abrahams, Robertson & White, 1949*b*; Mathieson, Robertson & Sinclair, 1950). An earlier note (Coulson, Higgs & March, 1951) has pointed out the dangers of making direct comparisons between the theoretical density, calculated for a stationary molecule, and the experimental density, measured for a molecule undergoing thermal agitation in a crystal. The present papers study quantitatively the influence of thermal motion on the measured distribution.

The most striking effect of vibration on the distribution in the neighbourhood of an atom is the smearing-out of the peak which marks the position of the nucleus: the sharp strong peak in the stationary atom becomes a broad weak maximum in a vibrating atom. The height of the peak depends quite strongly on the mean amplitude of vibration, so that variations from atom to atom due to bonding in a molecule may be augmented by variations due to different atomic vibration amplitudes. The bridge values of the density between bonded atoms undergo similar modifications, but the changes are less marked than those in the peak values. Thus in general, unless allowance is first made for the effects of thermal motion, the value of a comparison between theoretical and experimental distributions is somewhat dubious.

First of all, in § 2, the motion of a vibrating polyatomic system is discussed. In § 3 it is shown that the effective density ϱ^e derived from X-ray measurements is in fact the average $\bar{\varrho}$ of ϱ for all possible configurations of the atomic nuclei forming the crystal, in thermal equilibrium together at the temperature of the experiment. In § 4 $\bar{\varrho}$ at the mean centre of a carbon atom is computed as a function of the r.m.s. amplitude of isotropic atomic vibrations, and in § 5 an estimate is made of the effect on $\bar{\varrho}$ of anisotropy. The electron distribution in carbon corresponding to a selected value of the mean amplitude is calculated in § 6 and is compared with an experimental distribution found in naphthalene; in § 7 an estimate is made of the effect on such a comparison of the termination of the Fourier series from which the experimental distribution is derived. The results are discussed in § 8.

The results will be applied to the interpretation of the observed peaks in naphthalene, anthracene and other molecules in Part II.

2. Harmonic vibrations of a polyatomic system

Let us first consider the motion of a crystal as a system of N atoms vibrating about an equilibrium configuration. Let the instantaneous displacement of the rth atomic nucleus, of mass m_r, have cartesian components (x_r, y_r, z_r). Then in matrix notation, the order of the coordinates being

$$(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)\,,$$

the kinetic energy of the system is

$$T = \tfrac{1}{2}\dot{\mathbf{x}}'\mathbf{M}\dot{\mathbf{x}}\,, \tag{1}$$

where

$$\mathbf{M} = \operatorname{diag}(m_1, m_1, m_1, m_2, m_2, m_2, \ldots, m_N, m_N, m_N)\,.$$

The potential energy is, to a first approximation,

$$V = \tfrac{1}{2}\mathbf{x}'\mathbf{F}\mathbf{x}\,, \tag{2}$$

where $\mathbf{F}$ is the matrix of force constants. From the symmetric matrices, $\mathbf{M}$ and $\mathbf{F}$, another may be constructed, namely the dynamical matrix (Born, 1942),

$$\mathbf{D} = \mathbf{M}^{-\frac{1}{2}}\mathbf{F}\mathbf{M}^{-\frac{1}{2}}\,. \tag{3}$$

The vibration frequencies ν of the system are then the $3N$ solutions of the secular equation,

$$|\mathbf{D}-\omega^2\mathbf{I}| = 0\,,$$

in which $\mathbf{I}$ is the unit matrix and $\omega = 2\pi\nu$. Normal coordinates $\mathbf{q}$ are obtained from $\mathbf{x}$ by the transformation,

$$\mathbf{x} = \mathbf{M}^{-\frac{1}{2}}\mathbf{U}\mathbf{q}\,. \tag{4}$$

The ith column of $\mathbf{U}$ consists of the normalized amplitudes of $\mathbf{x}$ in the ith normal mode of vibration, that is, $\mathbf{U}$ is an orthogonal matrix ($\mathbf{U}'\mathbf{U}=\mathbf{I}=\mathbf{U}\mathbf{U}'$) which satisfies the equation,

$$\mathbf{D}\mathbf{U} = \mathbf{U}\mathbf{\Lambda}\,,$$

where $\mathbf{\Lambda} = \operatorname{diag}(\omega_i^2)$. It follows from the last equation that

$$\mathbf{D}^n = \mathbf{U}\mathbf{\Lambda}^n\mathbf{U}'\,,$$

where n is any integer, positive or negative, and more generally that

$$f(\mathbf{D}) = \mathbf{U}f(\mathbf{\Lambda})\mathbf{U}'\,, \tag{5}$$

where $f(z)$ is any regular function of z.

Expressed in terms of normal coordinates, the hamiltonian of the system is

$$H = T+V = \tfrac{1}{2}\sum_{i=1}^{3N}(\dot{q}_i^2+\omega_i^2 q_i^2)\,.$$

Now Bloch (1932) has shown, for a harmonic oscillator of hamiltonian $\frac{1}{2}(\dot{q}^2+\omega^2q^2)$ in thermal equilibrium with its environment at temperature T, that the probability that q lies in the range $(q, q+dq)$ is

$$P(q)dq = (\gamma/2\pi)^{\frac{1}{2}}\exp(-\tfrac{1}{2}\gamma q^2)\,dq\,, \tag{6}$$

in which

$$\gamma^{-1} = \overline{q^2} = (\hbar/2\omega)\coth(\hbar\omega/2kT)\,,$$

where k is Boltzmann's constant and $\hbar$ is Planck's constant divided by 2π. Since the normal coordinates are dynamically independent (in the sense that $H(\mathbf{q}) = \sum_i H_i(q_i)$, so that any total eigenfunction has the form $\psi(\mathbf{q}) = \prod_i \psi_i(q_i)$), the probability that all the q_i lie in the corresponding ranges (q_i, q_i+dq_i) equals the product of the probabilities of the individual situations:

$$P(\mathbf{q})d\mathbf{q} = \prod_{i} P_i(q_i)dq_i$$
$$= \{|\mathbf{\Gamma}|/(2\pi)^{3N}\}^{\frac{1}{2}} \exp(-\tfrac{1}{2}\mathbf{q}'\mathbf{\Gamma}\mathbf{q})d\mathbf{q} ,$$

in which

$$d\mathbf{q} = \prod_{i=1}^{3N} dq_i$$

and

$$\mathbf{\Gamma}^{-1} = \overline{\mathbf{q}\mathbf{q}'} = \varphi(\mathbf{\Lambda}) ,$$

where

$$\varphi(z) = \tfrac{1}{2}\hbar z^{-\frac{1}{2}} \coth(\hbar z^{\frac{1}{2}}/2kT) .$$

Transforming to the coordinates **x** according to equation (4) and using the consequent relation $d\mathbf{x} = |\mathbf{M}^{-\frac{1}{2}}\mathbf{U}|d\mathbf{q}$, we find that the probability that **x** lies in the range $(\mathbf{x}, \mathbf{x}+\mathbf{dx})$ is

$$P(\mathbf{x})d\mathbf{x} = P(\mathbf{q})d\mathbf{q}$$
$$= \{|\mathbf{A}|/(2\pi)^{3N}\}^{\frac{1}{2}} \exp(-\tfrac{1}{2}\mathbf{x}'\mathbf{A}\mathbf{x})d\mathbf{x} , \qquad (7)$$

in which

$$\mathbf{A}^{-1} = \mathbf{M}^{-\frac{1}{2}}\mathbf{U}\mathbf{\Gamma}^{-1}\mathbf{U}'\mathbf{M}^{-\frac{1}{2}}$$
$$= \overline{\mathbf{x}\mathbf{x}'}$$
$$= \mathbf{M}^{-\frac{1}{2}}\varphi(\mathbf{D})\mathbf{M}^{-\frac{1}{2}} , \qquad (8)$$

by equation (5). More generally it follows from (6) that the probability distribution for any subset $\mathbf{x}_1$ of the coordinates **x**, irrespective of the values of the remaining coordinates, has the gaussian form,

$$P(\mathbf{x}_1)d\mathbf{x}_1 = \{|\mathbf{A}_1|/(2\pi)^n\}^{\frac{1}{2}} \exp(-\tfrac{1}{2}\mathbf{x}_1'\mathbf{A}_1\mathbf{x}_1)d\mathbf{x}_1 , \qquad (7a)$$

where

$$\mathbf{A}_1^{-1} = \overline{\mathbf{x}_1\mathbf{x}_1'} \qquad (8a)$$

and n is the dimension of $\mathbf{x}_1$.

3. Effects of thermal motion on the scattering of X-rays by crystals

The influence of thermal motion on X-ray scattering has been discussed fully by Born & Sarginson (1941); some of their conclusions will be quoted here. Broadly, two effects may be distinguished: first, the Laue spots are weakened by the smearing-out of the electron density; secondly, there is a diffuse background intensity due to the relaxation of strict periodicity in the crystal lattice. We are concerned here with the former effect.

The modified Laue scattering is derived from that for a rigid crystal by changing the scattering factor for the jth atom in the unit cell from the value f_j for a stationary atom to the value

$$g_j = f_j \exp(-L_j) \qquad (9)$$

for a vibrating one. The simplest formula for L_j is that given by Born (1943):

$$L_j = \frac{2\pi^2}{m_j} \sum_{x,y} S_{ll,jj,xy}k_xk_y , \qquad (10)$$

where $\mathbf{k} = (\mathbf{k}_s - \mathbf{k}_i)$ is the difference between the wave-vectors of the scattered and incident radiation ($|\mathbf{k}_s| = |\mathbf{k}_i| = \lambda^{-1}$, where λ is the wavelength) and $\mathbf{S} = \varphi(\mathbf{D})$ is the scattering matrix (Born, 1942) for the crystal (the suffix l numbers the unit cells). Combining (8) and (10) we obtain the relation,

$$L_j = 2\pi^2 \sum_{x,y} \overline{x_jy_j}k_xk_y$$
$$= 2\pi^2\mathbf{k}'\overline{\mathbf{u}_j\mathbf{u}_j'}\mathbf{k} , \qquad (11)$$

in which $\mathbf{u}_j$ is the column vector with components (x_j, y_j, z_j). Alternatively, equation (11) may be written as

$$L_j = \frac{8\pi^2 \sin^2\theta}{\lambda^2}\overline{u_{j,\mathbf{k}}^2} , \qquad (11a)$$

where θ is the Bragg angle and $u_{j,\mathbf{k}}$ is the component of the displacement of the jth atom parallel to **k** (*i.e.* normal to the reflecting plane).

Let us now consider the electron distribution in atom j. The density in a stationary atom is the Fourier transform of f_j: at a point $\mathbf{r}_j$ from the nucleus it is

$$\varrho_j(\mathbf{r}_j) = \int f_j(\mathbf{k}) \exp(2\pi i\mathbf{k}'\mathbf{r}_j)d\mathbf{k}; \qquad (12)$$

conversely

$$f_j(\mathbf{k}) = \int \varrho_j(\mathbf{r}_j) \exp(-2\pi i\mathbf{k}'\mathbf{r}_j)d\mathbf{r}_j . \qquad (12a)$$

The effective density derived from the actual Laue intensities is similarly

$$\varrho_j^e(\mathbf{r}_j) = \int g_j(\mathbf{k}) \exp(2\pi i\mathbf{k}'\mathbf{r}_j)d\mathbf{k} . \qquad (13)$$

From (9), (11), (13) and (12*a*) we find

$$\varrho_j^e(\mathbf{r}_j)$$
$$= \iint \varrho_j(\mathbf{t}_j) \exp[-2\pi^2\mathbf{k}'\overline{\mathbf{u}_j\mathbf{u}_j'}\mathbf{k}+2\pi i\mathbf{k}'(\mathbf{r}_j-\mathbf{t}_j)]d\mathbf{k}d\mathbf{t}$$
$$= \int \varrho_j(\mathbf{t}_j)Q(\mathbf{r}_j-\mathbf{t}_j)d\mathbf{t}_j$$
$$= \int \varrho_j(\mathbf{r}_j-\mathbf{u}_j)Q(\mathbf{u}_j)d\mathbf{u} , \qquad (14)$$

in which

$$Q(\mathbf{u}_j) = \int \exp(-2\pi^2\mathbf{k}'\mathbf{A}_j^{-1}\mathbf{k}+2\pi i\mathbf{k}'\mathbf{u}_j)d\mathbf{k}$$
$$= \exp(-\tfrac{1}{2}\mathbf{u}_j'\mathbf{A}_j\mathbf{u}_j) \int \exp(-2\pi^2\mathbf{k}_1'\mathbf{A}_j\mathbf{k}_1)d\mathbf{k} ,$$

where

$$\mathbf{A}_j^{-1} = \overline{\mathbf{u}_j\mathbf{u}_j'} \qquad (15)$$

and

$$\mathbf{k}_1 = \mathbf{k}+(2\pi i)^{-1}\mathbf{A}_j\mathbf{u}_j .$$

Now

$$\int \exp(-2\pi^2\mathbf{k}_1'\mathbf{A}_j^{-1}\mathbf{k}_1)d\mathbf{k} = \{|\mathbf{A}_j|/(2\pi)^3\}^{\frac{1}{2}} ,$$

so that

$$Q(\mathbf{u}_j) = \{|\mathbf{A}_j|/(2\pi)^3\}^{\frac{1}{2}} \exp(-\tfrac{1}{2}\mathbf{u}_j'\mathbf{A}_j\mathbf{u}_j)$$
$$= P(\mathbf{u}_j) , \qquad (16)$$

as is evident from (7*a*) and (8*a*) with $\mathbf{x}_1 = \mathbf{u}_j$, and the definition (15). Combining (14) and (16) we find that

$$\varrho_j^e(\mathbf{r}_j) = \int \varrho_j(\mathbf{r}_j-\mathbf{u}_j)P(\mathbf{u}_j)\,d\mathbf{u}_j = \overline{\varrho_j}(\mathbf{r}_j)\,, \qquad (17)$$

the thermal average of the density. Thus the distribution which is derived from X-ray diffraction measurements is

$$\bar{\varrho}(\mathbf{r}) = \{|\mathbf{A}|/(2\pi)^3\}^{\frac{1}{2}} \int \varrho(\mathbf{r}-\mathbf{u}) \exp\left(-\tfrac{1}{2}\mathbf{u}'\mathbf{A}\mathbf{u}\right) d\mathbf{u}\,, \qquad (18)$$

where $\mathbf{A}^{-1} = \overline{\mathbf{u}\mathbf{u}'}$ and the suffix j has been dropped.

4. Calculation of $\bar{\varrho}$ for carbon

The calculation of $\bar{\varrho}$ for a given atom such as carbon falls into two distinct parts. In general $\bar{\varrho}$ is to be found as a function of $\mathbf{r}$ and $\mathbf{A}$; in particular problems $\mathbf{A}$ has to be derived from the geometry and force constants of the crystal by means of equation (8). At present we are concerned with the former problem; an example of the latter will be considered in Part II.

It is necessary to make certain assumptions about ϱ, the stationary density. Already, by using atomic scattering factors f_j in the theory, we have implicitly neglected bonding. As is customary in X-ray scattering theory, we shall derive ϱ from the Hartree self-consistent field for free carbon. The field will be taken as that for the spherically symmetric valence state, $(1s)^2(2s)(2p_x)(2p_y)(2p_z)$, which predominates in bonded carbon: in terms of the radial distribution functions, R, S and T, computed by Torrance (1934) $\varrho(\mathbf{r})$ is given by

$$\varrho(\mathbf{r}) = (4\pi r^2)^{-1}(2R^2+S^2+3T^2)\,. \qquad (19)$$

When ϱ is a spherically symmetric function such as (19), it is convenient to use a coordinate system whose axes lie along the principal axes of $\mathbf{A}$: the probability distribution then assumes the simpler form,

$$P(\mathbf{u})d\mathbf{u} = \{abc/(2\pi)^3\}^{\frac{1}{2}} \exp\left[-\tfrac{1}{2}(a\xi^2+b\eta^2+c\zeta^2)\right]d\mathbf{u}\,, \qquad (20)$$

in which (ξ, η, ζ) are the components of $\mathbf{u}$,

$$d\mathbf{u} = d\xi\, d\eta\, d\zeta\,,$$

and

$$a^{-1} = \overline{\xi^2},\quad b^{-1} = \overline{\eta^2},\quad c^{-1} = \overline{\zeta^2}\,.$$

Thus $\bar{\varrho}(\mathbf{r})$ may be expressed as a function of (x, y, z), the components of $\mathbf{r}$ along the principal axes of $\mathbf{A}$, and of (a, b, c), the principal values of $\mathbf{A}$.

Inspection of (18) shows that when $\varrho(\mathbf{r})$ is an even function, so also is $\bar{\varrho}(\mathbf{r})$: it therefore has a symmetrical maximum at $\mathbf{r} = 0$, the mean centre of the atom. The value of this peak density is, according to (18), (19) and (20),

$$\bar{\varrho}(0) = \{abc/(2\pi)^3\}^{\frac{1}{2}} \iiint_{-\infty}^{+\infty} (4\pi u^2)^{-1}\left[2R^2(u)+S^2(u)+3T^2(u)\right] \times \exp\left[-\tfrac{1}{2}(a\xi^2+b\eta^2+c\zeta^2)\right] d\xi\, d\eta\, d\zeta\,,$$

in which u is the radial atomic displacement ($u^2 = \xi^2+\eta^2+\zeta^2$). On transformation to spherical polar coordinates this integral becomes

$$\bar{\varrho}(0) = \int_0^\infty (2R^2+S^2+3T^2)F(u)\,du\,, \qquad (21)$$

in which

$$F(u) = (4\pi)^{-1}\{abc/(2\pi)^3\}^{\frac{1}{2}} \int_0^{2\pi} \left\{\int_0^\pi \exp\left[-\tfrac{1}{2}u^2(\alpha+\beta\cos^2\theta)\right] \times \sin\theta\, d\theta\right\} d\varphi\,,$$

where

$$\alpha(\varphi) = a\cos^2\varphi + b\sin^2\varphi$$

and

$$\beta(\varphi) = c - \alpha(\varphi)\,. \qquad (22)$$

The integration with respect to θ may be carried out and yields the formula,

$$F(u) = (abc)^{\frac{1}{2}}(8\pi^2 u)^{-1} \int_0^{2\pi} \exp\left(-\tfrac{1}{2}u^2\alpha\right)\beta^{-\frac{1}{2}} H\left(u\sqrt{\tfrac{1}{2}\beta}\right) d\varphi\,, \qquad (23)$$

where H is the error function defined by

$$H(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2)\,dt\,.$$

In the present section we shall consider only the simplest case of (23), that which occurs when the vibration is isotropic. When $\overline{\xi^2} = \overline{\eta^2} = \overline{\zeta^2} = \frac{1}{3}\overline{u^2}$, then also $a = b = c = 3(\overline{u^2})^{-1}$, so that $\mathbf{A} = a\mathbf{I}$. It follows that $\alpha = a$, $\beta = 0$, and (23) may be integrated to give

$$F(u) = (a/2\pi)^{\frac{3}{2}} \exp\left(-\tfrac{1}{2}au^2\right)\,. \qquad (24)$$

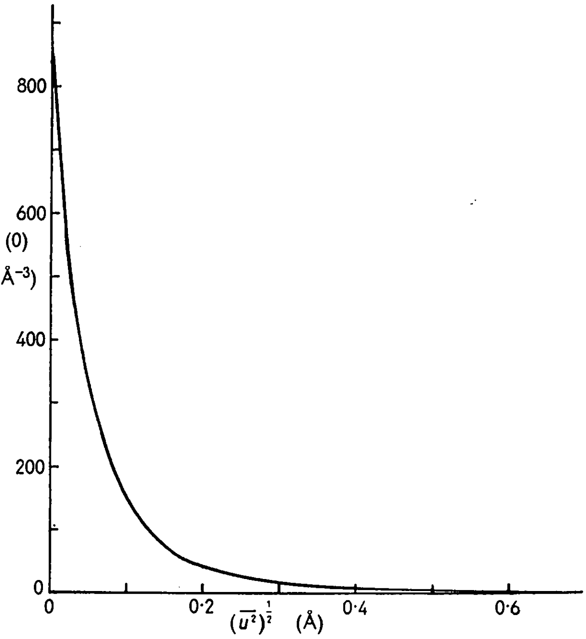

Fig. 1. Peak density in carbon as a function of thermal amplitude.

Table 1. *Peak density in carbon for various r.m.s. displacements*

$(\overline{u^2})^{\frac{1}{2}}$ (Å)	$\bar{\varrho}_{1s}(0)$ (e.Å^{-3})	$\bar{\varrho}_{2s}(0)$ (e.Å^{-3})	$\bar{\varrho}_{2p}(0)$ (e.Å^{-3})	$\bar{\varrho}(0)$ (e.Å^{-3})	v (%)
0	413·3	20·4	0	847	2·4
0·008	352·4	17·3	0·00	722	2·4
0·016	298·5	14·6	0·01	612	2·4
0·023	262·2	12·8	0·02	537	2·4
0·032	219·6	10·7	0·04	450	2·4
0·046	172·9	8·3	0·07	354	2·4
0·065	125·9	5·9	0·11	258	2·4
0·084	93·79	4·23	0·15	192	2·4
0·091	83·38	3·70	0·16	171	2·4
0·102	71·35	3·10	0·18	146	2·5
0·129	49·43	2·03	0·23	102	2·7
0·155	35·96	1·40	0·26	74·1	2·9
0·205	20·70	0·77	0·30	43·1	3·9
0·264	11·70	0·47	0·33	24·8	5·8
0·373	4·972	0·316	0·314	11·2 (11·2)	11·2
0·457	2·908	0·281	0·286	6·95 (6·95)	16·4
0·647	1·114	0·223	0·213	3·09 (3·10)	27·9

Table 2. *Analytical approximation to* $\bar{\varrho}(0)$.

$(\overline{u^2})^{\frac{1}{2}}$ (Å)	$\bar{\varrho}(0)$ (e.Å^{-3})	$(\overline{u^2})^{\frac{1}{2}}$ (Å)	$\bar{\varrho}(0)$ (e.Å^{-3})	$(\overline{u^2})^{\frac{1}{2}}$ (Å)	$\bar{\varrho}(0)$ (e.Å^{-3})
0·30	18·5	0·42	8·45	0·54	4·72
0·31	17·1	0·43	8·00	0·55	4·52
0·32	15·9	0·44	7·59	0·56	4·34
0·33	14·8	0·45	7·20	0·57	4·16
0·34	13·8	0·46	6·85	0·58	4·00
0·35	12·9	0·47	6·51	0·59	3·84
0·36	12·1	0·48	6·20	0·60	3·70
0·37	11·4	0·49	5·91	0·61	3·56
0·38	10·7	0·50	5·64	0·62	3·43
0·39	10·0	0·51	5·39	0·63	3·30
0·40	9·47	0·52	5·15	0·64	3·18
0·41	8·94	0·53	4·93	0·65	3·07

$\bar{\varrho}(0)$ was computed for a series of values of a by using (21) and (24): it is tabulated in Table 1, and in Fig. 1 it is plotted against $(\overline{u^2})^{\frac{1}{2}}$, the r.m.s. amplitude of vibration $(\overline{u^2} = 3a^{-1})$. The other quantities in Table 1 are $\bar{\varrho}_{1s}(0)$, $\bar{\varrho}_{2s}(0)$ and $\bar{\varrho}_{2p}(0)$, the contributions to $\bar{\varrho}(0)$ per $1s$, $2s$ and $2p$ electron respectively, and $v(0)$, the percentage contribution from all the valence electrons $(\bar{\varrho} = 2\bar{\varrho}_{1s}+\bar{\varrho}_{2s}+3\bar{\varrho}_{2p}$; $v = (100/\bar{\varrho})[\varrho_{2s}+3\bar{\varrho}_{2p}])$. A graph of v against $(\overline{u^2})^{\frac{1}{2}}$ is plotted in Fig. 2. When a is small, i.e. when $(\overline{u^2})^{\frac{1}{2}}$ is large,

$$F(u) \doteqdot (a/2\pi)^{\frac{3}{2}},$$

provided that u is not too large. Since R, S and T fall off rapidly at large distances from the nucleus, it follows from (21) that the asymptotic form of $\bar{\varrho}(0)$ for large $(\overline{u^2})^{\frac{1}{2}}$ is

$$\begin{aligned}\bar{\varrho}(0) &\simeq (a/2\pi)^{\frac{3}{2}}\int_0^\infty (2R^2+S^2+3T^2)\,du \\ &= 6(2\pi\overline{u^2}/3)^{-\frac{3}{2}}\,, \qquad (25)\end{aligned}$$

since R, S and T are normalized to unity. This result suggests that it may be possible to approximate to $\bar{\varrho}(0)$ over a moderate range of values of $(\overline{u^2})^{\frac{1}{2}}$ by a function of the form $C(\overline{u^2})^{-n}$. In fact it was found that the curve of Fig. 1 is fitted closely over the range $(\overline{u^2})^{\frac{1}{2}} = 0\cdot30$–$0\cdot65$ Å ($\bar{\varrho}(0) = 18$–3 e.A^{-3}) by the formula

$$\bar{\varrho}(0) \doteqdot 1\cdot13(\overline{u^2})^{-1\cdot16}; \qquad (26)$$

this function is tabulated in Table 2. The numbers in brackets in Table 1, column 5 are approximate values of $\bar{\varrho}(0)$ calculated from (26): comparison with the directly computed values indicates that (26) yields values which are accurate to less than 1% in the range covered by Table 2.

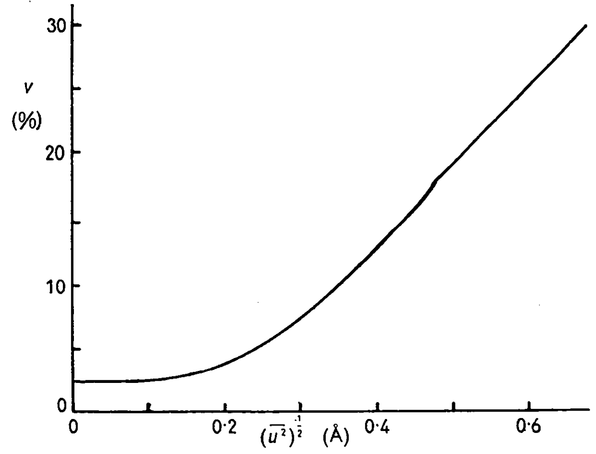

Fig. 2. Percentage valence-electron contribution to $\bar{\varrho}(0)$ as a function of thermal amplitude.

5. Effect of anisotropy

An estimate of the effect on $\bar{\varrho}(0)$ of anisotropy in the atomic motion may be made by considering the special case of anisotropy in one direction only. If $b = a$ and $c = a(1+\Delta)$, where Δ is an anisotropy parameter, then in (22) $\alpha(\varphi) = a$ and $\beta(\varphi) = a\Delta$, so that (23) may be integrated to give

$$F(u) = \left(\frac{1+\Delta}{\Delta}\right)^{\frac{1}{2}} \frac{a}{4\pi u} \exp\left(-\tfrac{1}{2}au^2\right) H\left(u\sqrt{\tfrac{1}{2}a\Delta}\right) . \qquad (27)$$

The r.m.s. amplitude is then

$$(\overline{u^2})^{\frac{1}{2}} = \left[\frac{3+2\Delta}{a(1+\Delta)}\right]^{\frac{1}{2}} .$$

$\bar{\varrho}(0)$ was calculated from (21) and (27) for the special values, $a = 4$ atomic units, $\Delta = \frac{1}{2}$: these correspond to $(\overline{u^2})^{\frac{1}{2}} = 0{\cdot}431$ Å, $(\overline{\zeta^2}/\overline{\xi^2})^{\frac{1}{2}} = 0{\cdot}82$. The value found was 8·13 e.Å^{-3}, which differs by less than 2% from the value 8·00 e.Å^{-3} for isotropic motion. It appears that a considerable degree of anisotropy would be required to produce a serious change in $\bar{\varrho}(0)$. Conversely, $\bar{\varrho}(0) = 8{\cdot}13$ e.Å^{-3} corresponds to an isotropic r.m.s. amplitude of 0·427 Å (Table 2), which differs by 1% from the anisotropic value, 0·431 Å. Thus, for such a degree of anisotropy, the error in $(\overline{u^2})^{\frac{1}{2}}$, calculated from $\bar{\varrho}(0)$ on the assumption of isotropy, is quite small.

6. Isotropic motion: the electron distribution

When the atomic motion is isotropic ($\mathbf{A} = a\mathbf{I}$) and the stationary distribution has spherical symmetry, equation (18) becomes

$$\bar{\varrho}(\mathbf{r}) = (a/2\pi)^{\frac{3}{2}} \int \varrho(t) \exp\left(-\tfrac{1}{2}au^2\right) d\mathbf{t} ,$$

in which $\mathbf{t} = \mathbf{r} - \mathbf{u}$ (see Fig. 3). On transforming to spherical polar coordinates in $\mathbf{t}$-space with the polar axis along $\mathbf{r}$, and using the relation,

$$u^2 = r^2 + t^2 - 2rt\cos\theta ,$$

we obtain

$$\bar{\varrho}(\mathbf{r}) = (a/2\pi)^{\frac{3}{2}} \exp\left(-\tfrac{1}{2}ar^2\right) \int_0^\infty \varrho(t) \exp\left(-\tfrac{1}{2}at^2\right) \times \left\{\int_0^\pi \exp\left(art\cos\theta\right) \sin\theta\, d\theta\right\} t^2 dt \int_0^{2\pi} d\varphi .$$

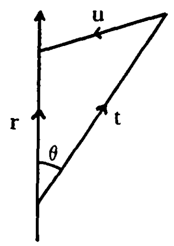

Fig. 3. Coordinates used in integration of $\bar{\varrho}(r)$.

On carrying out the θ and φ integrations, we find that $\bar{\varrho}$ has the spherically symmetric form,

$$\bar{\varrho}(r) = 4\pi(a/2\pi)^{\frac{3}{2}} \exp\left(-\tfrac{1}{2}ar^2\right) \int_0^\infty \varrho(t) \exp\left(-\tfrac{1}{2}at^2\right) \times \frac{\sinh(art)}{(art)} t^2 dt . \qquad (28)$$

In terms of the radial distribution function,

$$D(r) = 4\pi r^2 \varrho(r) = 2R^2 + S^2 + 3T^2 ,$$

this may be written as

$$\bar{\varrho}(r) = (a/2\pi)^{\frac{3}{2}} \exp\left(-\tfrac{1}{2}ar^2\right) \int_0^\infty D(t) \exp\left(-\tfrac{1}{2}at^2\right) \times \frac{\sinh(art)}{(art)} dt . \qquad (28a)$$

By expanding the function $(art)^{-1}\sinh(art)$ as a power series we obtain a formal series expansion of $\bar{\varrho}(r)$:

$$\bar{\varrho}(r) = \exp\left(-\tfrac{1}{2}ar^2\right) \sum_{n=0}^{\infty} \frac{\varrho_n(a)}{(2n+1)!} (ar^2)^n , \qquad (28b)$$

where

$$\varrho_n(a) = (a/2\pi)^{\frac{3}{2}} \int_0^\infty (at^2)^n D(t) \exp\left(-\tfrac{1}{2}at^2\right) dt . \qquad (29)$$

From (28b) we derive formulae for the height of the density peak and its curvature:

$$P(a) \equiv \bar{\varrho}(0) = \varrho_0 , \qquad (30)$$

the function computed in § 4;

$$C(a) \equiv -\left(\frac{d^2\bar{\varrho}}{dr^2}\right)_{r=0} = a\left(\varrho_0 - \tfrac{1}{3}\varrho_1\right) . \qquad (31)$$

The asymptotic form of $\bar{\varrho}(r)$ for large r.m.s. amplitudes may be obtained from (28a) by allowing a to tend to zero: the integral tends to the value $\int_0^\infty D(t)\,dt = 6$, so the asymptotic form of the distribution is

$$\bar{\varrho}(r) \cong 6(a/2\pi)^{\frac{3}{2}} \exp\left(-\tfrac{1}{2}ar^2\right) . \qquad (32)$$

This result indicates that when $(\overline{u^2})^{\frac{1}{2}}$ is large the distribution approximates closely to a gaussian peak, a fact which has long been known empirically by X-ray crystallographers (see Costain, 1941). When $(\overline{u^2})^{\frac{1}{2}}$ is finite, the gaussian function which is the best fit to the actual distribution for small r (i.e. which has the same peak height and curvature) is

$$\bar{\varrho}_g(r) = P\exp\left(-\tfrac{1}{2}a'r^2\right) , \qquad (33)$$

where

$$a' = C/P = a\left(1 - \tfrac{1}{3}\varrho_1/\varrho_0\right) .$$

The function $\bar{\varrho}(r)$ was computed from formula (28a) with $a = 4$ atomic units, corresponding to $(\overline{u^2})^{\frac{1}{2}} = 0{\cdot}457$ Å. The integral ϱ_1 was computed for the same value of a, and from it and ϱ_0 (Table 1, column 5) the parameters in the gaussian function $\bar{\varrho}_g$ were found:

$$P = 6{\cdot}955 \text{ e.Å}^{-3} ,$$
$$a' = 11{\cdot}24 \text{ Å}^{-2} ,$$
$$C = a'P = 78{\cdot}16 \text{ e.Å}^{-5} .$$

Both functions are tabulated in Table 3 and displayed graphically in Fig. 4: it is seen that $\bar{\varrho}(r)$ is closely gaussian up to about 0·4 Å from the centre.

Table 3. *Electron distribution in carbon*

$(\overline{u^2})^{\frac{1}{2}} = 0{\cdot}457$ Å

r (Å)	$\bar{\varrho}$ (e.Å^{-3})	$\bar{\varrho}_g$ (e.Å^{-3})
0	6·955	6·955
0·132	6·309	6·306
0·264	4·744	4·700
0·396	3·030	2·880
0·528	1·730	1·450
0·660	0·956	0·600

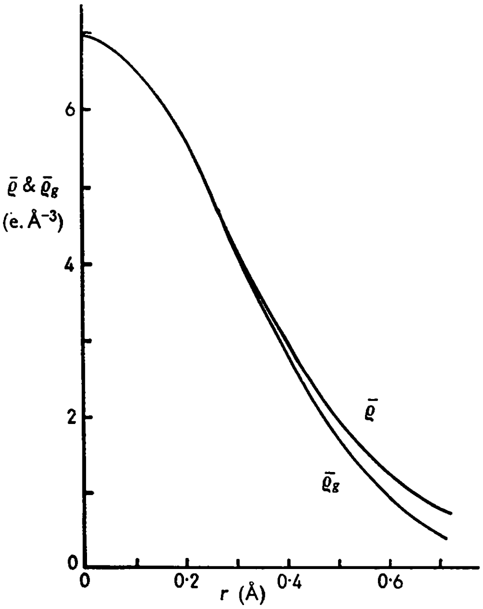

Fig. 4. Electron distribution $\bar{\varrho}(r)$ for carbon at $(\overline{u^2})^{\frac{1}{2}} = 0{\cdot}457$ Å, and gaussian curve $\bar{\varrho}_g(r)$.

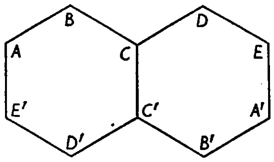

Fig. 5. Labelling of carbon atoms in naphthalene.

The carbon atom A in naphthalene (Fig. 5) on the contour map drawn by Abrahams, Robertson & White (1949*b*) has a peak density of 6·9 e.Å^{-3}; it is therefore suitable for a comparison with the computed distribution. A graph of $\ln \bar{\varrho}$ against r^2 (Fig. 6), plotted from measurements on the map along a line from the centre of atom A towards the centre of the ring (to reduce the effect of overlap from neighbouring atoms), is roughly linear up to $r = 0{\cdot}6$ Å: thus the experimental distribution is closely gaussian. However, the curvature of the experimental peak is 57 e.Å^{-5}, considerably less than the calculated 78 e.Å^{-5}. The source of this discrepancy probably lies in the use of a finite Fourier series in the calculation of the experimental distribution: this point is discussed more fully below in § 7.

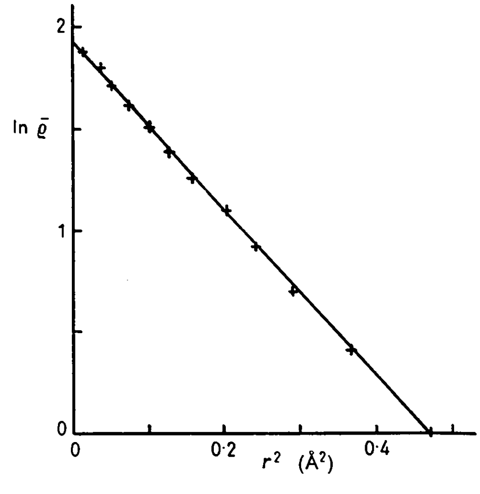

Fig. 6. Plot of $\ln \bar{\varrho}$ $v.$ r^2 for atom A of naphthalene (from measurements on Robertson's map).

The foregoing calculations permit us to estimate the effect of thermal motion on the bridge value of the density in a bond between two carbon atoms. If the change in the distribution due to bonding is neglected and the r.m.s. amplitudes of the two atoms are assumed to be equal, the bridge density is

$$B(a) = 2\bar{\varrho}(\tfrac{1}{2}l) , \qquad (34)$$

where l is the bond-length. Taking $l = 1{\cdot}4$ Å (a value typical of bonds belonging to benzene rings) and $(\overline{u^2})^{\frac{1}{2}} = 0{\cdot}457$ Å (corresponding to the peak, $P = 6{\cdot}9$ e.Å^{-3}, in atom A of naphthalene), we find $B = 1{\cdot}60$ e.Å^{-3} by extrapolating the data of Table 3 to $r = 0{\cdot}7$ Å. This value may be compared with $B = 1{\cdot}27$ e.Å^{-3}, computed directly from the Hartree field for stationary atoms. The motion increases B by 0·33 e.Å^{-3}.

An estimate of the accuracy of the approximate equation (34) may be made by considering the electron distribution in benzene calculated by March (1952). For the bridge density in a stationary C–C bond according to the molecular-orbital theory March gives the value 1·9 e.Å^{-3}. A calculation using the same analytical wave-functions (Slater, 1930) and the 'overlapping atom' approximation (34) yields the value 1·58 e.Å^{-3} for the same density. The difference, about 0·3 e.Å^{-3}, represents the effect of bonding: it is roughly equal to the increase in the Hartree-field density due to thermal motion. Clearly an adequate treatment of bridge densities must take both effects into account.

It may be remarked that the bridge values without, bonding or vibration, calculated from Hartree and Slater atomic wave-functions also differ by 0·3 e.Å^{-3}. Thus the choice of wave-functions is another important factor.

7. The effect of finite-series errors on the distribution

Ideally the experimental distribution is the sum of an infinite Fourier series, whose coefficients are obtained from the intensities of the diffracted X-rays. In practice the series used is finite, since the reciprocal radius, $k = |\mathbf{k}| = 2\lambda^{-1}\sin\theta$ (in the notation of equation (10) *et seq.*), cannot exceed the limiting value,

$$k_0 = 2\lambda^{-1}; \tag{35}$$

moreover, not all the spectra lying within this radius are actually recorded.

In order to estimate the errors introduced into peaks and curvatures by such a finite series let us consider the simpler problem of an isolated atom. The density distribution and the atomic scattering factor are then related by the reciprocal Fourier equations,

$$\left.\begin{aligned} \varrho(\mathbf{r}) &= \int f(\mathbf{k}) \exp(2\pi i \mathbf{k}'\mathbf{r}) d\mathbf{k}, \\ f(\mathbf{k}) &= \int \varrho(\mathbf{r}) \exp(-2\pi i \mathbf{k}'\mathbf{r}) d\mathbf{r}. \end{aligned}\right\} \tag{36}$$

When the distribution has spherical symmetry, the integrations over angular coordinates may be carried out: the transforms become

$$\left.\begin{aligned} \varrho(r) &= 2r^{-1}\int_0^\infty f(k)\sin(2\pi kr)kdk, \\ f(k) &= 2k^{-1}\int_0^\infty \varrho(r)\sin(2\pi kr)rdr. \end{aligned}\right\} \tag{36a}$$

From the former equation we derive formulae for the peak height and curvature:

$$\left.\begin{aligned} P &= 4\pi\int_0^\infty f(k)k^2dk, \\ C &= \frac{16\pi^3}{3}\int_0^\infty f(k)k^4dk. \end{aligned}\right\} \tag{37}$$

The corresponding parameters of the distribution obtained by restricting the range of integration to the sphere, $k < k_0$, in reciprocal space are

$$\left.\begin{aligned} P(k_0) &= 4\pi\int_0^{k_0} f(k)k^2dk, \\ C(k_0) &= \frac{16\pi^3}{3}\int_0^{k_0} f(k)k^4dk. \end{aligned}\right\} \tag{37a}$$

Let us simplify further by using the gaussian approximation (33) to the distribution. Then the second of equations (36) may be integrated to give

$$f(k) = P(2\pi/a')^{\frac{3}{2}} \exp(-2\pi^2k^2/a'). \tag{38}$$

Let us define the fractional errors introduced into P and C by the finite reciprocal radius:

$$\mathcal{E}(P) = \{P - P(k_0)\}/P,$$
$$\mathcal{E}(C) = \{C - C(k_0)\}/C.$$

Then from (33), (37), (37a) and (38) we find

$$\left.\begin{aligned} \mathcal{E}(P) &= (2/\sqrt{\pi})\gamma(\tfrac{3}{2}; 2\pi^2k_0^2/a'), \\ \mathcal{E}(C) &= (4/3\sqrt{\pi})\gamma(\tfrac{5}{2}; 2\pi^2k_0^2/a'), \end{aligned}\right\} \tag{39}$$

where γ is the incomplete gamma function,

$$\gamma(n;\, x) = \int_x^\infty e^{-t}t^{n-1}dt.$$

An application of the recursion formula,

$$\gamma(n+1;\, x) = n\gamma(n;\, x) + x^n e^{-x},$$

to (39) shows that

$$\mathcal{E}(C) = \mathcal{E}(P) + (4/3\sqrt{\pi})(2\pi^2k_0^2/a')^{\frac{3}{2}} \exp(-2\pi^2k_0^2/a'),$$

i.e. the error in C is always greater than that in P.

It is of interest to apply equation (39) to the distribution ϱ_g computed in § 6: then $a' = 11{\cdot}24$ Å^{-2}. The wave-length used in the experimental work on naphthalene was $\lambda = 1{\cdot}54$ Å (Abrahams, Robertson & White, 1949*a*), so the appropriate limiting reciprocal radius is not greater than that given by (35), $k_0 = 1{\cdot}30$ Å^{-1}. The corresponding errors are computed to be

$$\mathcal{E}(P) = 0{\cdot}112,\quad \mathcal{E}(C) = 0{\cdot}306.$$

The parameters of $\bar{\varrho}_g$ are $P = 6{\cdot}955$ e.Å^{-3}, $C = 78{\cdot}16$ e.Å^{-5}; thus the parameters of the modified distribution are

$$P(k_0) = 6{\cdot}18 \text{ e.Å}^{-3},\quad C(k_0) = 54{\cdot}2 \text{ e.Å}^{-5},$$

which may be compared with the experimental parameters,

$$P = 6{\cdot}9 \text{ e.Å}^{-3},\quad C = 57 \text{ e.Å}^{-5}.$$

The theoretical peak has been reduced slightly below the comparable experimental peak, but the agreement between the curvatures is now much more satisfactory. It seems likely that the theoretical distribution having the same $P(k_0)$ as the experimental one would also have approximately the same $C(k_0)$.

8. Discussion

Fig. 1 shows that the effect of vibration on the peak density is considerable: an amplitude of ½ Å reduces it by a factor of more than 100. This is of course due to the sharpness of the peak in the stationary atom. The effect on the bridge densities in bonds is less pronounced, but the calculations of § 6 show that these may be increased by more than 25%. It is therefore impossible to make any useful comparisons between the densities calculated by quantumtheoretical methods for stationary molecules and the corresponding densities derived from X-ray diffraction measurements, unless the latter are first corrected adequately for thermal motion.

The closeness of $\bar{\varrho}$, as calculated in § 6, to the gaussian curve $\bar{\varrho}_g$ suggests that the distribution at an amplitude such as that which occurs in naphthalene is not very sensitive to the shape of ϱ; for $\bar{\varrho}_g$ depends on ϱ only through the two integrals, ϱ_0 and ϱ_1. Thus many details of the electron distribution in a stationary molecule are likely to be lost in the distribution occurring in a molecular crystal at ordinary temperatures.

The $(\overline{u^2})^{\frac{1}{2}}-\bar{\varrho}(0)$ curve may be used to determine the r.m.s. amplitude of a carbon atom having a given observed peak density. It is of interest therefore to examine the assumptions used in the calculations of § 4. These are as follows:

(i) The wave-functions used are those for a free carbon atom. Bonding is neglected except as the source of the potential energy for motion of the nuclei. Since it is mainly the valence $(2s)\,(2p)^3$ electrons which take part in bonding, the inner-shell $(1s)^2$ electrons being practically unaffected, the quantity v (Fig. 2) provides an index of the probable effect of bonding on $\bar{\varrho}(0)$. So long as v is small, the contribution from the valence electrons is relatively unimportant. The range of values of $(\overline{u^2})^{\frac{1}{2}}$ occurring in molecular crystals such as naphthalene and anthracene is 0·4–0·5 Å, corresponding to $\bar{\varrho}(0) = 9{\cdot}5\text{–}5{\cdot}5$ e.Å^{-3} (data from Abrahams *et al.*, 1949*a*, *b*; Mathieson *et al.*, 1950); in this region $v = 13\text{–}19\%$, so the effect of bonding may be appreciable.

(ii) The atomic wave-functions are those derived by the Hartree method. These are the ones which it is customary to employ in X-ray scattering theory.* Recently McWeeny (1951) has discussed the use of analytical wave-functions in calculating scattering factors for stationary atoms, and in a later paper (1952) he deals with the effects of bonding.

An idea of the importance of the choice of wave-functions may be gained by comparing the value 847 e.Å^{-3}, calculated in § 4 for the stationary peak density, with the value 797 e.Å^{-3}, derived from analytical wave-functions of the form,

$$\psi_{1s}(\mathrm{r}) = g_1 \exp(-\gamma r)\,,$$
$$\psi_{2s}(\mathrm{r}) = g_2(r-\alpha) \exp(-\delta r)\,,$$

where $g_1, g_2, \alpha, \gamma, \delta$ are constants: the difference is about 6%. Now when $(\overline{u^2})^{\frac{1}{2}}$ is large, $\bar{\varrho}$ tends towards the asymptotic form (32), which is independent of the choice of wave-functions. Therefore it is reasonable to suppose that the error in $\bar{\varrho}$ due to any special choice of wave-functions tends to decrease as $(\overline{u^2})^{\frac{1}{2}}$ increases. It is probable then that the error in $\bar{\varrho}(0)$ caused by the assumption (ii) is not worse than, say, 5%.

(iii) Anharmonicity of the vibrations is neglected. The influence of this can be assessed only by a detailed analysis of the spectra of particular crystals. It is probably not important, provided that the amplitudes are not too large.

(iv) The motion is assumed to be isotropic. The effect of anisotropy has been discussed in § 5, where it was found to be small in the example which was examined.

(v) The density at the centre of one atom due to its neighbours has been neglected. This is justified if the bridge densities between the atom and each of its neighbours are small in comparison with the peak density, for the contribution to the peak from a neighbour is presumably much less than half the bridge density.

When all these sources of error have been taken into account, one may conclude that the accuracy of $\bar{\varrho}(0)$ corresponding to a given $(\overline{u^2})^{\frac{1}{2}}$ is probably not worse than 20% in the range covered by Table 2. It follows from equation (26) that the value of $(\overline{u^2})^{\frac{1}{2}}$ corresponding to a given $\bar{\varrho}(0)$ may be calculated with an accuracy not worse than about 10% in the same range.

Finally it may be remarked that the considerations of § 7 indicate that even a comparison between a thermally averaged electron density, such as that which has been computed in this paper, and an experimental density is of little value unless the latter has first been corrected for finite-series errors.

It is a pleasure to record my gratitude to Prof. C. A. Coulson, F.R.S., who suggested this problem to me, for his advice and encouragement throughout the course of the investigation. I am glad to have had an opportunity to discuss the problem with Dr D. W. J. Cruickshank, who first showed me the importance of the finite-series error. My thanks are also due to the University of London for the award of a Postgraduate Studentship and to King's College for a Layton Studentship, during the tenure of which the work was carried out.

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* Actually, the scattering factor for carbon tabulated by James & Brindley (1931), which is frequently used by crystallographers, was derived by interpolation from the Hartree-field scattering factors of various other atoms; the Hartree-field for carbon was not computed until several years later (Torrance, 1934). Moreover the JB factor is designed for the ground state, whereas it seems more reasonable on chemical grounds to consider the valence state, as has been done in this paper.

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The Crystal Structure of DL-Serine*

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The crystal structure of DL-serine has been determined by the use of complete data accessible with Cu $K\alpha$ radiation. A satisfactory trial structure was quickly obtained from a three-dimensional Patterson function by the application of a new method for interpreting these functions. This method, called the *Patterson superposition method*, is related to several other methods recently proposed, such as the vector convergence method of Beevers & Robertson, but differs from them in procedure and criteria employed.

The atomic parameters were refined by three-dimensional Fourier and least-squares procedures. Interatomic distances and interbond angles are close to those expected, and there is a satisfying system of hydrogen bonding throughout the crystal.

Introduction

Within the past decade and a half, determinations have been made in these Laboratories of the crystal structures of a number of amino acids and related substances by X-ray diffraction methods. The crystal structures of diketopiperazine (Corey, 1938), glycine (Albrecht & Corey, 1939), DL-alanine (Levy & Corey 1941), L_s-threonine (Shoemaker, Donohue, Schomaker & Corey, 1950), acetylglycine (Carpenter & Donohue, 1950), β-glycylglycine (Hughes & Moore, 1949) and hydroxy-L-proline (Donohue & Trueblood, 1952) have been determined, and the positional parameters for DL-alanine (Donohue, 1950) have been further refined. The bond distances and bond angles, modes of hydrogen bonding, and steric relationships of the molecules of these substances have been found very useful in the formation of conceptions and definite conclusions regarding the configurations of polypeptide chains in proteins (Corey & Donohue, 1950; Corey, 1940, 1948). These past investigations, together with the present one and others now in progress, are a part of a current program of research on the structure of protein molecules at this Institute. Because of its importance to the amino acid and protein program, DL-serine (α-amino-β-hydroxypropionic acid) received attention in these Laboratories first in 1942, when its unit cell and space group were determined (Lu, unpublished work). Continuation of that work was unsuccessful in revealing the structure, which did not appear to be amenable to treatment by the two-dimensional methods which were used.

In the investigation of the crystal structure of threonine (Shoemaker *et al.*, 1950) the use of the three-dimensional Patterson function enabled the determination of the approximate structure to be made in the face of a complexity that had defied two-dimensional methods and trial-and-error procedures. Consequently the decision was made to resume work on DL-serine with the intention of applying the three-dimensional Patterson method. This method led quickly to the approximate structure and was, moreover, also used to advantage in carrying out a preliminary refinement of parameters, thereby obviating altogether the use of Fourier projections and trial-and-error procedures for this purpose, since parameters of sufficient precision to justify immediate use of three-dimensional least-squares and Fourier refinement methods were obtained. These methods quickly converged to give the final atomic positional parameters.

Experimental

The DL-serine used in this work was prepared by Dr Roland N. Icke, and was made available to us by Prof. Carl Niemann of this Institute. Crystals for use

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