

symmetrical intensity distribution (§ 4, equations (7) and (8)) is verified as follows:

$$J(s) = 2 \int_0^{\infty} I(\sqrt{s^2 + y^2}) q(y) dy .$$

Equation (7) postulates

$$4 \int_0^{\infty} g(s) \int_0^{\infty} I(\sqrt{s^2 + y^2}) q(y) dy \cos 2\pi rs ds \\ = 2\pi \int_0^{\infty} sf(s) I(s) J_0(2\pi rs) ds . \quad (11)$$

Proceeding as in the case of equation (9) one finds for the left-hand side

$$4 \int_0^{\infty} z I(z) dz \int_0^{z^2} g(s) \cdot q(\sqrt{z^2 - s^2}) \frac{\cos 2\pi rs}{\sqrt{z^2 - s^2}} ds .$$

The integral in s yields

$$\int_0^{\pi/2} g(z \cos \varphi) q(z \sin \varphi) \cos(2\pi rz \cos \varphi) d\varphi .$$

If, as postulated in § 4,

$$g(z \cos \varphi) q(z \sin \varphi) = f(z)$$

this integral yields

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The Effect of Thermal Motion on the Estimation of Bond Lengths from Diffraction Measurements

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Diffraction studies of crystals locate the centroids or maxima of the distributions of atoms undergoing thermal motion, and separations computed from these positions cannot, in general, be interpreted directly as interatomic distances. Methods are presented for calculating the mean separation of two atoms given the isotropic or anisotropic temperature factor coefficients. In order to apply these methods, it is necessary that the joint distribution which describes the motion of the atoms in question be known or assumed.

The atomic coordinates resulting from a crystal structure analysis represent the maximum or the centroid of a distribution of scattering density arising from the combined effects of atomic structure and thermal displacement. It has been common practice to compute an interatomic distance as the distance between a pair of these 'atomic positions'. With improvement in the accuracy of experimental techniques, it has be-

$$\frac{1}{2} \pi f(z) J_0(2\pi rz)$$

which confirms equation (7).

Equation (8) is easily verified by combining the above procedure with that adopted for equation (10).

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come clear that this estimate is valid only in the limit of negligibly small thermal displacements. For example, a discrepancy between spectroscopic and diffraction estimates of the C-C distance in benzene has been shown by Cox, Cruickshank & Smith (1955, 1958) to arise from the large rotatory oscillation of this molecule about its hexad axis. Cruickshank (1956a, 1961) has discussed in detail the effect of the oscillations of a rigid molecule on the positions of maxima in a density distribution, and consequently on the estimation of bond lengths. The present authors (Busing & Levy,

1957) have discussed the O-H distance in $\text{Ca}(\text{OH})_2$, using two methods to account for the effect of libration of the OH^- ion.

While it is clear that errors introduced by neglect of thermal effects will frequently be appreciable, it is seldom possible, on the basis of available information, to make the rigorously appropriate corrections. Specifically, a knowledge of the correlation in thermal displacements of the two atoms, that is their joint distribution, is needed, and this in general would require a detailed analysis of the dynamics of the atomic system. However, it frequently happens that useful estimates can be made from simplified models of the vibrating system, and these estimates may serve as acceptable approximations to the actual system; it is also possible to place rigorous upper and lower bounds upon the corrections.

It is proposed that a suitable measure of an interatomic distance is the mean separation, the average being taken over the joint distribution of the two atoms. This approach to the problem is *different in principle* from that taken by Cruickshank (1956a, 1961). Cruickshank seeks to establish the equilibrium position of the point of maximum scattering density of an individual atom, the correction being applied to the apparent position of maximum density. It is believed that the present treatment, in dealing with the mean separation of a pair of atoms, in contrast with the equilibrium position of an individual, often has the advantage of being closer to the physical problem of interest. Further, the use of the centroid, rather than the density maximum, is more nearly in accord with the atomic coordinates determined experimentally, at least if they are obtained by least-squares refinement. A consequence of the use of the density maximum in Cruickshank's treatment is the need for peak-shape parameters of the atom at rest; no such parameters enter into the present treatment. A general expression will be presented for the mean interatomic separation in terms of the parameters describing the distribution of instantaneous separation. Equations for upper and lower bounds to this mean will be derived. The result will then be specialized for two simple joint distributions, expressing the desired quantities in terms of the parameters of the individual atomic distributions. The application of the correction to the case of rigid-body rotary oscillation is next considered. Finally, the evaluation of the pertinent quantities in terms of temperature factor coefficients and in terms of principal-axis displacements is given.

The mean separation of two atoms

Let the distribution of the instantaneous separation \mathbf{S} of two atoms be described by the function $\varrho(\mathbf{S} - \mathbf{S}_0) \equiv \varrho(\mathbf{s})$, in which \mathbf{S}_0 represents the separation of the mean positions of the two atoms. For convenience, and without loss of generality, consider a cylindrical coordinate system with origin at $\mathbf{s}=0$ and cylinder

axis z in the direction of \mathbf{S}_0 . Then since $\mathbf{S} = \mathbf{S}_0 + \mathbf{s}$, and $S = [(S_0 + z)^2 + w^2]^{\frac{1}{2}}$, where w is the radial component of \mathbf{s} in this system, a Taylor-Maclaurin expansion of S yields

$$S = S_0 + z + w^2/2S_0 + \dots$$

The remaining linear and quadratic terms vanish identically. The mean interatomic separation obtained by averaging S over the distribution $\varrho(\mathbf{s})$ is then

$$\bar{S} = S_0 + \bar{w}^2/2S_0 + \dots$$

since $\bar{z} = 0$ if \mathbf{S}_0 is chosen as described above.

The error in terminating the series, approximately $(\bar{z}^3 - \bar{s}^2 z)/2S_0^2$, will be satisfactorily small in cases of interest. If $\varrho(\mathbf{s})$ is symmetric with respect to inversion through the origin, this remainder vanishes, and the next term is of the order of $\bar{s}^4/2S_0^3$.

It is clear that \mathbf{w} is the relative vector displacement of two atoms projected on the plane normal to the line of mean positions. The value of \bar{w}^2 will now be expressed in terms of quantities which are experimentally accessible; namely, the mean components of displacements of the atoms individually. While this can be done explicitly only by making a specific choice of the joint distribution function of the displacements of the individual atoms, the upper and lower bounds to \bar{S} may be derived without such a specification. Let \mathbf{w}_B and \mathbf{w}_A be the projected instantaneous displacement of the two atoms, so that $\mathbf{w} = \mathbf{w}_B - \mathbf{w}_A$ and

$$\bar{w}^2 = \bar{w}_B^2 - 2\overline{\mathbf{w}_B \cdot \mathbf{w}_A} + \bar{w}_A^2.$$

A well-known theorem of statistics places bounds upon the second term of the right-hand member; namely,

$$-(\bar{w}_B^2 \bar{w}_A^2)^{\frac{1}{2}} \leq \overline{\mathbf{w}_B \cdot \mathbf{w}_A} \leq (\bar{w}_B^2 \bar{w}_A^2)^{\frac{1}{2}}.$$

It follows that

$$w_L^2 \equiv [(\bar{w}_B^2)^{\frac{1}{2}} - (\bar{w}_A^2)^{\frac{1}{2}}]^2 \leq \bar{w}^2 \leq [(\bar{w}_B^2)^{\frac{1}{2}} + (\bar{w}_A^2)^{\frac{1}{2}}]^2 \equiv w_U^2$$

and

$$S_0 + w_L^2/2S_0 \leq \bar{S} \leq S_0 + w_U^2/2S_0.$$

Since the quantities involved are all observable, it is possible to place upper and lower bounds upon the mean separation of two atoms without any assumptions as to their correlated motion. The lower bound corresponds to highly correlated parallel displacements of the two atoms and the upper bound to highly correlated antiparallel displacements. Neither of these extremes is to be expected to describe the actual displacements of atoms in crystals.

We next present expressions for \bar{S} in two simple special cases which are, of course, intermediate between the foregoing extremes.

'Riding' motion

Let the vector separation be independent of the position of one of the atoms, A , and let this position be

expressed in terms of \mathbf{r}_A , the displacement of A from its mean position. Then the second atom B , at a position similarly defined by \mathbf{r}_B , will be distributed according to the convolution of the distribution function $\rho_A(\mathbf{r}_A)$ of the first atom with that of the separation vector, $\rho(\mathbf{s}) = \rho(\mathbf{r}_B - \mathbf{r}_A)$, for independence of \mathbf{r}_A and $\mathbf{r}_B - \mathbf{r}_A$ implies that the joint distribution of A and B is

$$\rho_J(\mathbf{r}_A, \mathbf{r}_B) = \rho_A(\mathbf{r}_A)\rho(\mathbf{r}_B - \mathbf{r}_A)$$

and, hence,

$$\rho_B(\mathbf{r}_B) = \int d\mathbf{r}_A \rho_J(\mathbf{r}_A, \mathbf{r}_B) = \int \rho_A(\mathbf{r}_A)\rho(\mathbf{r}_B - \mathbf{r}_A) d\mathbf{r}_A,$$

the convolution of ρ_A with ρ . It is shown in the Appendix that the mean-square components are additive on convolution so that

$$\overline{w^2} = \overline{w_B^2} - \overline{w_A^2}$$

and

$$\overline{S} = S_0 + (\overline{w_B^2} - \overline{w_A^2})/2S_0.$$

The 'riding' case may be expected to provide a useful model of atomic motion in a number of real situations. For example, if atom B is much lighter than atom A and is strongly linked only to A , the lighter atom may be thought to 'ride' on the heavier in the manner described. This situation occurs in hydrogenous crystals frequently. (Strictly, one must exclude the possibility of rigid-body rotations of A and B about a center removed from A and this will be discussed below.)

A related application of this case is the following: let A represent not an individual atom, but the center of mass of a reasonably rigid, isolated molecule, and let B represent an atom of the molecule. Atom B may then be described as 'riding' on the motion of the center of mass.

If the motion of the center of mass or of atom A should be very small, a possible condition at low temperature, then the motion of B would be described by this case with $\overline{w_A^2} = 0$.

Non-correlated motion

Let the positions of atoms A and B be distributed independently; then their joint distribution is

$$\rho_J(\mathbf{r}_A, \mathbf{r}_B) = \rho_A(\mathbf{r}_A)\rho_B(\mathbf{r}_B).$$

Let their relative displacement be $\mathbf{s} = \mathbf{r}_B - \mathbf{r}_A$. The distribution of \mathbf{s} is given by

$$\begin{aligned} \rho(\mathbf{s}) &= \int \rho_J(\mathbf{r}_A, \mathbf{s} + \mathbf{r}_A) d\mathbf{r}_A \\ &= \int \rho_A(\mathbf{r}_A)\rho_B(\mathbf{s} + \mathbf{r}_A) d\mathbf{r}_A \end{aligned}$$

which is the convolution of ρ_A with the inversion of ρ_B through its origin. Again invoking the general properties of convoluted distributions derived in the Appendix we have

$$\overline{w^2} = \overline{w_A^2} + \overline{w_B^2}$$

and

$$\overline{S} = S_0 + (\overline{w_A^2} + \overline{w_B^2})/2S_0.$$

This case is a description of the motion of non-interacting atoms and may be a reasonable approximation for non-bonded atoms in a molecular crystal.

Molecular libration

The case of molecular libration may correspond to large-amplitude correlated motion and therefore may often require appreciable corrections to interatomic distances. The mean separation may be computed in this situation provided the principal axes and amplitudes of rotation are known. Unfortunately, it is not possible, in general, to derive this information directly from observed quantities. A procedure usually applicable to rigid-body molecular motion has been described by Cruickshank (1956b).

Assume that such a procedure has been used to determine an axis defined by the unit vector \mathbf{a} about which a group of atoms involving the interatomic vector \mathbf{S} oscillates with mean square amplitude $\overline{\varphi^2}$. Then S_0 , the observed value of this interatomic distance, will be foreshortened by an amount which depends on $\overline{w^2}$, where w is the component perpendicular to \mathbf{S} of the change in \mathbf{S} produced by a small rotation φ . Since $d\mathbf{S}/d\varphi = \mathbf{a} \times \mathbf{S}$ is itself perpendicular to \mathbf{S} it follows that $\overline{w^2} = S^2 \sin^2 \psi \overline{\varphi^2}$, where ψ is the angle subtended by \mathbf{a} and \mathbf{S} . Then $\overline{S} = S_0 + \overline{\varphi^2} S_0 \sin^2 \psi / 2$, where S_0 has been substituted for the approximately equal quantity S . For independent oscillations about more than one principal axis, the corrections are additive.

Note on the correction of angles

Thermal displacements may be expected to produce distortions in apparent angles as well as distances. A sensible measure of an angle is its mean value over the joint distribution describing correlated motion of the three atoms involved, but the evaluation of this mean angle is a more complex problem than that of computing mean distances. It is to be emphasized that angles computed by triangulation from mean separations are not in general proper measures of mean angles. An extreme example is the case of a linear molecule undergoing pure bending motion: triangulation from mean separations will yield a non-linear configuration, while averaging over the proper joint distribution must, of course, give a 180° angle. Unless the atomic motion is correctly analyzed in detail, it appears preferable to compute angles from the uncorrected distances.

Evaluation in terms of temperature factor coefficients

Since the characteristic parameters of atomic distributions are usually available in the form of temperature

factor coefficients, the expression for $\overline{w^2}$ will be evaluated in these terms. For this purpose it is noted that $\overline{w^2} = \overline{r^2} - \overline{z^2}$ where r is the instantaneous displacement of the atom from its centroid, and z is the component of displacement parallel to the interatomic vector.

Let the anisotropic temperature factor be represented by the matrix β in which the elements β_{ij} are coefficients in the quadratic form

$$M = \sum_{i,j=1}^3 \beta_{ij} h_i h_j; \quad h_i = h, k, l.$$

In matrix notation,

$$M = \tilde{\mathbf{h}} \beta \mathbf{h}$$

in which the column matrix \mathbf{h} represents the three reciprocal-axis coordinates, h, k, l .

Let \mathbf{g} be the metric matrix with components $g_{ij} = \mathbf{a}_i \cdot \mathbf{a}_j$, the scalar products of the unit cell vectors. The quantity $\tilde{\mathbf{h}} \beta \mathbf{h} / 2\pi^2 \tilde{\mathbf{h}} \mathbf{g}^{-1} \mathbf{h}$ is the mean square component of displacement of the atom in the direction corresponding to \mathbf{h} . We desire this quantity for the direction of the interatomic vector separation \mathbf{S}_0 which will ordinarily be described in terms of the direct lattice components

$$\mathbf{S}_0 = \sum_{i=1}^3 S_{0i} \mathbf{a}_i.$$

The reciprocal axis components are given by the matrix product $\mathbf{g} \mathbf{S}_0$, where \mathbf{S}_0 represents the column matrix with components S_{0i} . Hence

$$\overline{z^2} = (\tilde{\mathbf{g}} \mathbf{S}_0) \beta (\mathbf{g} \mathbf{S}_0) / 2\pi^2 \tilde{\mathbf{S}}_0 \mathbf{g} \mathbf{S}_0,$$

or, in algebraic notation

$$\overline{z^2} = \sum_{i,j=1}^3 \beta_{ij} U_i U_j / 2\pi^2 \sum_{i=1}^3 S_{0i} U_i$$

where

$$U_i = \sum_{k=1}^3 (\mathbf{a}_i \cdot \mathbf{a}_k) S_{0k}.$$

The value of $\overline{r^2}$ is proportional to the sum of the eigenvalues, and hence to the trace, of the matrix $\beta \mathbf{g}$ (Busing & Levy, 1958) or

$$\overline{r^2} = \text{Tr}(\beta \mathbf{g}) / 2\pi^2$$

and $\overline{w^2}$ may be calculated.

In algebraic notation

$$r^2 = \sum_{i,j=1}^3 \beta_{ij} (\mathbf{a}_j \cdot \mathbf{a}_i) / 2\pi^2.$$

If the thermal motion of the atoms is known only in terms of isotropic temperature factors, $\overline{M} = B(\sin \theta / \lambda)^2$, the above expressions reduce to $\overline{w^2} = 2B/8\pi^2$.

Evaluation in terms of principal axis displacements

It may happen that a description of the atomic distributions in terms of principal axis displacements is available. Let μ_i^2 represent the mean square displacement parallel to principal axis i of the distribution, and let γ_i be the direction cosine of \mathbf{S}_0 with respect to this axis. Then

$$\overline{w^2} = \sum_{i=1}^3 (1 - \gamma_i^2) \mu_i^2.$$

Examples and discussion

It is again emphasized that proper application of the correction discussed in this paper, except for evaluating the bounds, calls for physical insight into the dynamics of the crystal, and this is not always possible to obtain. The considerations involved are illustrated in the following examples.

Calcium hydroxide. This crystal (Busing & Levy, 1957) contains discrete O-H groups, presumably ions, separated from each other and from Ca by distances great enough to preclude strong bonding. The hydrogen atom shows pronounced anisotropic displacements which are considerably greater than those of oxygen. In this situation, and in view of the 16-fold greater mass of oxygen, it is reasonable to suppose that three independent modes of motion obtain: (1) translational oscillations of the ion as a whole, (2) rotary oscillations about a pair of axes substantially passing through O and normal to O-H, and (3) stretching of O-H. All of these modes are encompassed by postulating that the displacements of H with respect to O are uncorrelated with those of O; in other words, H 'rides' upon O. Making use of the reported room-temperature parameters, the following values for the O-H distance are obtained:

| | |
|------------------|---------|
| Uncorrected: | 0.936 Å |
| Lower bound: | 0.956 |
| 'Riding' motion: | 0.983 |
| Upper bound: | 1.051 |

For the reasons given above, the value 0.983 Å is judged the best; however, it is of interest that the mean separation cannot be shorter than 0.956 Å, whatever the nature of the atomic motion.

The closest H-H distance in Ca(OH)₂ also provides an instructive example. The structure suggests that these atoms are in van der Waals contact. If it is supposed that the contact is a 'soft' one, that is, that the motion of one atom does not appreciably affect the motion of its neighbor, then the assumption of non-correlated displacements is appropriate. If, on the other hand, the contact is assumed to be 'hard' so that the atoms strongly repel each other and undergo correlated parallel motion, then the mean distance

approaches the lower bound which in this case is the same as the uncorrected separation. The values obtained follow:

| | |
|--------------------------------------|---------|
| Uncorrected distance or lower bound: | 2.201 Å |
| Uncorrelated motion: | 2.235 |
| Upper bound: | 2.279 |

It is of interest that even the upper bound is less than a nominal van der Waals contact of 2.34 Å.

Benzene. The structure of benzene (Cox, Cruickshank & Smith, 1958) illustrates the treatment of rigid-body oscillation and rotation. The thermal displacements are strongly anisotropic with principal components normal to the plane of the ring, radial to the ring and tangential to the ring. The large difference in magnitude between the tangential components and the others, together with the lack of restraining contacts in the structure, suggests a rotary oscillation of the molecule in its own plane. Most of the remaining motion may be assigned to translational oscillations of the molecule which are isotropic in the molecular plane, although this is no doubt something of an oversimplification. On this basis, the mean separation of two adjacent carbon atoms is computed as follows. We have $S_0=1.378$, and for libration about the hexad axis $\sin \psi=1$ and

$$\overline{\varphi^2} = (7.4 - 4.5) / 8\pi^2(1.378) = 0.0367 / 1.378.$$

Then $\overline{w^2} = 0.0367$, and the correction is 0.013 Å. A similar treatment of libration about axes in the plane of the molecule yields an additional correction of 0.001 Å and a mean distance of $\overline{S} = 1.392$ Å. Because hexagonal molecular symmetry is assumed, the lower bound is equal to the uncorrected value, 1.378 Å, and the upper bound, 1.56 Å, is clearly too large to correspond to a true separation. The value 1.392 is in agreement with Cruickshank's treatment, which makes parallel assumptions as to the nature and amplitude of the molecular rotation.

APPENDIX

Properties of convoluted distributions

Given two normalized distributions $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$, each with centroid at $\mathbf{r}=0$, their convolution is $\rho(\mathbf{r}) = \int \rho_1(\mathbf{s})\rho_2(\mathbf{r} \mp \mathbf{s})d\mathbf{s}$. The negative sign defines the convolution proper and is pertinent to the 'riding' case of the text; the positive sign defines the convolution of ρ_1 with the inversion of ρ_2 and is pertinent to the case of uncorrelated motion. Let z be any Cartesian component, $z = \mathbf{r} \cdot \mathbf{k}$, where \mathbf{k} is a unit vector. Then averaging over the convolution:

$$\begin{aligned} \overline{z^2} &= \int (\mathbf{r} \cdot \mathbf{k})^2 \rho(\mathbf{r}) d\mathbf{r} = \int (\mathbf{r} \cdot \mathbf{k})^2 \int \rho_1(\mathbf{s})\rho_2(\mathbf{r} \mp \mathbf{s}) d\mathbf{s} d\mathbf{r} \\ &= \int \rho_2(\mathbf{u}) \int (\mathbf{u} \cdot \mathbf{k} \pm \mathbf{s} \cdot \mathbf{k})^2 \rho_1(\mathbf{s}) d\mathbf{s} d\mathbf{u} \\ &= \int \rho_2(\mathbf{u}) \int [(\mathbf{u} \cdot \mathbf{k})^2 \pm 2(\mathbf{u} \cdot \mathbf{k})(\mathbf{s} \cdot \mathbf{k}) + (\mathbf{s} \cdot \mathbf{k})^2] \rho_1(\mathbf{s}) d\mathbf{s} d\mathbf{u} \\ &= \int \rho_2(\mathbf{u}) [(\mathbf{u} \cdot \mathbf{k})^2 \pm 2(\mathbf{u} \cdot \mathbf{k})\overline{z_1} + \overline{z_1^2}] d\mathbf{u} \\ &= \overline{z_2^2} \pm \overline{z_1^2} \end{aligned}$$

since $\overline{z_1} = \overline{z_2} = 0$.

Because z is any Cartesian component, the same consideration applies to x and y ; hence

$$\overline{r^2} = \overline{x^2} + \overline{y^2} + \overline{z^2} = \overline{r_2^2} \pm \overline{r_1^2}$$

and

$$\overline{w^2} = \overline{r^2} - \overline{z^2} = \overline{w_2^2} \pm \overline{w_1^2}.$$

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