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Least-Squares Estimates of Equivalent Isotropic Temperature Factors: An Application to H Atoms in Crystalline Sucrose

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An anisotropic harmonic oscillator has mean-square amplitudes of vibration U_1, U_2 and U_3. The geometric mean, $U_{\rm gm}$, is $(U_1U_2U_3)^{1/3}$ and the arithmetic mean $U_{\rm am}$, is $(U_1+U_2+U_3)/3$. It is shown that estimates of $U_{\rm iso}$ which minimize the least-square error of structure factors is bounded by the inequalities $U_{\rm gm}\le U_N\le U_X\le U_{\rm am}$ where U_N is the equivalent isotropic U for the neutron diffraction experiment and U_X is the corresponding estimate of $U_{\rm iso}$ for the X-ray diffraction experiment. The results have been applied to H atoms in sucrose where the U_1, U_2 and U_3 are taken from the neutron diffraction analysis of Brown & Levy [*Acta Cryst.* (1973). B**29**, 790–797]. It is found that $U_X\simeq 0{\cdot}75U_{\rm am}+0{\cdot}25U_{\rm gm}$. When U_X is compared to $U_{\rm iso}$ (X-ray) from Hanson, Sieker & Jensen [*Acta Cryst.* (1973). B**29**, 797–808], U_X's for the fourteen H atoms bonded to C atoms exceed $U_{\rm iso}$ (X-ray) by $\sim 0{\cdot}022$ Å^2 (or equivalently $\sim 1{\cdot}7$ Å^2 in B units, where $B=8\pi^2U$). A systematic trend for the eight hydroxyl hydrogens is not found; the average difference $U_X-U_{\rm iso}$ (X-ray) is $-0{\cdot}006$ Å^2. The discrepancy for H bonded to C is consistent with quantum-chemical calculations of small molecules; the apparent agreement of U_X and $U_{\rm iso}$ (X-ray) for H bonded to O may reflect the influence of hydrogen bonding in crystalline sucrose.

Introduction

It is desirable to compare atomic thermal parameters derived from neutron diffraction data to those obtained from X-ray diffraction analyses. Differences in the results have been interpreted as a deficiency in X-ray atomic form factors (Coppens, 1970). Presumably the charge cloud about the atom is sufficiently deformed by the molecular environment so that thermal parameters from X-ray data are not exclusively a function of the nuclear properties of the molecular crystal. For the case of bonded hydrogen atoms, isotropic temperature factors are spuriously low if free-atom form factors are used (Jensen & Sundaralingam, 1964; Mason, Philips & Robertson, 1965; Hvoslef, 1968). The use of a bonded-hydrogen-atom scattering factor (Stewart, Davidson & Simpson, 1965) generally gives larger thermal parameters.

Hanson, Sieker & Jensen (1973) have reported a detailed comparison of thermal parameters from X-ray and neutron (Brown & Levy, 1973) diffraction analyses of sucrose. In the X-ray refinement, isotropic temperature factors for the H atoms were introduced as least-squares parameters. In the neutron analysis, however, anisotropic temperature parameters were assigned to the protons. The question arises as to what is the equivalent isotropic temperature parameter from the neutron results which is to be compared to the X-ray result. Hanson *et al.* (1973) chose the arithmetic mean of the principal values of the neutron thermal ellipsoid tensor. In an earlier report, however, Hanson, Sieker & Jensen (1972) used the geometrical mean of the three principal values as the equivalent isotropic temperature parameter. Hamilton (1959) has shown that the arithmetic mean corresponds to an isotropic thermal motion with the same value of $\langle r^2\rangle$ as for the anisotropic harmonic oscillator. In the same paper it was acknowledged that this equivalent isotropic thermal parameter does not necessarily minimize the least-squares error. The geometrical mean is determinantinvariant. In this case the equivalent isotropic oscillator motion has the same total probability, $\langle 1 \rangle$, as the anisotropic oscillator. Or, stated in another way, this equivalent isotropic oscillator has the same sum of amplitudes of coherent X-ray scattering over an infinite Ewald sphere as does the anisotropic oscillator; that is,

$$\int \exp\left(-\tfrac{1}{2}U_{\text{iso}}S^2\right)\mathrm{d}\mathbf{S} = \int \exp\left[-\tfrac{1}{2}\left(U_1S_x^2 + U_2S_y^2 + U_3S_z^2\right)\right]\mathrm{d}\mathbf{S}\,.$$

But this U_{iso} also does not minimize the least-squares error. An analysis for the estimate of the equivalent isotropic temperature parameter that minimizes the least-squares error is given below.

Least-squares estimate of U_{iso}

In order to simplify the calculation it is assumed that the atom is at the origin of a cell and that the Ewald sphere is essentially infinite. It is further assumed that the X-ray and neutron data have the same statistical weights which at most decrease much less rapidly with $|\mathbf{S}|$ than do the intensities. The true amplitude of scattering for the anisotropic oscillator with atomic scattering factor $f(S)$ is $f(S)\exp\left(-\tfrac{1}{2}\mathbf{S}^t\mathbf{U}\mathbf{S}\right)$ where $\mathbf{S}$ is the Bragg vector with components $2\pi h, 2\pi k, 2\pi l$ and has magnitude $4\pi \sin\theta/\lambda$. The tensor $\mathbf{U}$ contains the mean-square amplitudes of vibration of the anisotropic oscillator. The equivalent least-squares isotropic oscillator has U_{iso} such that

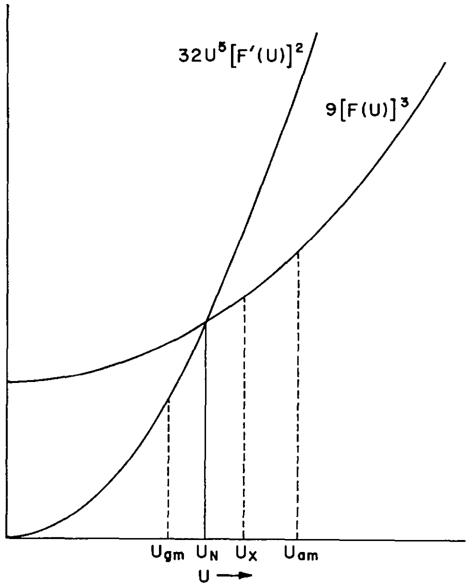

Fig. 1. Graph of the ninth-order polynomials from equation (3). U_N is the solution to (3). $U_{\text{gm}} = (U_1U_2U_3)^{1/3}$ and $U_{\text{am}} = U_1 + U_2 + U_3)/3$ are shown schematically. U_X is the solution to (2) for $[f(S)]^2$ a decreasing function with increasing S.

$$\varepsilon = \int [f(S)]^2\left[\exp\left(-\tfrac{1}{2}\mathbf{S}^t\mathbf{U}\mathbf{S}\right) - \exp\left(-\tfrac{1}{2}U_{\text{iso}}S^2\right)\right]^2\mathrm{d}\mathbf{S} = \text{minimum}\,. \quad (1)$$

By differentiating (1) with respect to U_{iso} and setting the result equal to zero,

$$\int [Sf(S)]^2 \exp\left[-\tfrac{1}{2}\left(\mathbf{S}^t\mathbf{U}\mathbf{S} + U_{\text{iso}}S^2\right)\right]\mathrm{d}\mathbf{S} - \int [Sf(S)]^2 \exp\left(-U_{\text{iso}}S^2\right)\mathrm{d}\mathbf{S} = 0\,. \quad (2)$$

It is clear from (2) or (1) that the value for U_{iso} depends on the nature of $f(S)$ as well as $\mathbf{U}$. First we consider the neutron case where $f(S)$ is a constant for all S. By straightforward integration of (2) and some tedious algebra it can be shown that (2), for $f(S) \equiv 1$, is,

$$32U^5[F'(U)]^2 - 9[(F(U)]^3 = 0 \quad (3)$$

where

$$F(U) = U^3 + (U_1 + U_2 + U_3)U^2 + (U_1U_2 + U_1U_3 + U_2U_3)U + U_1U_2U_3 \quad (4)$$
$$F'(U) = \mathrm{d}F/\mathrm{d}U$$

and U_1, U_2, U_3 are the principal values of $\mathbf{U}$. The ninth-order polynomial (3) has only one real and positive root since $U_1 \geq U_2 \geq U_3 > 0$. This is shown graphically in Fig. 1, where the root is denoted U_N. The left-hand side of (3) has a positive slope so U_N from (3) insures that (1) is a minimum. When U is taken as the arithmetic mean (U_{am}), then

$$32U_{\text{am}}^5[F'(U_{\text{am}})] \geq 9[F(U_{\text{am}})]^3 \quad (5)$$
$$U_{\text{am}} = (U_1 + U_2 + U_3)/3$$

and when U is the geometrical mean (U_{gm})

$$32U_{\text{gm}}^5[F'(U_{\text{gm}})] \leq 9[F(U_{\text{gm}})]^3 \quad (6)$$
$$U_{\text{gm}} = (U_1U_2U_3)^{1/3}\,.$$

The equalities in (5) and (6) hold when $U_1 = U_2 = U_3$. Thus we see that the least-squares estimate for the equivalent isotropic temperature factor in the neutron diffraction experiment is bracketed by the arithmetic and geometric means of the principal components of $\mathbf{U}$. The two means are schematically shown on the abscissa in Fig. 1.

For the X-ray diffraction case, $f(S)$ decreases with increasing S. If we approximate $f(S)$ with $\exp(-\alpha S^2)$ in (2) and take the limit of $\alpha \to \infty$, U_{iso} is the arithmetic mean, U_{am}. The solution to (2) from the X-ray diffraction experiment, U_X, is therefore between U_N and U_{am}. U_X is depicted schematically in Fig. 1. For a scattering factor that decreases relatively rapidly, such as the H atom, U_X will be rather closer to U_{am} than for a more extensive form factor such as for C or O atoms.

Hydrogen atoms in sucrose

As an example, the anisotropic thermal parameters for the 22 protons in sucrose have been analyzed. The thermal parameters, which are assumed to be correct, have been taken from the neutron diffraction results of Brown & Levy (1973). The principal values are tabulated in Table 1 under the headings U_1, U_2 and U_3. The arithmetic and geometric means are also listed. The mean-square amplitudes under U_N are the solutions to (3). These values are the least-squares estimates of the equivalent isotropic temperature factor for the protons from the neutron diffraction experiment. They are an estimate of the results Brown & Levy would find had they chosen to refine the protons as isotropic oscillators in a least-squares fit to observed structure factors. The column under U_X is a solution to (2) where $f(S)$ is a scattering factor for a bonded hydrogen atom. U_X are the values to compare to the corresponding isotropic U's from the X-ray results of Hanson, Sieker & Jensen (1973). For the rather moderate anisotropy in the motion of the protons in Table 1, $U_X \simeq 0{\cdot}75\ U_{\rm am}+0{\cdot}25\ U_{\rm gm}$. When the anisotropy is more extreme U_X is somewhat closer to $U_{\rm gm}$ (*e.g.* H(O4) in Table 1, $U_X=0{\cdot}64\ U_{\rm am}+0{\cdot}36\ U_{\rm gm}$).

The average U_X for H bonded to C from Table 1 is 0·04018 Å^2 and for H bonded to O, the average is 0·04697 Å^2. These estimates have $\bar{B}_{\rm iso}$ $(B=8\pi^2U)$ of 3·17 and 3·71, respectively, as compared to 3·23 and 3·84 reported in Table 6 by Hanson, Sieker & Jensen (1973). Thus the least-squares estimates are not greatly less than the equivalent isotropic temperature factor derived from the arithmetic mean. The average isotropic U for H bonded to C from Table 4 of Hanson, Sieker & Jensen (1973) is 0·018 Å^2 or $\bar{B}=1{\cdot}46$ and is not 1·33 as recorded in Table 6. A detailed comparison of Table 4 from Hanson, Sieker & Jensen with U_X in Table 1 here shows that for H bonded to C there is a systematic difference with $U_{\text{X-ray}} < U_X$. The average difference is $-0{\cdot}022$ Å^2 in U or $-1{\cdot}7$ in B. A similar comparison for H bonded to O does not show a systematic trend. For H(O3) and H(O4), $U_{\text{X-ray}} < U_X$; for H(O'1) and H(O'3), $U_{\text{X-ray}} = U_X$ and for the others $U_{\text{X-ray}} > U_X$, The average difference, $U_{\text{X-ray}} - U_X$, is 0·006 Å^2 or 0·45 in B units.

The hydrogen-atom scattering factor

The systematic discrepancy between $U_{\text{X-ray}}$ and U_X for H atoms bonded to C in sucrose probably reflects a deficiency in the bonded-H-atom scattering factor. It is of some interest to see if the discrepancy factor of 1·7 Å^2 in B units can be reconciled with quantum-chemical calculations. The difference $U_{\text{X-ray}} - U_X$ of $-1{\cdot}7$ Å^2 suggests that the charge density about the protons bonded to C atoms is more contracted than the charge density of H atoms in molecular hydrogen. The best floated spherical H-atom form factor from H_2 (Stewart, Davidson & Simpson, 1965) can be approximately represented by the Fourier–Bessel transform of a 1*s* orbital product with a ζ exponent of 1·16 bohr^{-1}. The 1*s* Slater-type orbital can be expanded with Gaussian functions by the method of least squares (Stewart, 1970). For the present discussion we will use a single Gaussian. In this case, the scattering factor for a 1*s* orbital product is simply,

$$f_{(1s)^2}=\exp\{-[2\pi^2a_0^2/(\alpha\zeta^2)]\,(\sin\theta/\lambda)^2\} \qquad (7)$$

where $a_0=0{\cdot}529177$ Å and $\alpha=0{\cdot}2709498091$ as taken from Stewart (1970). An estimate of ζ for the H atoms

Table 1. *Principal values of anisotropic thermal parameters for protons in sucrose, arithmetic and geometric means, and least-squares estimates of the equivalent isotropic mean-square amplitude of vibration*

Units in Å^2.

	U_1	U_2	U_3	$U_{\rm am}$*	$U_{\rm gm}$†	U_N	U_X
H(Cl)	0·03636	0·03056	0·02000	0·02898	0·02812	0·02839	0·02879
H(C2)	0·04453	0·04007	0·02039	0·03499	0·03313	0·03377	0·03459
H(C3)	0·05186	0·03684	0·02283	0·03718	0·03520	0·03582	0·03670
H(C4)	0·04926	0·03946	0·02444	0·03772	0·03621	0·03670	0·03736
H(C5)	0·04961	0·04055	0·02445	0·03821	0·03664	0·03715	0·03784
H(C6)	0·07681	0·05942	0·02528	0·05384	0·04869	0·05048	0·05255
H'(C6)	0·09225	0·04478	0·02868	0·05523	0·04911	0·05083	0·05337
H(C'1)	0·07063	0·04152	0·02118	0·04444	0·03960	0·04112	0·04319
H'(C'1)	0·05710	0·04331	0·02246	0·04096	0·03816	0·03909	0·04029
H(C'3)	0·03845	0·03247	0·02024	0·03039	0·02935	0·02968	0·03016
H(C'4)	0·03820	0·03692	0·01988	0·03166	0·03038	0·03081	0·03139
H(C'5)	0·04856	0·03558	0·02141	0·03518	0·03332	0·03391	0·03475
H(C'6)	0·08458	0·05221	0·02744	0·05474	0·04948	0·05114	0·05328
H'(C'6)	0·07212	0·05450	0·02201	0·04954	0·04423	0·04610	0·04827
H(O2)	0·05410	0·04465	0·02612	0·04163	0·03981	0·04041	0·04119
H(O3)	0·08558	0·03286	0·02699	0·04848	0·04234	0·04390	0·04658
H(O4)	0·18642	0·05267	0·02445	0·08785	0·06215	0·06905	0·07860
H(O6)	0·06430	0·04998	0·03749	0·05059	0·04939	0·04975	0·05025
H(O'1)	0·05796	0·03356	0·03051	0·04068	0·03900	0·03946	0·04021
H(O'3)	0·04872	0·03790	0·02438	0·03700	0·03557	0·03602	0·03666
H(O'4)	0·05136	0·04262	0·02072	0·03823	0·03566	0·03654	0·03766
H(O'6)	0·06035	0·04162	0·03293	0·04496	0·04357	0·04397	0·04458

* $U_{\rm am}=(U_1+U_2+U_3)/3$. † $U_{\rm gm}=(U_1U_2U_3)^{1/3}$.

bonded to C atoms in sucrose follows from the simple relation,

$$2\pi^2 a_0^2/(\alpha\zeta^2) = 2\pi^2 a_0^2/(\alpha\zeta_{\mathrm{SDS}}^2) - 1{\cdot}7 \qquad (8)$$

where $\zeta_{\mathrm{SDS}} = 1{\cdot}16$ bohr^{-1}. From (8) the value for ζ is $1{\cdot}23$ bohr^{-1}. This estimate is very close to the molecular optimized exponent of $1{\cdot}24$ bohr^{-1} reported by Hehre, Stewart & Pople (1969). We conclude from this analysis that an error of $-1{\cdot}7$ Å^2 in $B_{\text{X-ray}}$ for H atoms bonded to C is reasonable and is consistent with *ab initio* molecular-orbital calculations on a variety of small molecules that contain hydrogen and first-row atoms. It is not clear why a similar discrepancy for H atoms bonded to O in sucrose is not found. For $B_{\text{X-ray}} - B_X$ of $0{\cdot}45$ Å^2, the ζ exponent is $1{\cdot}14$ bohr^{-1}. From molecular-orbital calculations (Hehre, Stewart & Pople, 1969) one would expect ζ to be $\sim 1{\cdot}28$ bohr^{-1}. This would give rise to an error of $-2{\cdot}7$ Å^2 in $B_{\text{X-ray}}$. In the sucrose crystal, however, the H atoms in the hydroxyl groups are extensively hydrogen-bonded. It could well be that this perturbation makes the charge cloud about the proton rather more diffuse than for the isolated molecule. It is interesting to note that H(O4) has the largest negative value of $B_{\text{X-ray}} - B_X$ ($-1{\cdot}23$ Å^2) for the hydroxyl hydrogens. This hydrogen is the only non-hydrogen-bonded hydroxyl hydrogen in sucrose. For H(O3), $B_{\text{X-ray}} - B_X$ is $-0{\cdot}28$ Å^2 and for all other OH's the discrepancy is either zero or positive.

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Die Elektronendichte in Lithiumhydroxid (LiOH)

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The electron density in LiOH has been determined by X-ray diffraction. The intensities were measured on single-crystal plates and corrected for extinction, double reflexion and thermal diffuse scattering. The values found by integration over the electron density were 2·0 e in lithium (Li^+), 8·7 e in oxygen ($\mathrm{O}^{-0\cdot7}$) and 0·3 e in the hydrogen ($\mathrm{H}^{+0\cdot7}$). One electron is distributed over a wide range between the LiOH layers in the lattice.

Einleitung

Lithiumhydroxid bildet ein tetragonales Schichtgitter der Raumgruppe *P*4/*nmm*. Die Elementarzelle mit den Gitterkonstanten $a = b = 3{,}549$ und $c = 4{,}334$ Å enthält zwei Formeleinheiten LiOH. Die Lithiumatome liegen in der in Fig. 1 angegebenen Aufstellung in den Eckpunkten und auf der Mitte der Basisfläche, die Sauerstoffatome in $\frac{1}{2}0z(\mathrm{O})$ und $0\frac{1}{2}\bar{z}(\mathrm{O})$, die Wasserstoffatome in $\frac{1}{2}0z(\mathrm{H})$ und $0\frac{1}{2}\bar{z}(\mathrm{H})$, mit $z(\mathrm{O}) = 0{,}194$, $z(\mathrm{H}) = 0{,}407$. Die Lage- und Schwingungsparameter der Atome wurden von Dachs (1959) bestimmt, wobei gefunden wurde, dass die z-Komponenten der mittleren Schwingungsamplituden der Lithium- und Sauerstoffatome grösser sind als die Komponenten in der xy-Ebene. Für den Wasserstoffkern bestimmte Dachs erheblich grössere Schwingungsamplituden in Richtung x und y, die er als Drehschwingung der OH-Gruppe deutete.

Über die Ladung der Ionen liegen Informationen aus Kernquadrupolresonanzmessungen von Campbell & Coogan (1965) und von Coogan (1965) vor, die zu einem Modell mit zwei Elektronen im Bereich des Lithiums (Li^+), 8,7 Elektronen im Bereich des Sauerstoffs ($\mathrm{O}^{0{,}7-}$) und 1,3 Elektronen im Bereich des Wasserstoffs ($\mathrm{H}^{0{,}3-}$) führten. Die Ladungsverteilung in der OH-Gruppe wurde von Bader & Gangi (1971) quanten-