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Temperature Factors for Internuclear Density Units. 1. Theory in the Harmonic Approximation

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Expressions for the temperature factors of internuclear density units are derived in the harmonic approximation of lattice dynamics. The vibration tensors of internuclear density units are a linear combination of the vibration tensors of the adjacent nuclei and the corresponding coupling tensors. The coupling tensors cannot be determined by diffraction experiments but must be determined by other means. For molecular crystals, the coupling tensors for the internal modes can be calculated from a complete force-constant matrix, and the coupling tensors for the external modes can be determined by applying the model of rigid-body motions.

1. Introduction

In the experimental determination of electron density distributions, models with internuclear density units are often used for which temperature factors are needed, *e.g.* Hirshfeld & Rabinovich (1967); Brill, Dietrich & Dierks (1971); Coppens, Willoughby & Csonka (1971); Dietrich & Scheringer (1975). Since a bond peak between the nuclei cannot be attributed solely to any of the adjacent nuclei, one cannot expect the temperature factor of one of the adjacent nuclei to be appropriate. The purpose of this paper is to derive a general expression for the temperature factors of internuclear density units in the harmonic approximation of lattice dynamics.

2. Derivation of the temperature factors

One way of deriving the temperature factors for internuclear density units consists of a modification of the lattice-dynamical derivation of the Debye–Waller factors, such as given by Cochran & Cowley (1967). We have carried out this derivation, but the presentation of the general case becomes cumbersome. In this paper we use another approach which is shorter and leads to the same result. We start with the most general form of the dynamic density and derive the structure factors in the convolution approximation. Two assumptions will be made:

(1) The structure factor for any form of the density distribution in the crystal is the Fourier transform of the average density in the unit cell.

(2) The vibrations of the atomic nuclei are harmonic, *i.e.* in thermal equilibrium, the nuclei have a Gaussian distribution (Bloch, 1932; Maradudin, Montroll & Weiss, 1963).

The validity of the first assumption was proved by Marshall & Lovesey (1971, ch. 2) for neutron diffraction by crystals. If we replace the scattering potential for neutrons with the electron density distribution, we can adopt Marshall & Lovesey's proof for the diffraction of X-rays. Our derivation will show that the temperature factors for internuclear density units depend on the coupling of the nuclear vibrations. A by-product of our derivation will be a proof that the temperature factors of the nuclei do not depend on the internuclear vibrational coupling – a result which until now could only be established by means of lattice dynamics.

Within the limits of the Born–Oppenheimer approximation, we assume that the distribution of the bonding electrons rearranges itself instantly for every thermal configuration of the nuclear positions. The dynamic density of a molecule is the average of all densities which belong to the various configurations, positions and orientations of the molecule. Let the molecule have m nuclei; the m displacement vectors of the nuclei relative to their equilibrium positions are denoted by the vector $\mathbf{u}$. The frequency of the nuclear configuration $\mathbf{u}$ is $f(\mathbf{u})d\mathbf{u}$, and the respective density distribution at the position $\mathbf{x}$ is $\varrho(\mathbf{x},\mathbf{u})$. Then, the exact form of the dynamic density is

$$\varrho(\mathbf{x})_{\rm dyn} = \int_{-\infty}^{+\infty} \varrho(\mathbf{x},\mathbf{u}) f(\mathbf{u}) d\mathbf{u}. \tag{2.1}$$

$\varrho(\mathbf{x})_{\rm dyn}$ is uniquely defined for a given distribution function $f(\mathbf{u})$. In the convolution approximation, the total density distribution is divided into n rigid units, the kth unit being centred at the position $\mathbf{x}_k$. Its distribution is $\varrho_k(\mathbf{x}-\mathbf{x}_k)$. The dynamic density is then the average of all configurations of the vibrating rigid units, and (2.1) takes the form

$$\varrho(\mathbf{x})_{\rm dyn} = \sum_{k=1}^{n} \int_{-\infty}^{+\infty} \varrho_k(\mathbf{x}-\mathbf{x}_k-\mathbf{u}_k) f(\mathbf{u}) d\mathbf{u}. \tag{2.2}$$

$\mathbf{u}_k$ is the displacement vector of the kth unit from its equilibrium position. In contrast to the definition (2.1), the density is not determined solely by the distribution function $f(\mathbf{u})$. With (2.2), $\varrho(\mathbf{x})_{\rm dyn}$ depends also on the particular choice of the density units $\varrho_k(\mathbf{x}-\mathbf{x}_k)$ (number, size and shape).

In the harmonic approximation, the distribution function for a single nucleus r in thermal equilibrium is a Gaussian (Bloch, 1932), *i.e.*

$$f(\mathbf{u}_r)=(2\pi)^{-3/2}(\det \mathbf{U}_r)^{-1/2}\exp(-\tfrac{1}{2}\mathbf{u}_r^T\mathbf{U}_r^{-1}\mathbf{u}_r). \quad (2.3)$$

$\mathbf{U}_r$ is the 3×3 covariance matrix of the vector $\mathbf{u}_r$. If all the nuclei vibrate independently, $f(\mathbf{u})$ is given by

$$f(\mathbf{u})=\prod_{r=1}^{m} f(\mathbf{u}_r). \quad (2.4)$$

In a molecule, the nuclei usually do not vibrate independently; rather they are coupled to some extent. Then, in the harmonic approximation, $f(\mathbf{u})$ is a $3m$-dimensional Gaussian and is determined by the $3m\times 3m$ covariance matrix of the random vector $\mathbf{u}$. Hence, in the general case,

$$f(\mathbf{u})=(2\pi)^{-3m/2}(\det \mathbf{U})^{-1/2}\exp(-\tfrac{1}{2}\mathbf{u}^T\mathbf{U}^{-1}\mathbf{u}). \quad (2.5)$$

The difficulty in the further treatment of (2.2) and (2.5) is that the displacement vector $\mathbf{u}_k$ does not explicitly appear in the $3m\times 1$ displacement vector $\mathbf{u}$ of the nuclei. (2.2) can be worked out only if the relation between $\mathbf{u}_k$ and $\mathbf{u}$ is established and if the distribution function $f(\mathbf{u})$ is rewritten into the distribution function $f(\mathbf{u}_k)$. This program will form the essence of the following derivation.

We choose the general and primarily interesting case where the kth density unit is attached to several nuclei, say p, $p\le m$. For the displacement vector $\mathbf{u}_k$ we can assume a linear relation of the form*

$$\mathbf{u}_k=\sum_{r=1}^{p}\alpha_r\mathbf{u}_r,\quad \sum_{r=1}^{p}\alpha_r=1. \quad (2.6)$$

This means, physically, that the density unit k is 'carried along' with the p nuclei. The calculation of the coefficients α_r is discussed in §3. First we show that those parts of the covariance matrix $\mathbf{U}$ which belong to the $m-p$ non-relevant nuclei do not matter in the further calculation, even if the motions of the $m-p$ nuclei are coupled with those of the p relevant nuclei. In a second step, we show how the $3p\times 3p$ relevant submatrix of $\mathbf{U}$ contributes to the covariance matrix of the kth density unit. We combine the p displacement vectors $\mathbf{u}_r$ of the p relevant nuclei into a $3p\times 1$ column matrix $\mathbf{u}_p$, and formally describe the relation between $\mathbf{u}_p$ and $\mathbf{u}$ with a $3p\times 3m$ matrix $\mathbf{A}_p$ by the equation

$$\mathbf{u}_p=\mathbf{A}_p\mathbf{u}. \quad (2.7)$$

Now we refer to a theorem about the transformation of covariance matrices and Gaussian distribution functions (Linnik, 1961, p. 43). With (2.7) the covariance matrix $\mathbf{U}_p$ of the random vector $\mathbf{u}_p$ is given by $\mathbf{U}_p=\mathbf{A}_p\mathbf{U}\mathbf{A}_p^T$, and $\mathbf{u}_p$ is normally distributed. Inspection of this result shows that $\mathbf{U}_p$ is just the $3p\times 3p$ submatrix of $\mathbf{U}$, which belongs to the p relevant nuclei. The frequency of the random vector $\mathbf{u}_p$ is given by $f(\mathbf{u}_p)d\mathbf{u}_p$, where the integration over the displacement vectors of the $m-p$ non-relevant nuclei is assumed to have been carried out. This result is a generalization of the theorem that the marginal distributions of a multidimensional Gaussian distribution are equal to the corresponding one-dimensional distributions that are contained in the multidimensional Gaussian. We now apply the theorem about the transformation of covariance matrices and Gaussian distribution functions to $\mathbf{U}_p$ and $f(\mathbf{u}_p)$ with respect to the transformation (2.6). We obtain a 3×3 covariance matrix for the kth density unit according to

$$\mathbf{U}_k=\sum_{r=1}^{p}\sum_{r'=1}^{p}\alpha_r\alpha_{r'}\mathbf{U}_{rr'}, \quad (2.8)$$

and the displacement vector $\mathbf{u}_k$ is normally distributed as given by (2.3). $\mathbf{U}_{rr}$ is a 3×3 diagonal block and $\mathbf{U}_{rr'}$, $r'\ne r$, is an off-diagonal block of the covariance matrix $\mathbf{U}$. Instead of (2.2) we now obtain for the dynamic density

$$\varrho(\mathbf{x})_{\mathrm{dyn}}=\sum_{k=1}^{n}\int_{-\infty}^{+\infty}\varrho_k(\mathbf{x}-\mathbf{x}_k-\mathbf{u}_k)\times(2\pi)^{-3/2}(\det\mathbf{U}_k)^{-1/2}\exp(-\tfrac{1}{2}\mathbf{u}_k^T\mathbf{U}_k^{-1}\mathbf{u}_k)d\mathbf{u}_k. \quad (2.9)$$

Now we can derive the structure factor from (2.9). Let $\mathbf{h}$ be the vector in reciprocal space, and let the Fourier transform of $\varrho_k(\mathbf{x}-\mathbf{x}_k)$ with respect to the common origin be $g_k(\mathbf{h})\exp(2\pi i\mathbf{h}^T\mathbf{x}_k)$, and let the Fourier transform of $f(\mathbf{u}_k)$ with respect to the equilibrium position $\mathbf{x}_k$ ($\mathbf{u}_k=\mathbf{0}$) be $T_k(\mathbf{h})$. Fourier inversion of (2.9) yields

$$F(\mathbf{h})_{\mathrm{dyn}}=\sum_{k=1}^{m}g_k(\mathbf{h})T_k(\mathbf{h})\exp(2\pi i\mathbf{h}^T\mathbf{x}_k), \quad (2.10)$$

where

$$T_k(\mathbf{h})=\exp(-2\pi^2\mathbf{h}^T\mathbf{U}_k\mathbf{h}). \quad (2.11)$$

From its position in (2.10) we see that $T_k(\mathbf{h})$ is what is conventionally called the temperature factor. Hence, $\mathbf{U}_k$ is the vibration tensor of the kth density unit. For $p\ge 2$ not only the diagonal blocks of the covariance matrix $\mathbf{U}$, *i.e.* the vibrational tensors of the nuclei, contribute to $\mathbf{U}_k$ but also the off-diagonal blocks, *i.e.* the coupling tensors $\mathbf{U}_{rr'}$ (*cf.* 2.8). Thus, the temperature factors for the internuclear density units are also determined by the internuclear thermal coupling.

If, however, the density units are bound only to one nucleus, or are identical with the individual atoms, we obtain the known result for the structure factor: the coupling of the vibrations of the nuclei does not explicitly occur in the structure factor, since we have $p=1$, $\alpha_r=1$, and $\mathbf{U}_k=\mathbf{U}_r$. Thus, the off-diagonal blocks of the covariance matrix are ruled out, a result which

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* In the harmonic approximation only a linear relation is permitted. A non-linear relation, *e.g.* one containing the term $\beta\mathbf{u}_r.\mathbf{u}_r$, gives rise to deviations from the harmonic approximation for the displacements $\mathbf{u}_k$, if one assumes that the $\mathbf{u}_r$ satisfy the harmonic approximation. The normalization of the α_r in (2.6) arises from the condition that, in the limit $\mathbf{u}_k=\mathbf{u}_r$, the kth density unit is attached solely to the rth nucleus.

until now has only been established by means of lattice dynamics.

From (2.8) we can derive the general result that the vibration tensors of internuclear density units are smaller than the vibration tensors of the adjacent nuclei (except for the case of rigid translations). For this purpose we introduce the symmetric and positive definite tensors*

$$\mathbf{A}_{rr'}=\mathbf{U}_r+\mathbf{U}_{r'}-\mathbf{U}_{rr'}-\mathbf{U}_{r'r}, \tag{2.12}$$

(Scheringer, 1972*b*). We insert (2.12) into (2.8) and, after a reordering of terms, obtain

$$\mathbf{U}_k=\sum_{r=1}^{p}\alpha_r\mathbf{U}_r-\sum_{r=1}^{p}\sum_{r'=r+1}^{p}\alpha_r\alpha_{r'}\mathbf{A}_{rr'}. \tag{2.13}$$

The first term in (2.13) is the weighted average of the tensors $\mathbf{U}_r$. Since $\mathbf{A}_{rr'}$ is positive definite, a positive term is subtracted from this average. Neither the coupling tensors nor the tensors $\mathbf{U}_k$ can be determined from diffraction data; hence these tensors have to be determined by other methods.

The external modes of molecules in crystals can be represented by rigid-body motions. We shall now apply the methods used in this section to this model. A rigid body has not $3m$, but only six degrees of freedom, which can be described by three translation parameters $\mathbf{x}_t$ and three libration parameters $\boldsymbol{\varphi}$. The covariance matrix $\mathbf{U}$ being set up for the m nuclei of the molecule will become singular (of rank 6), and $\mathbf{U}^{-1}$ and $f(\mathbf{u})$ cannot be formed. Hence, the appropriate distribution function for the variables $\mathbf{x}_t$ and $\boldsymbol{\varphi}$ has to be used. The appropriate covariance matrix is

$$\mathbf{C}=\begin{pmatrix}\mathbf{T} & \mathbf{S}^T\\ \mathbf{S} & \mathbf{L}\end{pmatrix}, \tag{2.14}$$

and the displacement vector $\mathbf{u}_k^{\text{ext}}$ at the position $\mathbf{x}_k$ in the molecule is

$$\mathbf{u}_k^{\text{ext}}=\mathbf{x}_t-\mathbf{V}_k\boldsymbol{\varphi}. \tag{2.15}$$

$\mathbf{V}_k$ is an antisymmetric tensor and contains the components $\mathbf{x}_k$ in a Cartesian coordinate system. Applying the transformation law for covariance matrices and Gaussian distribution functions (Linnik, 1961) to (2.14) and (2.15) we obtain for the covariance matrix

$$\mathbf{U}_k^{\text{ext}}=\mathbf{T}+\mathbf{V}_k\mathbf{L}\mathbf{V}_k{}^T-\mathbf{V}_k\mathbf{S}-(\mathbf{V}_k\mathbf{S})^T, \tag{2.16}$$

and the displacement vector $\mathbf{u}_k$ is normally distributed according to (2.3) with $(\mathbf{U}_k^{\text{ext}})^{-1}$ in the exponent. If the density unit is attached to just one nucleus then (2.16) is identical with the result already derived by Schomaker & Trueblood (1968), and by Pawley (1968). Our derivation has the merit of being shorter than the derivations cited.

So far we have deliberately refrained from making use of any results of lattice dynamics. Now we would like to consider two points in the light of lattice dynamics. The coupling tensors $\mathbf{U}_{rr'}$ have been shown to be the off-diagonal blocks of the mean-square-amplitude matrix of the atoms in the unit cell (Scheringer, 1972*a*,*b*). Hence the coupling tensors can be calculated from the interatomic force constants or from the lattice frequencies and eigenvectors respectively. Furthermore, lattice-dynamical considerations confirm our linear relation (2.6). In the lattice-dynamical derivation of our results (2.8), we have used a corresponding linear approach, $\mathbf{u}(lk)=\Sigma\alpha_r\mathbf{u}(lr)$, for the displacements of the kth density unit in the lth cell. In the harmonic approximation, the equations of motion have a plane-wave solution for the displacements $\mathbf{u}(lr)$ of the nuclei. Only a linear relation yields a plane-wave description for the displacements $\mathbf{u}(lk)$. Thus, any non-linear approach for the displacements $\mathbf{u}(lk)$ violates the harmonic approximation.

3. Determination of the coefficients α_r

In the harmonic approximation we have to assume that the displacements $\mathbf{u}_r$ and $\mathbf{u}_k$ are small relative to the distances between the nuclei. For small variations $\mathbf{u}_r$ and $\mathbf{u}_k$, we can consider the α_r as constants. Putting $\mathbf{u}_r=d\mathbf{x}_r$, and $\mathbf{u}_k=d\mathbf{x}_k$, we obtain by integration of (2.6) from a common vector origin

$$\mathbf{x}_k=\sum_{r=1}^{p}\alpha_r\mathbf{x}_r,\quad \sum_{r=1}^{p}\alpha_r=1. \tag{3.1}$$

(3.1) is formally identical with the equation for the centre of gravity, whereby the α_r represent the 'masses' at the positions $\mathbf{x}_r$. We can interpret (3.1) so that the total mass of the density unit is distributed at the positions $\mathbf{x}_r$ with fractions α_r, whereby the centre of gravity of the density unit remains unchanged. With (2.6), the displacements $\mathbf{u}_k$ are then determined by the displacements $\mathbf{u}_r$ to the extent given by the mass fractions α_r at the positions $\mathbf{x}_r$. This determination of the $\mathbf{u}_k$ appears to be reasonable. (Such a picture of the dynamic behaviour of the density units is, of course, applicable only in the framework of the convolution approximation, and should not be conceived as being a physically exact statement about the dynamic behaviour of the bonding electrons.) In order to obtain the coefficients α_r, we first have to determine the centroid $\mathbf{x}_k$ of the density unit (by integration). From (3.1) we then obtain

$$\sum_{r=1}^{p-1}\alpha_r(\mathbf{x}_r-\mathbf{x}_p)=\mathbf{x}_k-\mathbf{x}_p \tag{3.2}$$

for the calculation of the $p-1$ unknown coefficients α_r. For $p=2$, the density unit should lie on the straight line through the two nuclei. For $p=3$ the three nuclei may not lie on a straight line, and the density unit should lie in the plane of the three nuclei. For $p=4$, the four nuclei may not lie in a plane, and for $p>4$, $p-4$

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* Since $\mathbf{U}_{r'r}=\mathbf{U}_{rr'}^T$, $\mathbf{A}_{rr'}$ is symmetric. From (3.2) and (3.3) of Scheringer (1972*b*) it follows that the diagonal components of $\mathbf{A}_{rr'}$ are positive, and are zero for the case of rigid translations. Since this holds true for any coordinate system, it also holds true for the system in which $\mathbf{A}_{rr'}$ is diagonal. Hence, $\mathbf{A}_{rr'}$ is positive (semi) definite.

coefficients α_r can be freely chosen. Hence, the covariance matrix $\mathbf{U}_k$ is not determined for the case $p>4$, and cannot, even when we know all the coupling tensors, be determined directly, but only with additional information about the α_r. If, for $p=2$, the density unit does not lie on the straight line through the two nuclei (bent two-centre bond), then the best we can do is calculate α_1 and α_2 from the point $\mathbf{x}_k$, which is the intersection of the straight line and the line through the centroid perpendicular to the straight line. A corresponding procedure should be used for a bent three-centre bond where the centroid of the density unit does not lie in the plane of the three nuclei. However, a unique solution for bent bonds can be derived from the model of rigid-body motions.

4. Determination of the coupling tensors

We restrict our discussion to the case of molecular crystals since the internuclear density units (overlap densities) appear mainly with molecules. With molecular crystals, one can often assume with reasonable certainty that the internal and external modes are separated and contribute separately to the vibration and coupling tensors. We shall make this assumption in the following.

The contribution of the internal modes $\mathbf{U}^{\text{int}}_{rr'}$ to the coupling tensors can be obtained from a complete force-constant matrix, but, for its determination, infrared and Raman measurements have to be made, possibly with several isotopic compositions of the molecule. However, there are two difficulties: firstly, the low-frequency modes make the largest contribution to the vibration tensors (Scheringer, 1972*c*), although their force constants can often be determined only with low accuracy. Secondly, for low temperatures, the vibration tensors are usually calculated with the matrix series expansion given by Cyvin (1968). At 100 K, this expansion is, however, only valid for frequencies smaller than 424 cm^{-1}, *i.e.* it does not hold for most of the high frequencies of the internal modes. Moreover, we found that the series converges badly (Fadini & Scheringer, 1977). A way out was indicated earlier, whereby the series expansion was circumvented (Scheringer, 1972*a*). The solutions of these difficulties are presently being studied with urea and thiourea (Fadini & Scheringer, 1977).

The external modes of the molecule can be described with the aid of the model of rigid-body motions which are described by the tensors **TLS**. For the coupling tensors $\mathbf{U}^{\text{ext}}_{rr'}$, and the tensors $\mathbf{A}^{\text{ext}}_{rr'}$, we obtain respectively

$$\mathbf{U}^{\text{ext}}_{rr'}=\mathbf{T}+\mathbf{V}_r\mathbf{L}\mathbf{V}^T_{r'}-\mathbf{V}_r\mathbf{S}-(\mathbf{V}_{r'}\mathbf{S})^T, \qquad (4.1)$$

$$\mathbf{A}^{\text{ext}}_{rr'}=(\mathbf{V}_r-\mathbf{V}_{r'})\mathbf{L}(\mathbf{V}_r-\mathbf{V}_{r'})^T, \qquad (4.2)$$

(Scheringer, 1972*b*). $\mathbf{V}_r$ is an antisymmetric tensor which contains the Cartesian coordinates of the rth nucleus, relative to an arbitrary origin. (4.2) and (2.13) show that an antiphase part which arises only from the librations of the molecule is subtracted from the average $\Sigma\alpha_r\mathbf{U}_r$. In actual practice, one must first determine the vibration tensors for the internal modes and subtract them from the tensors of the nuclei which have been determined experimentally, *i.e.* one should first calculate $\mathbf{U}^{\text{ext}}_r=\mathbf{U}_r-\mathbf{U}^{\text{int}}_r$, and then **TLS** from the $\mathbf{U}^{\text{ext}}_r$. (Omission of the procedure may be tolerated for room-temperature data where the internal modes contribute less than 10% to the vibration tensors.) In order to calculate the contributions of the external modes, one can select one of three possibilities, each of which has certain advantages and disadvantages:

(1) One uses (2.16). The advantage is that the α_r need not be known for the external modes; this is particularly favourable when there are difficulties in determining the α_r, *cf.* §3.
(2) One uses (2.13) and (4.2). The advantage is that only **L** (and the α_r) need be known, but not **T** and **S**. In this way one can prevent errors in **T** and **S** from falsifying the result.
(3) One uses (2.8) and (4.1). Here there are no advantages. [With the internal modes one is always forced to use (2.8) or, what is the same here, (2.12) and (2.13).]

In order to obtain the vibration tensors for the internuclear density units, one finally has to calculate, depending on the way the external modes were dealt with, $\mathbf{U}_k=\mathbf{U}^{\text{int}}_k+\mathbf{U}^{\text{ext}}_k$, or $\mathbf{A}_{rr'}=\mathbf{A}^{\text{int}}_{rr'}+\mathbf{A}^{\text{ext}}_{rr'}$, or $\mathbf{U}_{rr'}=\mathbf{U}^{\text{int}}_{rr'}+\mathbf{U}^{\text{ext}}_{rr'}$ respectively.

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