

sharpened Patterson map as the map to be shifted and a trial structure determination was carried out using the modified superposition approach described above. The resulting map readily identified the positions of all the larger atoms in the structure and the correct placement of the origin. (The midpoint of the diagonal vector coincided with the crystallographic center of symmetry.) Examination of the map revealed that of those 67 peaks greater than 70 in height on an arbitrary scale (with 435 as maximum) 74% of these corresponded to atoms in the structure (50 of the 64 atoms in the structure). A standard superposition using the same single vector (the diagonal) yielded 300 peaks over 70 in height on the same scale and only 21% of these corresponded to atoms in the structure.

As a second test case, $\text{Cp}_2\text{Fe}_2(\text{CO})_3\text{CS}$ [dicarbonylbis(η -cyclopentadienyl)- μ -carbonyl- μ -thiocarbonyldiiron] (Beckman & Jacobson, 1979*b*), another structure that had not previously been determined, was used. It contains 160 non-hydrogen atoms in a unit cell of $P2_1/c$ symmetry, *i.e.* 40 non-hydrogen atoms per asymmetric unit. Again a peak corresponding to a multiple vector was chosen from the sharpened Patterson map and a second shift-vector from the backshifted map. In this case the vector corresponding to the diagonal across the parallelogram did not contain the true inversion center and two images resulted. An additional vector was readily selected that belonged to one of these images and one further superposition using this vector yielded a map in which 87% of the peaks greater than 100 in height on an arbitrary scale corresponded to actual atomic positions.

Acta Cryst. (1979). A35, 340–342

X-ray Bragg scattering in the Born–Oppenheimer approximation. By C. SCHERINGER, *Institut für Mineralogie der Universität Marburg, D-3550 Marburg/Lahn, Federal Republic of Germany*

(Received 9 October 1978; accepted 10 November 1978)

Abstract

It is shown that for any type of motion of atomic nuclei the following hold in the Born–Oppenheimer approximation of the wave functions: (1) the structure factors for the Bragg intensities are given by the Fourier transform of the average density in the unit cell, (2) for the Bragg intensities, the Boltzmann weight factor of a thermal state appears as a factor of the amplitude (and not of the intensity).

The thermal motions of atomic nuclei constantly change the electron density distribution in a crystal. In electron density studies it is important to know which density distribution is related to the Bragg intensities. Marshall & Lovesey (1971) have shown, for neutron diffraction by crystals, that the Bragg intensities can be understood to be the coherent elastic scattering at average atomic nuclei, where the average is taken over all nuclear spin orientations and random isotope distributions in the crystal. One would expect that a corresponding result would hold for the thermal motions of the nuclei in the crystal. Marshall & Lovesey's

We have demonstrated that a modified Patterson superposition using multiple vectors is a viable method for obtaining a good trial structure and is especially applicable to those structures where size and/or low symmetry inhibits solution by other conventional techniques. The method also involves a relatively minimal amount of computer time. A program listing is available on request.

This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Materials Sciences Division.

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(1971) calculation was carried out in the convolution approximation, which holds rigorously for atomic nuclei. But for X-ray diffraction on the electron density distribution in the crystal, the convolution approximation breaks down in the regions of the chemical bonds, since one cannot assume that these density regions move rigidly with any of the adjacent nuclei. Hence, for X-ray diffraction, our question concerning which density distribution gives rise to Bragg scattering is posed in a more general form. In this paper we shall discuss it within the limits of the Born–Oppenheimer approximation of the wave functions.

In the Born–Oppenheimer approximation we assume that the electron density distribution $\rho(\mathbf{x}, \mathbf{Q})$ rearranges itself instantly for every configuration \mathbf{Q} of the nuclear positions. Hence, the average density is given by

$$\rho(\mathbf{x})_{\text{av}} = \int \rho(\mathbf{x}, \mathbf{Q}) f(\mathbf{Q}) d\mathbf{Q}, \quad (1)$$

where the distribution function of the nuclear coordinates, $f(\mathbf{Q})$, is assumed to be normalized, *i.e.*

$$\int f(\mathbf{Q}) d\mathbf{Q} = 1. \quad (2)$$

Since the scattering of X-rays occurs much faster than the thermal motions of the nuclei, every configuration of the density in the crystal, $\rho(\mathbf{x}, \mathbf{Q})$, gives rise to a coherent scattering process with the amplitude $F(\mathbf{K}, \mathbf{Q})$, with $|\mathbf{K}| = 4\pi(\sin \theta)/\lambda$. Since there occurs an independent scattering at the various configurations of the density, the average density diffracted by the crystal is obtained by summing over the intensities of all elementary scattering processes; *i.e.* a formula corresponding to (1) also holds for the intensity

$$J(\mathbf{K})_{\text{av}} = \int J(\mathbf{K}, \mathbf{Q}) f(\mathbf{Q}) d\mathbf{Q}, \quad (3)$$

where

$$J(\mathbf{K}, \mathbf{Q}) = |F(\mathbf{K}, \mathbf{Q})|^2. \quad (4)$$

It is our aim to derive an expression from (3), which explicitly contains the Bragg intensity. We start from (4) and state that $F(\mathbf{K}, \mathbf{Q})$ is the Fourier transform of the density distribution $\rho(\mathbf{x}, \mathbf{Q})$. Since, by definition, the crystal is on the average periodic, $\rho(\mathbf{x})_{\text{av}}$ must be periodic. In other words: in a time long compared to the oscillation periods of the lattice waves the density configurations in each cell of the crystal will add up to the same average. Hence, the following representation for a given density configuration is expedient (Marshall & Lovesey, 1971):

$$\rho(\mathbf{x}, \mathbf{Q}) = \rho(\mathbf{x})_{\text{av}} + \Delta\rho(\mathbf{x}, \mathbf{Q}). \quad (5)$$

$\Delta\rho(\mathbf{x}, \mathbf{Q})$ denotes the non-periodic deviation from the average density at the position \mathbf{x} . With (5), we have, by definition,

$$\int \Delta\rho(\mathbf{x}, \mathbf{Q}) f(\mathbf{Q}) d\mathbf{Q} = 0, \quad (6)$$

for all values of \mathbf{x} . In order to make use of (4), we now form the Fourier transform of $\rho(\mathbf{x}, \mathbf{Q})$ with the aid of (5),

$$\begin{aligned} F(\mathbf{K}, \mathbf{Q}) &= \int \rho(\mathbf{x})_{\text{av}} \exp(i\mathbf{K} \cdot \mathbf{x}) d\mathbf{x} \\ &\quad + \int \Delta\rho(\mathbf{x}, \mathbf{Q}) \exp(i\mathbf{K} \cdot \mathbf{x}) d\mathbf{x} \quad (7) \\ &\equiv F(\mathbf{K})_{\text{av}} + \Delta F(\mathbf{K}, \mathbf{Q}), \end{aligned}$$

whereby $F(\mathbf{K})_{\text{av}}$ and $\Delta F(\mathbf{K}, \mathbf{Q})$ are defined. With (4) and (7) we now obtain

$$\begin{aligned} J(\mathbf{K}, \mathbf{Q}) &= F(\mathbf{K})_{\text{av}} F^*(\mathbf{K})_{\text{av}} + F(\mathbf{K})_{\text{av}} \Delta F^*(\mathbf{K}, \mathbf{Q}) \\ &\quad + F^*(\mathbf{K})_{\text{av}} \Delta F(\mathbf{K}, \mathbf{Q}) + \Delta F(\mathbf{K}, \mathbf{Q}) \Delta F^*(\mathbf{K}, \mathbf{Q}). \quad (8) \end{aligned}$$

With (3), we have to integrate over the nuclear coordinates \mathbf{Q} . The two middle terms in (8) then become zero, as can be seen by virtue of (6):

$$\begin{aligned} \int \Delta F(\mathbf{K}, \mathbf{Q}) f(\mathbf{Q}) d\mathbf{Q} \\ = \iint \Delta\rho(\mathbf{x}, \mathbf{Q}) f(\mathbf{Q}) d\mathbf{Q} \exp(i\mathbf{K} \cdot \mathbf{x}) d\mathbf{x} = 0. \quad (9) \end{aligned}$$

The first term in (8) does not depend on \mathbf{Q} and remains unchanged because of the normalization (2). Hence we obtain from (3) and (8)

$$J(\mathbf{K})_{\text{av}} = |F(\mathbf{K})_{\text{av}}|^2 + \int |\Delta F(\mathbf{K}, \mathbf{Q})|^2 f(\mathbf{Q}) d\mathbf{Q}. \quad (10)$$

The second term in (10) arises from the deviations from the periodic density distribution and thus describes a thermal diffuse scattering (TDS). The first term arises from the periodic average of the density distribution and, therefore, it

represents Bragg scattering. With the division of $F(\mathbf{K}, \mathbf{Q})$ performed in (7), we have

$$J(\mathbf{K})_{\text{Bragg}} = |F(\mathbf{K})_{\text{av}}|^2, \quad (11a)$$

$$F(\mathbf{K})_{\text{av}} = \int \rho(\mathbf{x})_{\text{av}} \exp(i\mathbf{K} \cdot \mathbf{x}) d\mathbf{x}. \quad (11b)$$

Thus, the structure factor for calculating the Bragg intensities is the Fourier transform of the average density in the unit cell. Having assumed this situation to hold, we published applications in earlier works (Scheringer, 1977a,b, 1978).

So far we have made use of the periodicity of the average density distribution, and a consideration of the possible energy exchanges is missing.* We should show that, in the Born-Oppenheimer approximation, Bragg scattering is purely elastic and TDS purely inelastic. Hitherto, derivations were given (on the basis of lattice dynamics) only in the harmonic approximation of the nuclear motions and in the convolution approximation of the density distribution (see *e.g.* Maradudin, Montroll & Weiss, 1963; Cochran, 1964; Cooper, 1970; Willis & Pryor, 1975); a more general derivation is not known to the author. In this paper, we cannot give a complete derivation, but we shall combine our general equation (10) with the key equations of lattice dynamics which were derived in the harmonic and convolution approximations, in order to establish part of a general derivation. The key equations are the conservation of quasi-momentum;

$$\left. \begin{aligned} \mathbf{K} &= 2\pi\mathbf{H} + \mathbf{q}, \\ \mathbf{q} &= \mathbf{q}_1 \text{ for one-phonon scattering,} \\ \mathbf{q} &= \mathbf{q}_1 + \mathbf{q}_2 \text{ for two-phonon scattering, etc.,} \end{aligned} \right\} \quad (12a)$$

and the conservation of energy

$$\hbar\omega = \hbar\omega_0 \pm \Delta E(\mathbf{q}), \quad (12b)$$

where $\Delta E(\mathbf{q})$ represents the energy for the annihilation (+) or creation (−) of one or several phonons. \mathbf{H} is a point in the reciprocal lattice, \mathbf{q}_i are the wave vectors of the phonons. Obviously, (12b) is generally valid. If we assume that (12a) is also generally valid, we can easily show that the first term in (10) only represents elastic scattering and the second term only inelastic scattering. For $\mathbf{q} = \mathbf{0}$ the scattering is, on the one hand, elastic and, on the other hand, (12a) now expresses Bragg's law. Hence, the first term in (10), which was identified to represent Bragg scattering due to the average periodic density distribution in the crystal, can only represent elastic scattering. It is extended into small regions around the reciprocal lattice points in which the first few side maxima of Laue's interference function have also to be included (James, 1948). For $\mathbf{q} \neq \mathbf{0}$ the scattering is purely inelastic, and (12a) means that intensity can only be observed between the reciprocal lattice points. Hence, the second term in (10), which was identified to represent TDS due to the deviations from periodicity, can only represent inelastic scattering [as long as no other sources of deviations from periodicity (structural imperfections) occur, which we do not consider here]. We suppose that (12a) is generally valid, since its simple form suggests that the only essential requirements are the periodicity of the average crystal and, classically, the occurrence of the Doppler effect. Calculations of TDS with anharmonic motions, but retaining the convolution approxi-

* This part of the paper was initiated by a correspondence with Professor R. F. Stewart, Groningen.

mation, were performed by Hahn & Ludwig (1961), Hahn (1961) and Ludwig (1967). In these papers, (12a) was not explicitly established, but it appears that anharmonicity changes the intensity distribution of TDS, but neither its location between the reciprocal lattice points nor its inelastic nature.

In a recent paper, Stewart (1977) posed the question whether, for the Bragg intensities, the Boltzmann factor of a thermal state has to be applied as a factor to the amplitude or to the intensity. For the harmonic approximation and the convolution approximation (rigid pseudo-atoms), Stewart has shown that the Boltzmann factor is a factor of the amplitude, in agreement with earlier work of Born (1942–1943), but he could not prove this generally. With our results above, a general proof can be given.

We insert (1) into (11b) and obtain

$$F(\mathbf{K})_{\text{av}} = \iint \rho(\mathbf{x}, \mathbf{Q}) f(\mathbf{Q}) d\mathbf{Q} \exp(i\mathbf{K} \cdot \mathbf{x}) d\mathbf{x}. \quad (13)$$

Performing the Fourier transformation in (13) we obtain

$$F(\mathbf{K})_{\text{av}} = \int F(\mathbf{K}, \mathbf{Q}) f(\mathbf{Q}) d\mathbf{Q}. \quad (14)$$

To introduce the Boltzmann weight factor, we write with Stewart (1977)

$$f(\mathbf{Q}) = \sum_n W_n |\chi_n(\mathbf{Q})|^2, \quad (15)$$

$$W_n = \exp(-E_n/kT) / \sum_n \exp(-E_n/kT). \quad (16)$$

Note that our $f(\mathbf{Q})$ is identical with Stewart's $t(\mathbf{Q})/\int t(\mathbf{Q}) d\mathbf{Q}$. $\chi_n(\mathbf{Q})$ are the normalized vibrational eigenfunctions, and E_n the eigenvalues of the Hamiltonian of the nuclear motions. We insert (15) into (14) and obtain

$$F(\mathbf{K})_{\text{av}} = \sum_n W_n \int \chi_n^*(\mathbf{Q}) F(\mathbf{K}, \mathbf{Q}) \chi_n(\mathbf{Q}) d\mathbf{Q}. \quad (17)$$

Inserting (17) into (11a) we obtain Stewart's equation (17). Thus, with (17) and (11a) we have shown that, for the Bragg intensities, the Boltzmann factor W_n is a factor of $F(\mathbf{K}, \mathbf{Q})$,

but not a factor of $|\int \chi_n^* F \chi_n d\mathbf{Q}|^2$. Hence, Stewart's alternative equation (21) is not valid for the Bragg intensities, and, since it is incompatible with Stewart's equation (17), it is generally not correct. In the general formula (3) for the average intensity, the weighting is transferred from $\rho(\mathbf{x}, \mathbf{Q})$ to the intensities; whereas, for the Bragg intensities, the Fourier transform relations (11b) and (13) cause the weighting to be transferred from $\rho(\mathbf{x}, \mathbf{Q})$ to the amplitudes.

In our derivation of (10), (11) and (17) no model of the thermal motions of the nuclei has been assumed. Rather, the physical basis is that a crystal must have a mean periodic density distribution. A general derivation of (12a) by means of lattice dynamics appears to be a difficult project, although it seems that the only essential requirement is also the periodicity of the average crystal.

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Acta Cryst. (1979). **A35**, 342

Crystallographic pedigree of organic compounds: erratum. By MASAO HAISA, *Faculty of Science, Okayama University, Tsushima, Okayama 700, Japan*

(Received 2 January 1979)

Abstract

In Haisa [*Acta Cryst.* (1978), **A34**, 753–759], to correct a printer's error, the first ten lines in the left-hand column on page 758 should be moved to the bottom of that column.

All information is given in the Abstract.