

the partial derivative of (B8) with respect to y is equal to (5). Therefore, we have two proofs that Borie is wrong in his argument.

It may be quite difficult to obtain any analytical expression for $I(x, y)$. But remember that we are only interested in the integral (6) often with an extra integration over the divergence angle ε . Therefore the correct procedure is to look for numerical approximations to the integral (6). In the case of strong absorption, we have shown (Becker & Coppens, 1974) that no general solution can be found. However, when $\mu\bar{T}$ is not too large, we have shown that most of the coupling between absorption and multiple scattering can be dealt with by using the general extinction expressions and just replacing the mean path length $\bar{T} = \bar{t}_1 + \bar{t}_2$ by its absorption-weighted value

$$\bar{T}_\mu = \frac{1}{A_\nu} \int dv T \exp(-\mu T) dv, \quad (9)$$

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Improved Corrections for Thermal Diffuse Scattering

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Abstract

Programs have been written to calculate TDS corrections from Long Wave eigenvectors and modelled frequency Dispersion of the acoustic branches (LWD approximation). Calculations on naphthalene crystals with neutral and with charged atoms were carried out to check the convergence of the lattice dynamical calculations and of the numerical integration procedures used in the programs.

1. Introduction

It has been shown by Kroon & Vos (1979; referred to as KV) that corrections of X-ray diffraction intensities for thermal diffuse scattering (TDS) can be calculated in very good approximation by the LWD method. This method has in common with the long-wave (LW)

where A is the absorption factor. When dealing with accurate structure-factor determination, such conditions are generally fulfilled.

In conclusion, very complicated expressions such as those derived by Borie, using Werner's method, are believed to be of little practical use. In contrast, I want to repeat that the method of point sources, which eliminates boundary conditions, is certainly of strong potential usefulness (Becker & Dunstetter, 1982).

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method that only acoustic branches are taken into account and that eigenvectors for $g = g(\text{small})$ are used for all values of the wave vector \mathbf{g} . In contradistinction to the LW method, the LWD method accounts for the real frequency dispersion $v_j(\mathbf{g})$ instead of taking the linear relation

$$v_j(\mathbf{g}) = v_j(\hat{\mathbf{e}}) g \quad (1)$$

where $\hat{\mathbf{e}}$ is a unit vector along \mathbf{g} and $v_j(\hat{\mathbf{e}})$ is the acoustic velocity along $\hat{\mathbf{e}}$ for branch j ($j = 1-3$).

Frequency dispersion curves and eigenvectors can, in principle, be obtained by inelastic neutron scattering. Long-wave eigenvectors can also be deduced from the elastic constants of the crystal considered (Wooster, 1962; Born & Huang, 1968). In favourable cases both quantities can be obtained by lattice dynamical calculations. Such calculations can, for instance, be made for crystals consisting of rigid-body molecules with uncharged atoms with the program *LATDYN* written by Kroon (1977).

The LWD method can easily be incorporated in programs which compute TDS corrections according
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to the LW method (see, for instance, Helmholtz & Vos, 1977; referred to as HV). The present paper describes the transformation of the LW program *TDS2* of Helmholtz (1975) to the LWD program *TDS2/3*, and gives the changes applied to the program *LATDYN* to make it suitable for rigid-body molecules with charged atoms. TDS calculations in the LWD approximation have been performed on naphthalene to check the convergence of the numerical procedures in the computer programs.

2. Theory

2.1. Total TDS contribution to a reflection

The volume in reciprocal space swept out by a scan is given by HV for the $\theta/2\theta$ and the ω scan methods. In good approximation this volume can be represented by a parallelepiped for their experimental conditions. The (long-wave) program *TDS2* divides this volume into pyramids. The TDS contribution $\alpha(\mathbf{H})|F_o(\mathbf{H})|^2$ to the intensity of a reflection \mathbf{H} is obtained by analytical integration over each pyramid and numerical integration over the pyramids. For definitions and symbols not defined here, see HV. For linear frequency dispersion (formula 1) and neglect of quantum effects, $\alpha(\mathbf{H}, \mathbf{g}) d\eta(\mathbf{g})$ for the pyramids around \mathbf{g} and $-\mathbf{g}$, each having solid angle $d\eta(\mathbf{g})$, is given by HV (formula 11):

$$\alpha^{\text{LW}}(\mathbf{H}, \mathbf{g}) d\eta(\mathbf{g}) = \frac{2kTV(\text{cell})}{M(\text{cell})} H^2 G \times \sum_{j=1}^3 \frac{|\hat{\mathbf{u}}_j(\hat{\mathbf{e}}) \cdot \hat{\mathbf{p}}|^2}{v_j^2(\hat{\mathbf{e}})} d\eta(\mathbf{g}) \quad (2)$$

with k Boltzmann's constant, T absolute temperature, $V(\text{cell})$ volume of cell, $M(\text{cell})$ formula weight of cell, $H = 2 \sin \theta / \lambda$ length of diffraction vector \mathbf{H} , G maximum value of \mathbf{g} for pyramid concerned, $\hat{\mathbf{u}}_j(\hat{\mathbf{e}})$ polarization vector of mode j for direction $\hat{\mathbf{e}}$, $\hat{\mathbf{p}}$ unit vector along \mathbf{H} .

The derivation of (2) shows that the factor $1/v_j^2(\hat{\mathbf{e}})$ arises from the integral

$$I_j^{\text{LW}}(G, \hat{\mathbf{e}}) = G^{-1} \int_0^G \frac{g^2 dg}{v_j^2(\hat{\mathbf{e}}) g^2} = \frac{1}{v_j^2(\hat{\mathbf{e}})}. \quad (3)$$

According to (1), $v_j(\hat{\mathbf{e}})g$ is the approximated value for $v_j(\hat{\mathbf{e}})$. If this approximation is abandoned, the integral $I_j^{\text{LW}}(G, \hat{\mathbf{e}})$ has to be replaced by

$$I_j^{\text{LWD}}(G, \hat{\mathbf{e}}) = G^{-1} \int_0^G [g^2/v_j^2(\mathbf{g})] dg. \quad (4)$$

For practical calculations we have approximated (4) by its series expansion in G

$$I_{j, \text{ser}}^{\text{LWD}}(G, \hat{\mathbf{e}}) = \sum_{m=0}^{m(\text{max})} C_{j,m}(\hat{\mathbf{e}}) G^m. \quad (5)$$

According to HV, formula (12) for each independent bounding plane $l(1-3)$ of the scanned volume parallelepiped, the solid angle $d\eta_{l,n}$ of the n th surface element $\Delta O_{l,n} \equiv \Delta O_l$ is given by

$$d\eta_{l,n} = (\Delta O_l \cos^2 \beta_{ln}) / G d_l, \quad (6)$$

where d_l is the distance from the centre of the parallelepiped to plane l . Replacement of $1/v_j^2(\hat{\mathbf{e}})$ in (2) by (5) and summation over all pyramids gives

$$\alpha^{\text{LWD}}(\mathbf{H}) = \frac{2kTV(\text{cell})}{M(\text{cell})} H^2 \sum_l \frac{\Delta O_l}{d_l} \sum_n \cos^2 \beta_{ln} \times \sum_{j=1}^3 |\hat{\mathbf{u}}_j(\hat{\mathbf{e}}) \cdot \hat{\mathbf{p}}|^2 \sum_m C_{j,m}(\hat{\mathbf{e}}) G^m. \quad (7)$$

2.2. The TDS contribution to the background of a reflection

For symmetrical scans the TDS at the beginning and the end of a scan is obtained as

$$d\alpha(\mathbf{H})/d[d_s(\mathbf{H})] \quad (8)$$

with $l = s$ indicating the bounding planes of the parallelepiped seen at the beginning and the end of the scan. The total TDS background amounts to

$$\alpha_B^{\text{LWD}}(\mathbf{H}) = 2d_s(\mathbf{H}) d\alpha(\mathbf{H})/d[d_s(\mathbf{H})] = \frac{2kTV(\text{cell})}{M(\text{cell})} H^2 d_s(\mathbf{H}) \Delta O_s \sum_n \frac{1}{G_n^2} \times \sum_{j=1}^3 |\hat{\mathbf{u}}_j(\hat{\mathbf{e}}) \cdot \hat{\mathbf{p}}|^2 \sum_m (1+m) C_{j,m}(\hat{\mathbf{e}}) G^m. \quad (9)$$

Note that for $I_{j, \text{ser}}^{\text{LWD}}(G, \hat{\mathbf{e}}) = C_{j,0}(\hat{\mathbf{e}}) = 1/v_j^2(\hat{\mathbf{e}})$ formulae (7) and (9) reduce to the LW formulae (13) and (16) in HV if the correction for quantum effects $F(Y_j) = 1$; $2d_s = L(\text{HV})$.

2.3. The net TDS contribution

The net fractional TDS contribution to a reflection is given by

$$\alpha^{\text{LWD}}(\mathbf{H}; \text{net}) = \alpha^{\text{LWD}}(\mathbf{H}) - \alpha_B^{\text{LWD}}(\mathbf{H}). \quad (10)$$

3. Computer programs

The following changes have made the program *LATDYN* (KV) suitable for rigid bodies with charged atoms: (1) extension of the minimization procedure with convergence acceleration according to Williams

(1971) for the functions $1/R$ and $1/R^6$; (2) consideration of complete molecules rather than atoms within a certain summation limit in the calculation of the dynamical matrix. The directions $\hat{\mathbf{e}}$ for which the curves $\nu_j(\hat{\mathbf{e}}, g)$ and the long-wave eigenvectors are calculated are approximately equally spaced over a hemisphere. From a number N , which is about equal to the total number of directions for a hemisphere, the polar angles χ_m and φ_{mn} for each direction (m, n) are taken as

$$\chi_m = \pi/(2N_x) + (m + 1)\pi/N_x$$

$$\varphi_{mn} = n\pi/N_\omega(m)$$

with

$$N_x = \text{Int}[(\pi N/2)^{1/2} + 0.9]$$

$$N_\omega(m) = \text{Int}(N_x \sin \chi_m + 0.9).$$

The frequency dispersion curves $\nu_j(\hat{\mathbf{e}}, g)$, either obtained from *LATDYN* or from experimental data, are transformed to the integrals $I_j^{\text{WD}}(G, \hat{\mathbf{e}})$ and the series expansions $I_{j, \text{ser}}^{\text{WD}}(G, \hat{\mathbf{e}})$ by the program *LATFIT*.

The program *TDS2* (HV) has been changed to *TDS2/3* to accept the coefficients $C_{j,m}(\hat{\mathbf{e}})$ and the long-wave eigenvectors. In *TDS2/3* each reflection has its own scanned volume and its own pyramids τ with

direction $\hat{\mathbf{e}}_\tau$. The program takes as constants $C_{j,m}(\hat{\mathbf{e}}_\tau)$ and eigenvectors $\hat{\mathbf{u}}_j(\hat{\mathbf{e}}_\tau)$ the data for the directions $\hat{\mathbf{e}}$ closest to $\hat{\mathbf{e}}_\tau$. Also, an option has been added which deduces the eigenvectors $\hat{\mathbf{u}}_j(\hat{\mathbf{e}})$ from elastic constants and uses experimental $\nu_j(g)$ curves.

The set of programs was checked by reproducing the *LWD* results published by KV; apart from a factor of 1.31 which forms an error in their normalization.

4. Application to naphthalene

The calculations were performed for the naphthalene structure described by KV. The interaction functions used for the lattice dynamical models are given in Table 1. The interaction constants, which were taken from Williams (1970, 1974), are not specifically adjusted to the experimental elastic constants of naphthalene. The results obtained by *LATDYN* and *LATFIT* (Table 1, Fig. 1) show that the crystal with charged atoms is 'harder' than the crystal with neutral atoms.

Calculation of $\nu_j(\hat{\mathbf{e}}, g)$ at g intervals of 0.005 \AA^{-1} has given dispersion curves which are within 0.1% equal to dispersion curves calculated for very small intervals (0.001 \AA^{-1}). For $m(\text{max}) = 6$, $I_j^{\text{WD}}(G, \hat{\mathbf{e}})$ is approximated within 0.2% by $I_{j, \text{ser}}^{\text{WD}}(G, \hat{\mathbf{e}})$.

Table 1. Results obtained by *LATDYN* and *LATFIT* for naphthalene crystals with neutral and with charged atoms

The axes E_1, E_2, E_3 are unit vectors along $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}$.						
Neutral		Charged		Neutral	Charged	
				Minimization		
Old version of <i>LATDYN</i> (6-exp) potential functions (Williams, 1970)		Modified version of <i>LATDYN</i> Charges: C $-0.179e$, H $+0.179e$, plus corresponding potential functions (Williams, 1974)		Limit	7.0 \AA	7.0 \AA
				Number of contacts	2260	2260. Reciprocal limit 0.7 \AA^{-1}
						Convergence constant 0.35
						Number of reciprocal-lattice vectors 506
Rotation with respect to Kroon & Vos (1979)						
E_1	E_2	E_3	E_1	E_2	E_3	
0.00	0.00	0.00°	1.08	-1.96	-0.11°	
				Lattice dynamical calculations		
				Limit	7.0 \AA	7.0 \AA
				Fragmented molecules		Completed molecules
				Number of contacts	2260	11016

Results for $\hat{\mathbf{e}}/[4E_1 + E_3]$; $\hat{\mathbf{u}}_j$ = component eigenvector

	Neutral			Charged		
	$j = 1$	$j = 2$	$j = 3$	$j = 1$	$j = 2$	$j = 3$
\hat{u}_x	-0.2192	0.0001	-0.9757	-0.1085	0.0000	-0.9941
\hat{u}_y	0.0000	1.0000	0.0001	0.0001	1.0000	0.0000
\hat{u}_z	0.9757	0.0000	-0.2192	0.9941	0.0001	-0.1085
C_0	0.3530E - 5*	0.2861E - 5	0.1634E - 5	0.3378E - 5	0.2045E - 5	0.1335E - 3
C_1	-0.7455E - 6	-0.3851E - 5	0.9872E - 5	-0.2130E - 6	-0.6671E - 6	-0.1140E - 6
C_2	0.2865E - 3	0.1407E - 2	-0.2762E - 2	0.6521E - 4	0.2274E - 3	0.6352E - 4
C_3	-0.1877E - 1	-0.1445E + 0	0.2445E + 0	-0.2102E - 2	-0.2115E - 1	-0.8751E - 2
C_4	0.8433E + 0	0.7313E + 1	-0.8761E + 1	0.7247E - 1	0.1014E + 1	0.5965E + 0
C_5	-0.1717E + 2	-0.1693E + 3	0.1209E + 3	-0.1178E + 1	-0.2229E + 2	-0.1725E + 1
C_6	0.1326E + 3	0.1492E + 4	-0.3604E + 3	0.7660E + 1	0.1842E + 3	0.1784E + 1

* E - 5 is equivalent to $\times 10^{-5}$.

For the case with charged atoms and 640 directions $\hat{\mathbf{e}}$, the total computing time for *LATDYN* plus *LATFIT* is 500 CPU s on a CDC CYBER 176 at the computing centre of the University of Groningen.

For the TDS calculations the following measuring conditions were applied: ω scan, crystal-slit distance 173 mm, slit height 4 mm, scan width $(0.844 + 0.50 \tan \theta)^\circ$, slit width 3 mm, $T = 100$ K. Numerical integrations were performed for approximately 300, 500 and 1000 independent pyramids per scanned volume. After it had been proven that for 500 independent pyramids the accuracy is better than 1%, all further calculations were carried out for 500 pyramids. Table 2 illustrates the influence of the change of the number (Nre) of directions $\hat{\mathbf{e}}$ on a hemisphere. For naphthalene with uncharged atoms convergence to a level of 1% is reached for $Nre \simeq 640$ and for naphthalene with charged atoms for $Nre \simeq 325$.

For a division of the scanned volume into 500 pyramids plus their symmetrically related ones, the average computing time for *TDS2/3* is 0.6 CPU s plus 1.2 IO s for each reflection, on a CDC CYBER 175.

In Table 3, for a series of reflections, $\alpha^{LWD}(\mathbf{H};net)$ and $\alpha^{LW}(\mathbf{H};net)$ values are given. The experimental elastic constants are taken from Aleksandrov, Belikova, Ryzhenkov, Teslenko & Kitaigorodskii (1963). Comparison of the LWD and LW values for the model with charged atoms shows that the differences between corresponding values vary from -7% (reflection 18,6,-8) to +3% (reflection 11,4,4). Larger differences are observed for the model with neutral atoms. Earlier calculations by KV for the model with neutral atoms have shown that the 'exact' lattice dynamical values are approached much better by the LWD than by the LW method. This shows that, especially for large scan angles, it is worthwhile to

apply the LWD rather than the LW approximation, if reasonable models for the frequency dispersion are available.

The $\alpha^{LW}(\mathbf{H};net)$ values obtained for the model with charged atoms show considerable deviations from the

Table 2. Influence of number (Nre) of $\hat{\mathbf{e}}$ vectors per hemisphere on $\alpha(\mathbf{H}; net)$ values

Nre is given at the top of each α column in parentheses

(a) Naphthalene with neutral atoms

h	k	l	$\sin \theta/\lambda$ (\AA^{-1})	α (325)	α (640)	α (1270)
7	1	5	0.751	0.235	0.298	0.300
8	9	0	0.946	0.399	0.433	0.431
10	7	6	1.160	0.696	0.784	0.789
18	6	-8	1.211	0.888	1.137	1.123

For 27 reflections $R(640/325) = \sum |\Delta\alpha|/\sum |\alpha| = 0.190$, $R(1270/325) = 0.189$ and $R(1270/640) = 0.008$

(b) Naphthalene with charged atoms

h	k	l	$\sin \theta/\lambda$ (\AA^{-1})	α (325)	α (640)
7	1	5	0.751	0.176	0.177
8	9	0	0.946	0.302	0.306
10	7	6	1.160	0.517	0.512
18	6	-8	1.211	0.702	0.695

For 27 reflections $R(640/325) = 0.006$

Table 3. $\alpha^{LWD}(\mathbf{H}; net)$ and $\alpha^{LW}(\mathbf{H}; net)$ values ($\times 10^3$) for naphthalene, from the lattice dynamical models ($Nre = 640$), and from experimental elastic constants

Results are given for the arbitrary set of reflections adopted by Kroon & Vos (1979) to present their results.

h	k	l	$\sin \theta/\lambda$ (\AA^{-1})	Model neutral		Model charged		Elastic constants
				LWD	LW	LWD	LW	LW
0	1	3	0.222	3	3	2	2	3
4	5	-1	0.490	50	46	38	37	33
2	5	3	0.518	64	61	49	49	33
1	6	-4	0.556	59	59	49	49	50
6	0	-10	0.581	64	67	60	60	83
6	6	-5	0.628	109	100	80	78	80
12	1	-6	0.735	231	176	150	141	125
9	5	-9	0.738	191	175	144	141	136
7	1	5*	0.751	298	354	177	180	88
8	2	4*	0.778	341	401	208	212	103
7	8	-10	0.892	274	283	229	230	240
10	0	4*	0.898	531	656	309	315	162
8	9	0	0.946	433	372	306	299	239
0	5	13	0.983	259	266	228	230	294
3	6	-14	0.997	246	248	240	242	337
11	4	4*	1.024	702	856	425	436	253
17	1	-11	1.040	700	647	427	400	367
12	9	-3	1.077	689	557	457	434	363
0	13	1	1.085	408	411	328	330	317
2	13	-5	1.121	440	443	355	358	355
15	7	-14	1.146	656	702	493	501	496
10	7	6*	1.160	784	881	512	524	350
1	14	-1	1.168	475	482	370	376	362
3	13	5	1.190	566	592	440	446	371
13	8	-16	1.191	576	600	482	487	546
4	13	-9	1.202	486	488	406	410	445
18	6	-8	1.211	1137	1023	695	645	519

* \mathbf{H} roughly parallel to $7\mathbf{E}_1 + 2\mathbf{E}_2 + 2\mathbf{E}_3$ (see text).

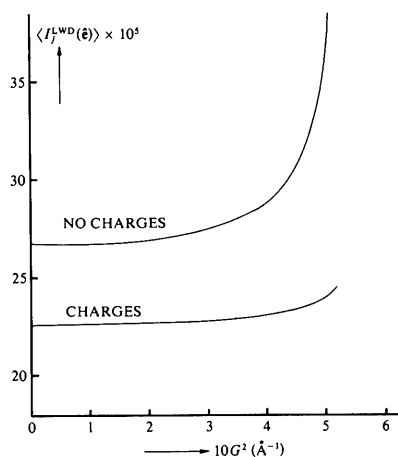


Fig. 1. $\langle I_j^{LWD}(\hat{\mathbf{e}}) \rangle$ averaged over j , for $\hat{\mathbf{e}}/[4\mathbf{E}_1 + \mathbf{E}_3]$ (for definition of $\mathbf{E}_1, \mathbf{E}_2, \mathbf{E}_3$ see Table 1).

$\alpha^{LW}(\mathbf{H};\text{net})$ values based on the experimental elastic constants (for neutral atoms the deviations are even larger). However, errors in the elastic constants strongly influence the $\alpha^{LW}(\mathbf{H};\text{net})$ values based on them. Changes of $\pm 25\%$ occur, if the elastic constants are changed by $\pm \sigma$ in a random way. Within this large experimental error $\alpha^{LW}(\mathbf{H};\text{net})$ for the charged-atom model shows reasonable agreement with the LW values calculated from the elastic constants for most reflections. Exceptions are the reflections with \mathbf{H} roughly parallel to $7\mathbf{E}_1 + 2\mathbf{E}_2 + 2\mathbf{E}_3$ (for definition of \mathbf{E}_1 , \mathbf{E}_2 and \mathbf{E}_3 , see Table 1), for which $\alpha^{LW}(\mathbf{H};\text{el})$ is relatively small.

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Incorporation of Experimental Phases in a Restrained Least-Squares Refinement

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Abstract

The least-squares refinement of macromolecular structures is characterized by a low ratio of observed data to refined parameters. Efforts have been made to compensate for this problem by incorporating subsidiary restraints into the observational equations. In this paper, a method is proposed and examples given for the introduction of additional observations into a least-squares refinement in the form of experimental phase information.

Introduction

The reciprocal-space least-squares refinement of atomic coordinates is becoming a routine procedure in the structure determination of macromolecules. The refinement of such structures is handicapped, however, by the comparatively low ratio of observed data to refined parameters. To increase the overdetermination of the refinement, efforts have been made to incorporate additional sources of information into the least-squares equations (Waser, 1963). These extra terms are generally in the form of molecular geometry restraints or constraints, using stereochemical data

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obtained from small-molecule structures. The quantity, Φ , minimized by the least-squares method may then be expressed as the sum of several terms:

$$\Phi = \sum \omega_h [|F_o| - |F_c|]^2 + \sum \omega_p (p_o - p_{\text{model}})^2, \quad (1)$$

where the first summation is the residual between observed and calculated structure factors, while the second summation contains the restraints between observed and model values for various stereochemical parameters. The weighting functions ω_h and ω_p control the contribution of each term to the least squares.

Traditionally, the role of experimental phases in a structure determination was limited to calculation of the electron density. Phases have been excluded from least-squares refinements, although inclusion of the experimental phases in a structure refinement could approximately double the number of observations. In addition, several protein structure refinements suggest that the experimental phases may indeed contribute useful information to the structure refinement. Phases calculated from a refined model agree more closely with the experimental phases than phases calculated from the preliminary model (Watenpaugh, Sieker, Herriot & Jensen, 1973; Rees, Lewis & Lipscomb, 1982).

Experimental phases usually contain significant random errors, but are free of systematic errors due to misinterpretation of the electron density map. We wish to demonstrate in this paper that by using appropriate selection criteria, experimental phases may indeed

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