

COMPUTER CALCULATIONS FOR A PERFECT CRYSTAL OF MULTIPOLES*

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Abstract — A general method is proposed, which tests have shown to be convenient, for the study of how the following quantities vary with molecular orientation at the lattice sites: (1) the potential produced by a perfect crystal of multipoles; (2) the interaction energy with a second multipole; (3) the self-energy and self-potential of a primitive lattice. To make a study of the variation with molecular orientation feasible, it has been necessary to decompose the calculation into three stages: stage Ia is a function solely of crystal geometry; stage Ib, which involves the most calculation, can be greatly shortened by the use of any molecular symmetry; stage II, which is very short compared with stage I, is the only one which requires a quantitative knowledge of the multipole moments, and, therefore, of the charge distribution. The form of the proposed procedure — the result of a study of the ice lattice — has been shown to reduce markedly the computation required and to permit convenient error checks. Numerical constants required for calculations of orders ≤ 5 are given.

1. INTRODUCTION

Many problems involving the interaction of forces arising from discrete or continuous charge distributions can be simplified by using a Taylor Series Expansion around a conveniently chosen reference point. For example, although the direct evaluation of the second virial coefficient is not feasible if part of the potential energy is assumed to arise from point charges within each molecule, the problem can be solved using multipoles which characterize the charge distribution (i.e., using a Taylor Series Expansion).⁽¹⁾

In the study of crystal structures, such an expansion permits a decomposition into the three stages specified in the abstract. In some cases, conclusions might then be deduced from stage I which depends solely upon crystal geometry and molecular symmetry. In any case, the segregation of all use of the uncertain data on the quantitative charge distribution to a final short step has been shown to make feasible the study of a range of models and parameters.

The object of the present paper is to present the general equations and techniques for a procedure which has been shown to reduce markedly the computation required and to permit convenient error checks. One form of the method is to be used when a single orientation is to be studied; a second form has been shown to be adapted to the study of sets of orientations.

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2. FORMULATION OF THE PROBLEM AND BASIC NOTATION

Consider two continuous or discrete charge distributions T_A and T_B contained in two nonintersecting closed spheres, C_A and C_B , centered at O_A and O_B , respectively. Since for each \mathbf{r}_α in C_A and \mathbf{r}_β in C_B $\|\mathbf{r}_\beta - \mathbf{r}_\alpha\|^{-1}$ possesses a Taylor Series at $\langle O_A, O_B \rangle$ which converges absolutely and uniformly, the interaction energy has a Taylor Series Expansion which it will be convenient to write in the form

$$E(\langle T_A, T_B \rangle) = \sum_{N=0}^{\infty} E^N(\langle T_A, T_B \rangle) \quad (1)$$

$$E^N(\langle T_A, T_B \rangle) = \sum_{n=0}^N E_{\langle n, N-n \rangle}^N(\langle T_A, T_B \rangle)$$

$E_{\langle n, N-n \rangle}^N(\langle T_A, T_B \rangle)$: the sum of all terms involving N th order partial derivatives, where n are evaluated at O_A and $(N - n)$ at O_B .

Moreover, it has been shown⁽²⁾ that n unit vectors, $\langle \mathbf{s}_{A,1}, \dots, \mathbf{s}_{A,n} \rangle$, can be found for T_A and $(N - n)$ for T_B , $\langle \mathbf{s}_{B,1}, \dots, \mathbf{s}_{B,N-n} \rangle$ such that the sum of all the Taylor Series terms in $E_{\langle n, N-n \rangle}^N$ can be replaced by a single term of the same form.* Thus, if \mathbf{s}_i denotes the i th member of a sequence formed from these vectors, then

$$E_{\langle n, N-n \rangle}^N(\langle T_A, T_B \rangle) = \frac{(-1)^{n_B} p_A^{(n)} p_B^{(N-n)}}{n!(N-n)!} \times \left\{ \prod_{i=1}^N (\mathbf{s}_i \cdot \nabla_\alpha) \|\mathbf{r}_\beta - \mathbf{r}_\alpha\|^{-1} \right\}_{\langle O_A, O_B \rangle} \quad (2)$$

$$= \frac{(-1)^{n_A} p_A^{(n)} p_B^{(N-n)}}{n!(N-n)!} \times \left\{ \prod_{i=1}^N (\mathbf{s}_i \cdot \nabla_\beta) \|\mathbf{r}_\beta - \mathbf{r}_\alpha\|^{-1} \right\}_{\langle O_A, O_B \rangle}$$

$$\nabla_{r_\gamma} \equiv \nabla_\gamma \equiv \langle \partial/\partial X_\gamma^1, \partial/\partial X_\gamma^2, \partial/\partial X_\gamma^3 \rangle \text{ (in rectangular Cartesian coordinates)}$$

$p_A^{(n)}, p_B^{(N-n)}$: scalars.

Conventionally, any term of this form is said to be an N th order interaction energy between an n th order multipole of moment $p_A^{(n)}$ and characteristic directions $\mathbf{s}_{A,1}, \dots, \mathbf{s}_{A,n}$ located at O_A and an $(N - n)$ th order multipole of moment $p_B^{(N-n)}$ and characteristic directions $\mathbf{s}_{B,1}, \dots, \mathbf{s}_{B,N-n}$ located at O_B , while the potential at O_B defined by the multipole at O_A is just $E_{\langle N,0 \rangle}^N$ with $p_B^{(0)} = 1$.

In the application of a Taylor Series Expansion to the calculation of the interaction energy between a given charge distribution and a lattice whose sites are centers of non-overlapping charge distributions, it is convenient to invert the order of limiting operations. First the terms for each order N are summed over the lattice sites, and then the results are summed over N . However, since the lattice sums for $N \leq 2$ converge only conditionally, it has been shown that the physically observed value for these orders must be computed using a summation order corresponding to the growth of a crystal of the physically specified shape.⁽⁴⁾ If the crystal has a shape parallel to the translation axes for the unit cell, then the series for $N = 1$ converges only if the unit cell has zero net dipole moment. It has been proven⁽⁴⁾ that the limits of the conditionally convergent series for $N = 1, 2$ of this shape as well as of the absolutely convergent series for higher orders can be computed as the unique sums given by the absolutely convergent series which occur in an extension of EWALD'S work,⁽⁵⁾ proposed (but not justified⁽⁴⁾) by KORNFELD⁽⁶⁾. Reasons why it is convenient to use this extension are discussed in Section 4.

The remainder of this section is devoted to the basic equations which are transformed into computationally useful forms in Section 3. To facilitate reference to a previous paper⁽⁴⁾ on the justification of the

* Explicit formulae are given for the special case $N = 2$.⁽³⁾

methods used here, the same notation is maintained here. In the proposed procedure the lattice is decomposed into sub-lattices, each of which is a simple (primitive) translation lattice in the sense that each site for the sub-lattice is equivalent to any other site. Consider the directional derivatives for the interaction between a multipole of order $n_{\mathbf{r}}$ located at

$$\mathbf{r} = \langle r_1, r_2, r_3 \rangle \quad (3)$$

and a crystal c of multipoles of order n_c , each with the same set of characteristic directions.

Let:

$\langle \mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3 \rangle$: vectors which define a unit cell for the crystal, c

$L = \langle L_1, L_2, L_3 \rangle$, an arbitrary ordered triple of integers

$$r_L = L_1 \mathbf{a}_1 + L_2 \mathbf{a}_2 + L_3 \mathbf{a}_3; \quad r_L = \|\mathbf{r}_L\|$$

\mathbf{r}_T : a vector whose endpoint lies at that site of the translation lattice, T , for which $L = \langle 0, 0, 0 \rangle$

\mathbf{b}_i : the vector reciprocal to \mathbf{a}_i , $i = 1, 2, 3$; i.e.,

$\mathbf{b}_i = (\mathbf{a}_j \times \mathbf{a}_k) / (\mathbf{a}_i \cdot \mathbf{a}_j \times \mathbf{a}_k)$, where $\langle i, j, k \rangle$ may undergo any cyclic permutation

$\mathbf{q}_L = 2\pi(L_1 \mathbf{b}_1 + L_2 \mathbf{b}_2 + L_3 \mathbf{b}_3)$, a vector of magnitude, q_L

$$\mathbf{R}_{L,T} = \mathbf{r} - (\mathbf{r}_L + \mathbf{r}_T); \quad R_{L,T} = \|\mathbf{R}_{L,T}\|. \quad (4)$$

It has been shown⁽⁴⁾ that under the stipulated hypotheses about summation order and dipole moment, the directional derivatives summed over the points of c can be computed as

$$\sum_{\{L\}} \left\{ \sum_{\{T\}} \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) R_{L,T}^{-1} \right\} = \sum_{\{T\}} \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) U_T'(\mathbf{r}, 0) \quad (5a)$$

$$U_T'(\mathbf{r}, 0) = U_{T,1}'(\mathbf{r}, 0, \epsilon) + U_{T,2}'(\mathbf{r}, 0, \epsilon) \quad (5b)$$

where \mathbf{r} is not a lattice point of T , and

ϵ : an arbitrary parameter with units of reciprocal distance (*cf.* Section 4) (6a)

$$U_{T,1}'(\mathbf{r}, 0, \epsilon) = \frac{4\pi}{(\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)} \sum'_{\{L\}} (q_L)^{-2} \times \exp[-(q_L)^2/4\epsilon^2 + i(\mathbf{q}_L \cdot \mathbf{r} - \mathbf{r}_T)] \quad (6b.1)$$

$$\sum'_{\{L\}} \text{ summation over } L \text{ such that } L \neq \langle 0, 0, 0 \rangle \quad (6b.2)$$

$$U_{T,2}'(\mathbf{r}, 0, \epsilon) = \sum_{\{L\}} G(\epsilon R_{L,T}) / R_{L,T} \quad (6c.1)$$

$$G(X) = 1 - \phi(X) \quad (6c.2)$$

$$\phi(X) = 2\pi^{-1/2} \int_0^X \exp(-\alpha^2) d\alpha \quad (6c.3)$$

The modification of equation (6) which is required when \mathbf{r} is a point of one of the translation lattices is given in Section (3.13).

3. DEVELOPMENT OF COMPUTATIONALLY USEFUL EQUATIONS

Since in practice there is little accurate information about charge distributions (i.e., about the coefficients of more than the first partial derivatives in the Taylor Series Expansion), it is desirable to conduct as much of the calculation as possible without using such data. Although this prohibits the reduction of $E_{(n,N-n)}^N$ the single term of equation (2), it may still be possible to use merely molecular symmetry to reduce the number of terms in the Taylor Series Expansion. For example, if a molecule has a symmetry plane, then for an expansion about a point in the plane, the moments involving odd numbers of characteristic directions perpendicular to the plane vanish. In any case, the Taylor Series Expansion allows the separation of the calculation into two stages:

Stage I: Calculations involving solely crystal geometry and molecular symmetry.

Stage II: Far shorter calculations involving the In general, define by induction, multipole moments and, therefore, a quantitative knowledge of the charge distribution.

The equations for stage I, which are developed in Section 3.1, are useful in the study of a single or a sufficiently small number of orientations of (6a) molecules centered at the lattice sites. However, as the number of molecular orientations increases, practice has shown that it is imperative to use equations developed in Section 3.2 which subdivide stage I:

Stage Ia: Calculations of 'crystal' constants which depend solely on crystal geometry;

Stage Ib: Calculations which involve the characteristic directions and, therefore, depend upon molecular symmetry.

Obviously, the particular number of orientations at which this decomposition becomes advantageous depends upon the particular lattice being studied.

3.1 Development of computationally useful equations for the study of a sufficiently small number of orientations

3.1.1. Recursion relations for directional derivatives of a function of a vector length; specialization for $U_{T,2}(\mathbf{r}, 0, \epsilon)$ and r^{-1} . It is convenient to develop the formulae for the directional derivatives of a general function of a vector magnitude since: (a) equation (5) requires explicit formulae for the directional derivatives of $U'_{T,2}(\mathbf{r}, 0, \epsilon)$ which depend only upon the magnitudes, $R_{L,T}$; (b) Appendix A requires the directional derivatives of another function of a vector length, r^{-1} .

Let:

$f(R)$: any function with derivatives of an arbitrary order

$$\mathbf{R} \equiv \mathbf{r} - \mathbf{r}'; \quad R \equiv \|\mathbf{R}\| \quad (7)$$

Then

$$(\mathbf{s}_1 \cdot \nabla_{\mathbf{r}})f(R) = [df(R)/dR] \cdot [(\mathbf{s}_1 \cdot \nabla_{\mathbf{r}})R] = \{R^{-1}[df(R)/dR]\} \cdot (\mathbf{s}_1 \cdot \mathbf{R}) \quad (8)$$

Let:

$$F_1(f) \equiv R^{-1} \cdot [df(R)/dR]. \quad (9a)$$

In general, define by induction

$$F_j(f) \equiv R^{-1}[dF_{j-1}[f(R)]/dR], \quad j \geq 2. \quad (9b)$$

First the successive directional derivatives for $f(R)$ will be given as functions of the $F_n(f)$. Then simple recursion relations will be given for the $F_n(f)$ for the two different $f(R)$.

Mathematical induction upon n shows that the successive directional derivatives can be written as the following linear combinations of the $F_j(f)$:

$$\prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) f(r) = \sum_{j=q}^N a_j^N(\{\mathbf{s}_k\}, \mathbf{R}) F_j(j) \quad (10)$$

$$q = \begin{cases} N \text{ odd} : & (N+1)/2 \\ N \text{ even} : & N/2 \end{cases}$$

To define the a_j^N , let

$$\eta_N : \text{set of all positive integers } \leq N \quad (11a)$$

$$D_j^N \equiv \{c_1(D_j^N), \dots, c_{N-j+1}(D_j^N)\} \quad (11b)$$

any set of subsets of η_N which satisfy the following four conditions :

(1) the subsets are disjoint

$$(2) \bigcup_{g=1}^{N-j+1} c_g(D_j^N) = \eta_N$$

$$(3) j = N : D_N^N = \{c_1(D_N^N)\}, c_1(D_N^N) = \eta_N$$

is a subset of two elements of η_N , which will be denoted by $\{k_1^g, k_2^g\}$

(4) $g = N - j + 1$:

N even, $j = q = N/2$: $c_{(N/2)+1}(D_{(N/2)}^N)$ is empty

otherwise: $c_{N-j+1}(D_j^N)$: a subset of $(2j - n)$ elements of η_N which will be denoted by

$$\{k_1^{N-j+1}, \dots, k_{2j-N}^{N-j+1}\}$$

$$C_j^N : \text{the class of all } D_j^N \text{ (i.e., no account is taken of the order of the first } (N - j) \text{ subsets)}. \quad (11c)$$

For each D_j^N define the products

$$j = N : P(D_j^N, \{\mathbf{s}_k\}, \mathbf{R}) = \prod_{k=1}^N (\mathbf{s}_k \cdot \mathbf{R}) \quad (11d.1)$$

$$j \neq N, j \neq N/2 : P(D_j^N, \{\mathbf{s}_k\}, \mathbf{R}) = \left[\prod_{g=1}^{N-j} (\mathbf{s}_{k_1^g} \cdot \mathbf{s}_{k_2^g}) \right] \times \prod_{g=1}^{2j-N} (\mathbf{s}_{k_f^{N-j+1}} \cdot \mathbf{R}) \quad (11d.2)$$

$$j = N/2 : P(D_j^N, \{\mathbf{s}_k\}, \mathbf{R}) = \prod_{g=1}^{N/2} (\mathbf{s}_{k_1^g} \cdot \mathbf{s}_{k_2^g}) \quad (11d.3)$$

Then mathematical induction upon N and finite induction upon j establishes the formula:

$$a_j^N(\{\mathbf{s}_k\}, \mathbf{R}) = \sum_{C_j^N} P(D_j^N, \{\mathbf{s}_k\}, \mathbf{R}). \quad (11e)$$

Thus, a_j^N is a sum of products formed from $(N - j)$ inner products, of the form $(\mathbf{s}_i \cdot \mathbf{s}_k)$, and $(2j - N)$ factors of the form $(\mathbf{s}_i \cdot \mathbf{R})$. The sum is made over all permutations which divide N indices into $(N - j)$ distinct unordered subsets of two elements each and another unordered subset of the remaining $(2j - N)$ elements. No account is taken of the ordering of the subsets.

The formulae for the $F_N(f)$ which occur in the derivatives of $U_{T,2}(\mathbf{r}, 0, \epsilon)$ will now be given. According to equation (6), $U_{T,2}(\mathbf{r}, 0, \epsilon)$ is a summation over $\{L\}$ of terms of the form:

$$g(R) \equiv [G(\epsilon R)]/R. \quad (12)$$

For $f(R) = g(R)$ differentiation and use of the definition (9) give

$$F_1(g) = -R^{-3}G(\epsilon R) - R^{-2}[2\epsilon/\sqrt{(\pi)}] \exp(-\epsilon^2 R^2) \quad (13a)$$

$$F_2(g) = -3R^{-5}G(\epsilon R) + 3R^{-4}[2\epsilon/\sqrt{(\pi)}] \exp(-\epsilon^2 R^2) + R^{-2}[2^2\epsilon^3/\sqrt{(\pi)}] \exp(-\epsilon^2 R^2) \quad (13b)$$

The latter equation can be rewritten in terms of elements of $F_1(g)$ as:

$$F_2(g) = \frac{-3F_1(g) + [(-2)^2\epsilon^3/\sqrt{(\pi)}] \exp[-\epsilon^2 R^2]}{R^2} \quad (13c)$$

The general recursive equation for $N \geq 2$ is:

$$F_N(g) = \frac{-(2N - 1)F_{N-1}(g) + [(-2)^N\epsilon^{2N-1}/\sqrt{(\pi)}] \exp[-\epsilon^2 R^2]}{R^2} \quad (13d)$$

The proof of (13d) by mathematical induction is immediate. According to (13c) it holds for $N = 2$ and differentiation shows that the hypothesis that it holds for $N = h$ implies that it is valid for $N = (h + 1)$.

Next, the equations will be given for the function $f(R) = R^{-1}$ whose directional derivatives define multipoles:

$$\begin{aligned} F_1(R^{-1}) &= -R^{-3}; \\ F_2(R^{-1}) &= 3R^{-5} = -3R^{-2}F_1(R^{-1}). \end{aligned} \quad (14a)$$

In general for $N \geq 2$

$$F_N(R^{-1}) = -(2N - 1)R^{-2}F_{N-1}(R^{-1}) = R^{-(2N+1)} \prod_{l=1}^N [-(2l - 1)]. \quad (14b)$$

3.1.2. *Equations when \mathbf{r} is not a lattice point of T .* Since the series converges absolutely and uniformly, the equations of the preceding section can be applied at once to obtain

$$\prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) U_{T,2}(\mathbf{r}, 0, \epsilon) = \sum_{j=q}^N \left\{ \sum_{\{L\}} a_j^N(\{\mathbf{s}_k\}, \mathbf{R}_{L,T}) F_j(g_{L,T}) \right\} \quad (15a)$$

$$g_{L,T} \equiv g(R_{L,T}) = G(\epsilon R_{L,T})/R_{L,T} \quad (15b)$$

$$F_j(g) : cf. \text{ equation (13)} \quad (15c)$$

$$q : cf. \text{ equation (10)}. \quad (15d)$$

Since $U'_{T,1}(\mathbf{r}, 0, \epsilon)$ is not solely a function of the magnitude of $\mathbf{r} - \mathbf{r}_T$, the formulae of the preceding section do not apply. However, mathematical induction applied to the differentiation of equation (6a) gives the desired formulae:

$$\prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) U'_{T,1}(\mathbf{r}, 0, \epsilon) = \begin{cases} N \text{ even} : & \frac{4\pi(-1)^{N/2}}{(\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)} \times \sum_{\{L\}}' \frac{\cos(\mathbf{q}_L \cdot [\mathbf{r} - \mathbf{r}_T]) [\exp[-(q_L)^2/4\epsilon^2]] \prod_{j=1}^N (\mathbf{q}_L \cdot \mathbf{s}_j)}{q_L^2} \\ N \text{ odd} : & \frac{4\pi(-1)^{(N+1)/2}}{(\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)} \times \sum_{\{L\}}' \frac{\sin(\mathbf{q}_L \cdot [\mathbf{r} - \mathbf{r}_T]) [\exp[-(q_L)^2/4\epsilon^2]] \prod_{j=1}^N (\mathbf{q}_L \cdot \mathbf{s}_j)}{q_L^2} \end{cases} \quad (16)$$

3.1.3. *Equations when \mathbf{r} is a lattice point, \mathbf{r}_{T_0} .* Consider now the case when \mathbf{r} is a lattice point so that there is a translation lattice $T = T_0$ for which $\mathbf{r} = \mathbf{r}_{T_0}$. The ‘self-energy’ is defined as the energy of interaction between a multipole at a lattice point and all other multipoles of a translation lattice. Similarly, the ‘self-potential’ is defined as the potential produced at a lattice point by all other multipoles of the translation lattice. Without loss in generality, suppose that the coordinate system has been so chosen that

$$\mathbf{r}_{T_0} = \mathbf{0} \quad (17)$$

Furthermore, as a first step in the calculation of the lattice sums of directional derivatives for the self-energy or the self-potential, suppose that the multipole at the origin, $\mathbf{r}_{T_0} = \mathbf{0}$, is displaced to $\mathbf{r} \neq \mathbf{0}$ which lies in a sphere containing no other lattice point except the origin. Then the summation over all sites but the origin can be computed as:

$$\begin{aligned} \sum_{\{L\}}' \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) \|\mathbf{r} - \mathbf{r}_L\|^{-1} &= \left\{ \sum_{\{L\}}' \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) \|\mathbf{r} - \mathbf{r}_L\|^{-1} \right\} - \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) r^{-1} \\ &= \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) [U'_{T_0,1}(\mathbf{r}, 0, \epsilon) + U_{T_0,2}(\mathbf{r}, 0, \epsilon) - R^{-1}] \\ &\quad \sum_{\{L\}}' : cf. \text{ equation (6b.2)}. \end{aligned} \quad (18)$$

Under the assumption that the right hand side is a continuous function of \mathbf{r} , the desired summation can be computed as the limit of equation (18) as $\mathbf{r} \rightarrow \mathbf{r}_{T_0} = \mathbf{0}$:

$$\left\{ \sum_{\{L\}}' \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) \|\mathbf{r} - \mathbf{r}_L\|^{-1} \right\}_{\mathbf{r}=\mathbf{0}} = \lim_{\mathbf{r} \rightarrow \mathbf{0}} \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) \times [U'_{T_0,1}(\mathbf{r}, 0, \epsilon) + U_{T_0,2}(\mathbf{r}, 0, \epsilon) - r^{-1}]. \quad (19)$$

In Appendix A it is shown that this limit is [cf. equations (A3, 11, 12)]:

$$\left\{ \sum_{\{L\}}' \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) \|\mathbf{r} - \mathbf{r}_L\|^{-1} \right\}_{\mathbf{r}=\mathbf{0}} = \begin{cases} N \text{ odd} : & \text{zero} \\ N \text{ even} : & \left\{ \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) [U'_{T_0,1}(\mathbf{r}, 0, \epsilon) + U'_{T_0,2}(\mathbf{r}, 0, \epsilon)] \right\}_{\mathbf{r}=\mathbf{0}} \\ & + R_{T_0,2}^N(\{\mathbf{s}_k\}, \epsilon) \end{cases} \quad (20a)$$

$$\left\{ \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) [U'_{T_0,1}(\mathbf{r}, 0, \epsilon)] \right\}_{\mathbf{r}=\mathbf{0}} = \frac{4\pi(-1)^{(N/2)}}{(\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)} \times \sum'_{\{L\}} q_L^{-2} \prod_{j=1}^N (\mathbf{q}_L \cdot \mathbf{s}_j) \exp[-q_L^2/4\epsilon^2] \quad (20b)$$

$$\left\{ \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) [U'_{T_0,2}(\mathbf{r}, 0, \epsilon)] \right\}_{\mathbf{r}=\mathbf{0}} = \sum_{j=q}^N \left\{ \sum'_{\{L\}} a_j^N(\{\mathbf{s}_k\}, \mathbf{R}_{L,T_0}) F_j(g_{L,T_0}) \right\} \quad (20c)$$

$$R_{T_0,2}^N(\{\mathbf{s}_j\}, \epsilon) = \frac{(-2)^{q+1} \epsilon^{(2q+1)} a_q^N(\{\mathbf{s}_k\})}{(2q+1)\pi^{1/2}} \quad (20d.1)$$

$$\sum'_{\{L\}} : cf. \text{ equation (6b.2)} \quad (20d.2)$$

$$q : cf. \text{ equation (10)} \quad (20d.3)$$

$$a_j^N : cf. \text{ equation (11)} \quad (20d.4)$$

$$F_j(g_{L,T_0}) : cf. \text{ equations (13, 15)}. \quad (20d.5)$$

3.2 Development of computationally useful equations for the study of a larger number of molecular orientations

The equations for one or a sufficiently small number of orientations were given in the preceding Section 3.1. To make calculations for larger numbers of orientations feasible, this section gives the equations for the stages la, b so that most of the computation involving crystal geometry will be done independently of orientation. For this purpose, it is necessary to expand the scalar products of equations (15, 16). To maintain generality the scalar products will be expressed using the contravariant and covariant vector components. The following sections giving the specific equations will use the standard sub- and superscript notation:

$$s_j^i \equiv i\text{th contravariant component of } \mathbf{s}_j$$

$$R_{L,T,i}, q_{L,i} \equiv i\text{th covariant components of } \mathbf{R}_{L,T}, \text{ and } \mathbf{q}_L, \text{ respectively.} \quad (21)$$

3.2.1. *Equations for the directional derivatives of $U_{T,1}$.* Consider first equations (16, 20b) for

$$\prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) U'_{T,1}(\mathbf{r}, 0, \epsilon)$$

Expansion of the scalar products gives:

$$\prod_{j=1}^N (\mathbf{q}_L \cdot \mathbf{s}_j) = \sum_{\{\{i_1, \dots, i_N\}\}} \left[\prod_{j=1}^N s_j^{i_j} \right] \cdot \left[\prod_{j=1}^N q_{L,i_j} \right] \quad (22)$$

$\{\{i_1, \dots, i_N\}\}$: the set of all ordered N -tuples which can be formed using the integers 1, 2, 3

Since $\prod_{j=1}^N (q_{L,i_j})$ is independent of the index j , it is convenient to regroup the terms of equation (22) to obtain

$$\prod_{j=1}^N (\mathbf{q}_L \cdot \mathbf{s}_j) = \sum_{\{\nu\}} (q_{L,1})^{\nu_1} (q_{L,2})^{\nu_2} (q_{L,3})^{\nu_3} \sigma(\{\mathbf{s}_j\}, \nu) \quad (23a)$$

$$\{\nu\} : \text{the set of all } \nu = \langle \nu_1, \nu_2, \nu_3 \rangle \text{ for which } \nu_1 + \nu_2 + \nu_3 = N \quad (23b)$$

$$\sigma(\{\mathbf{s}_j\}, \nu) = \sum_{\{\langle i_1, \dots, i_N \rangle\}_\nu} \prod_{j=1}^N s_j^{i_j} \quad (23c)$$

$\{\langle i_1, \dots, i_N \rangle\}_\nu$: the subset of $\{\langle i_1, \dots, i_N \rangle\}$ for which i_j has the value one for ν_1 distinct j , the value two for ν_2 distinct j , the value three for ν_3 distinct j .

Before substituting equation (23) into equations (16, 20b), it is desirable to regroup the terms of the latter to reduce the number of numerical operations by separating that part of the calculation (25) which depends only upon the magnitudes, q_L , from that part which depends upon the components, $q_{L,i}$.

Therefore, suppose $\{\mathbf{q}_L\}$ is divided into subsets of vectors of equal non-vanishing magnitudes:

$$C(M_1), C(M_2), \dots \quad (24)$$

M_i : the common magnitude of the \mathbf{q}_L in the subset $C(M_i)$.

Then substitution of equation (23) into equations (16, 20b) gives

$$\prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) U'_{T,1}(\mathbf{r}, 0, \epsilon) = \sum_{\{\nu\}} \sigma(\{\mathbf{s}_j\}, \nu) K_{T,1}^N(\nu, \mathbf{r}, \epsilon) \quad (25a)$$

$$K_{T,1}^N(\nu, \mathbf{r}, \epsilon) = B_N \sum_{\{M_i\}} P(\nu, \mathbf{r}, C(M_i)) M_i^{-2} \exp(-M_i^2/4\epsilon^2) \quad (25b)$$

$$\nu : \text{equation (23b)} \quad (25b.1)$$

$$B_N = \begin{cases} N \text{ even} : & [4\pi(-1)^{N/2}/(\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)] \\ N \text{ odd} : & [4\pi(-1)^{(N+1)/2}/(\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)] \end{cases} \quad (25b.2)$$

$$P(\nu, \mathbf{r}, C(M_i)) = \begin{cases} N \text{ even} : & \sum_{C(M_i)} \left[\prod_{i=1}^3 (q_{L,i})^{\nu_i} \right] \cos(\mathbf{q}_L \cdot [\mathbf{r} - \mathbf{r}_T]) \\ N \text{ odd} : & \sum_{C(M_i)} \left[\prod_{i=1}^3 (q_{L,i})^{\nu_i} \right] \sin(\mathbf{q}_L \cdot [\mathbf{r} - \mathbf{r}_T]) \end{cases} \quad (25b.3)$$

For $T = T_0$, $\mathbf{r} = \mathbf{r}_{T_0} = \mathbf{0}$, this reduces to

$$P(\nu, \mathbf{0}, C(M_i)) = \begin{cases} N \text{ even} : & \sum_{C(M_i)} \left[\prod_{i=1}^3 (q_{L,i})^{\nu_i} \right] \\ N \text{ odd} : & \text{zero} \end{cases} \quad (25b.4)$$

3.2.2. *Equations for the directional derivatives of $U_{T,2}(\mathbf{r}, 0, \epsilon)$.* While the preceding section developed the desired regrouping of terms in the directional derivatives of $U'_{T,1}(\mathbf{r}, 0, \epsilon)$, this section is devoted to the regrouping for $U_{T,2}(\mathbf{r}, 0, \epsilon)$. Each $a_j^N(\{\mathbf{s}_k\}, \mathbf{R}_{L,T})$, of equation (15) is a sum of products, $P(D_j^N, \{\mathbf{s}_k\}, \mathbf{R}_{L,T})$, defined by equation (11). As a first step in the regrouping, consider the factor $\prod_{j=1}^{2j-N} (\mathbf{s}_{k_f^{N-j+1}} \cdot \mathbf{R}_{L,T})$ of $P(D_j^N, \{\mathbf{s}_k\}, \mathbf{R}_{L,T})$ which occurs whenever $j \neq N/2$, N even. Expansion of the scalarproducts gives

$$j \neq N/2 : \prod_{j=1}^{2j-N} (\mathbf{s}_{k_f^{N-j+1}} \cdot \mathbf{R}_{L,T}) = \sum_{\{\langle i_1, \dots, i_{2j-N} \rangle\}} \left[\prod_{f=1}^{2j-N} s_{k_f^{N-j+1}}^{i_f} \right] \cdot \left[\prod_{f=1}^{2j-N} R_{L,T,i_f} \right] \quad (26)$$

$\{\langle i_1, \dots, i_{2j-N} \rangle\}$: the set of all ordered $(2j - N)$ -tuples such that $i_f = 1, 2$, or 3 .

Since the second factor in the sum is independent of any permutation of the k_f^{N-j+1} , it is convenient to define

$$s(c_{N-j+1}) \equiv \text{set of } s_{k_f^{N-j+1}} \text{ such that } k_f^{N-j+1} \text{ is in } c_{N-j+1}(D_j^N) \quad (27)$$

and to regroup the terms of equation (26) to obtain

$$j \neq N/2 : \prod_{f=1}^{2j-N} (s_{k_f^{N-j+1}} \cdot \mathbf{R}_{L,T}) = \sum_{H(\langle j, N \rangle)} \left[\prod_{i=1}^3 R_{L,T,i} \right]^{h_i} \sigma(\mathbf{s}(c_{N-j+1}), \mathbf{h}) \quad (28a)$$

$$\sigma(\mathbf{s}(c_{N-j+1}), \mathbf{h}) = \sum_{\{\langle i_1, \dots, i_{2j-N} \rangle\}_{\mathbf{h}}} \prod_{f=1}^{2j-N} s_{k_f^{N-j+1}}^{i_f} \quad (28b)$$

$$\{\langle i_1, \dots, i_{2j-N} \rangle\}_{\mathbf{h}} : \text{the subset of } \{\langle i_1, \dots, i_{2j-N} \rangle\} \text{ for which} \quad (28c)$$

$$i_f = 1 \text{ for } h_1 \text{ values of } f, 2 \text{ for } h_2 \text{ values of } f, \text{ and } 3 \text{ for } h_3 \text{ values of } f$$

$$H(\langle j, N \rangle) \equiv \text{set of all } \mathbf{h} = \langle h_1, h_2, h_3 \rangle \text{ such that } h_1 + h_2 + h_3 = 2j - N. \quad (28d)$$

It is convenient to introduce, notation for the products of the $(\mathbf{s}_\alpha \cdot \mathbf{s}_\beta)$ which occur as factors of the $P(D_j^N, \{\mathbf{s}_k\}, \mathbf{R}_{L,T})$. Define

$$\begin{cases} j = N : P(D_j^N, \{\mathbf{s}_k\}, \mathbf{R}_{L,T}) = 1 \\ j \neq N : P(D_j^N, \{\mathbf{s}_k\}, \mathbf{R}_{L,T}) = \prod_{g=1}^{N-j} (\mathbf{s}_{k_1^g} \cdot \mathbf{s}_{k_2^g}). \end{cases} \quad (29a)$$

Also, to simplify the writing of the equations, introduce the special definition:

$$j = N/2, \sigma(\mathbf{s}(c_{N/2+1}), \mathbf{0}) \equiv 1. \quad (29b)$$

Then, for all j :

$$a_j^N(\{\mathbf{s}_k\}, \mathbf{R}_{L,T}) = \sum_{H(\langle j, N \rangle)} \prod_{i=1}^3 [R_{L,T,i}]^{h_i} \times \left\{ \sum_{C_j^N} P(D_j^N, \{\mathbf{s}_k\}, \mathbf{R}_{L,T}) \sigma(\mathbf{s}(c_{N-j+1}), \mathbf{h}) \right\} \quad (30)$$

Before substituting equation (30) into equation (15), it is desirable to regroup terms to reduce the number of numerical operations. For this purpose, the vectors, $\mathbf{R}_{L,T}$, are partitioned into classes of equal non-vanishing magnitudes,

$$\mathcal{C}(\mathcal{M}_1), \mathcal{C}(\mathcal{M}_2) \dots \quad (30)$$

\mathcal{M}_i : the common magnitude of all vectors in $\mathcal{C}(\mathcal{M}_i)$.

Define the sum over $\mathcal{C}(\mathcal{M}_i)$:

$$K_{T,2}^N(\mathbf{r}, \mathbf{h}, \mathcal{M}_i) = \sum_{\mathcal{C}(\mathcal{M}_i)} \prod_{i=1}^3 (R_{L,T,i})^{h_i} \quad (32)$$

Then for each \mathbf{h} in $H(\langle j, N \rangle)$ define the sum over the set $\{\mathcal{M}_i\}$ required by equation (15):

$$K_{T,2}^N(\epsilon, \mathbf{r}, \mathbf{h}, j) = \sum_i K_{T,2}^N(\mathbf{r}, \mathbf{h}, \mathcal{M}_i) F_j[g(\mathcal{M}_i)] \quad (33)$$

g : cf. equation (15b).

Use of equations (15, 30, 32, 33) gives:

$$\begin{aligned} \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) [U_{T,2}(\mathbf{r}, 0, \epsilon)] &= \sum_{j=q}^N \left\{ \sum_{\{L\}} a_j^N(\{\mathbf{s}_k, \mathbf{R}_{L,T}\}) F_j(g_{L,T}) \right\} \\ &= \sum_{j=q}^N \sum_{H(\langle j, N \rangle)} K_{T,2}^N(\epsilon, \mathbf{r}, \mathbf{h}, j) \times \left\{ \sum_{C_j^N} P(D_j^N, \{\mathbf{s}_k\})(\mathbf{s}_{(C_{N-j+1})}, \mathbf{h}) \right\}. \end{aligned} \quad (34)$$

The preceding equation, which holds for general coordinate systems, requires a significantly greater number of numerical operations and greater amount of machine storage than the equations specialized for orthogonal Cartesian systems. Comparison of the general equation (34) with the special form which will now be developed will show that the latter is in general to be preferred even when the crystal axes are not orthogonal. Thus, it has been used in the calculations on ice discussed in Section 4, despite the fact that the lattice is hexagonal.

Since for orthogonal Cartesian systems, covariant and contravariant components are identical, it is convenient to expand the scalar products of the $P(D_j^N, \{\mathbf{s}_k\})$ of equation (29a) to introduce the $\sigma(\{\mathbf{s}_k\}, \nu)$ required for the directional derivatives of $U_{T,1}$. This gives

$$P(D_j^N, \{\mathbf{s}_k\})(\mathbf{s}_{(C_{N-j+1})}, \mathbf{h}) = \left\{ \sum_{\{\langle i_1, \dots, i_{N-j} \rangle\}} \prod_{g=1}^{N-j} s_{k_1^g}^{i_g} s_{k_2^g}^{i_g} \right\} \sigma(\mathbf{s}_{(C_{N-j+1})}, \mathbf{h}) \quad (35)$$

$\{\langle i_1, \dots, i_{N-j} \rangle\}$: set of all ordered $(N-j)$ -tuples such that for each g , $i_g = 1, 2$, or 3 .

Any one of the products can have the i th components of ν_i different \mathbf{s}_j as factors $\leftrightarrow \nu_i - h_i$ is an even positive integer or zero. Therefore, define

$$\begin{aligned} H(\langle j, N, \nu \rangle) &: \text{the subset of } H(\langle j, N \rangle) \text{ of equation (28d) for which } (\nu_i - h_i) \text{ is} \\ &\text{an even positive integer or zero for a fixed } \nu. \end{aligned} \quad (36)$$

Consider any ν which satisfies equation (23b) and any \mathbf{h} which satisfies equations (28d, 36), (i.e., \mathbf{h} in $H(\langle j, N, \nu \rangle)$). Then the summation of equation (34) over the D_j^N in the class C_j^N defined by equation (11) presents an elementary combinatorial problem which has as its solution:

$$\begin{aligned} \sum_{C_i^N} P(D_j^N, \{\mathbf{s}_k\}) \sigma(\mathbf{s}_{(C_{N-j+1})}, \mathbf{h}) &= \sum_{C_j^N} \left\{ \sum_{\{\langle i_1, \dots, i_{N-j} \rangle\}} \prod_{g=1}^{N-j} s_{k_1^g}^{i_g} s_{k_2^g}^{i_g} \right\} \times \sum_{\{\langle i_1, \dots, i_{2j-N} \rangle\}_{\mathbf{h}}} \prod_{f=1}^{2j-N} s_{k_f^i}^{i_{N-j+1}} \\ &= I(\nu, \mathbf{h}) \sigma(\{\mathbf{s}_k\}, \nu) \end{aligned} \quad (37a)$$

$$I(\nu, \mathbf{h}) = \prod_{i=1}^3 [\nu_i! / (2^{t_i} t_i! h_i!)] \quad (37b)$$

$$t_i = (\nu_i - h_i) / 2 \quad (37c)$$

Substitution of equation (37a) into (30) and use of the definition (36) for $H(\langle j, N, \nu \rangle)$ gives

$$a_j^N(\{\mathbf{s}_k\}, \mathbf{R}_{L,T}) = \sum_{\{\nu\}} \sigma(\{\mathbf{s}_k\}, \nu) \sum H(\langle j, N, \nu \rangle) I(\nu, \mathbf{h}) \prod_{i=1}^3 [R_{L,T,i}]^{h_i}. \quad (38)$$

The same procedure used in the case of the general coordinate systems now gives equations which have been broken down into convenient computational steps:

$$\prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) [U_{T,2}(\mathbf{r}, 0, \epsilon)] = \sum_{\{\nu\}} K_{T,2}^N(\nu, \mathbf{r}, \epsilon) \sigma(\{\mathbf{s}_k\}, \nu) \quad (39a)$$

$$K_{T,2}^N(\nu, \mathbf{r}, \epsilon) = \sum_{j=q}^N K_{T,2}^N(j, \nu, \mathbf{r}, \epsilon) \quad (39a.1)$$

$$K_{T,2}^N(j, \nu, \mathbf{r}, \epsilon) = \sum_i K_{T,2}^N(j, \nu, \mathbf{r}, \mathcal{M}_i) F_j[g(\mathcal{M}_i)] \quad (39a.2)$$

$$K_{T,2}^N(j, \nu, \mathbf{r}, \mathcal{M}_i) = \sum_{H(\langle j, N, \nu \rangle)} K_{T,2}^N(j, \nu, \mathbf{r}, \mathcal{M}_i, \mathbf{h}) \quad (39a.3)$$

$$K_{T,2}^N(j, \nu, \mathbf{r}, \mathcal{M}_i, \mathbf{h}) = I(\nu, \mathbf{h}) \sum_{\mathcal{C}(\mathcal{M}_i)} \prod_{i=1}^3 (R_{L,T,i})^{h_i} \quad (39a.4)$$

Finally, consider the values for the directional derivatives of $U'_{T_0,2}$ which occur in equation (20c). Since by definition each $\mathcal{M}_i \neq 0$ comparison with equation (34) shows that these limits have the form which occurs in (39):

$$\left\{ \prod_{j=1}^n U'_{T_0,2}(\mathbf{r}, 0, \epsilon) \right\}_{\mathbf{r}=\mathbf{0}} = \sum_{\{\nu\}} K_{T_0,2}^N(\nu, \mathbf{0}, \epsilon) \sigma(\{\mathbf{s}_k\}, \nu). \quad (39b)$$

3.2.3. *Introduction of constants independent of ϵ and introduction of dimensionless forms.* In using the preceding formulae, it is important to remember that the lattice sum for a given translation lattice fails to converge for the summation order corresponding to crystal growth for $N = 1$. Nevertheless, even for a conditionally convergent series, the desired limit for the entire lattice has been obtained using absolutely convergent series. In the final equations for the contribution which each lattice, T , makes to the absolutely convergent series, it is convenient to define the sums $K_T^N(\nu, \mathbf{r})$ which are independent of the arbitrary parameter, ϵ :

$$\text{Contribution of each } T \text{ to the lattice sum} = \sum_{\{\nu\}} K_T^N(\nu, \mathbf{r}) \sigma(\{\mathbf{s}_k\}, \mathbf{r})$$

$$K_T^N(\nu, \mathbf{r}) \begin{cases} T \neq T_0 & : K_{T,1}^N(\nu, \mathbf{r}, \epsilon) + K_{T,2}^N(\nu, \mathbf{r}, \epsilon) \\ T = T_0 & : (i.e., \mathbf{r} = \mathbf{r}_{T_0} = \mathbf{0}) \end{cases} \begin{cases} N \text{ odd} & : \text{zero} \\ N \text{ even} & : [K_{T_0,2}^N(\nu, \mathbf{0}, \epsilon) + R_{T_0,2}^N(\{\mathbf{s}_k\}, \epsilon)] \end{cases} \quad (40)$$

$$K_{T,1}^N(\nu, \mathbf{r}, \epsilon) \text{ cf. equation (25)}$$

$$K_{T,2}^N(\nu, \mathbf{r}, \epsilon) \text{ cf. equation (39a)}$$

$$K_{T_0,1}^N(\nu, \mathbf{0}, \epsilon) \text{ cf. equation (25b.4)}$$

$$K_{T_0,2}^N(\nu, \mathbf{0}, \epsilon) \text{ cf. equation (39b)}$$

$$R_{T_0,2}^N(\{\mathbf{s}_k\}, \epsilon) \text{ cf. equation (20d.1)}$$

For clarity and convenience, the computational steps that are used to evaluate equation (40) are summarized in Appendix B.

To simplify numerical input for the multipole calculation it is convenient to change to dimensionless variables by introducing a parameter, r_0 :

$$r_0 : \text{ a convenient standard distance within the crystal.} \quad (41)$$

Let all distances be scaled by r_0 and ϵ be replaced by a dimensionless parameter ϵ_0 defined by the equation

$$\epsilon = \epsilon_0 / r_0 \quad (42)$$

Then, it can be shown that

$$K_{T,i}^N(\nu, \mathbf{r}, \epsilon) = [K_{T,i}^N(\nu, \mathbf{r}/r_0, \epsilon_0)] / r_0^{N+1}. \quad (43)$$

Thus, whenever the crystal structure has only one variable parameter, r_0 , the dimensionless $K_T^N(\nu, [\mathbf{r}/r_0])$ are independent of measured lengths.

3.3. Use of molecular symmetry

To separate out all dependence upon the quantitative charge distribution, it is convenient to proceed as follows. As noted previously, in general, it is not possible to reduce the $E_{(n, N-n)}^N(\langle T_A, T_B \rangle)$ to the single term of equation (2) without introducing a specific assumption about the quantitative charge distribution. In such a case, the best that can be done is to select a molecular coordinate system to reduce the number of terms with nonvanishing moments. Let:

$\mathbf{u}_1^\alpha, \mathbf{u}_2^\alpha, \mathbf{u}_3^\alpha$: unit vectors defining the 3 axes for the molecular system of a molecule of type α .

$\{s\}_\alpha^m$: any set of m characteristic directions for a molecule of type α for which the moment, $p(\{s\}_\alpha^m) \neq 0$

$n_{\alpha,i}$: the number of the m characteristic directions which lie along \mathbf{u}_i^α . (44)

In this case, the furthest the calculation can proceed without an assumption about the quantitative charge distribution is to compute the relative energy for each pair $\{\{\mathbf{s}\}_A^n, \{\{\mathbf{s}\}_B^{N-n}\}$, i.e., the energy when $p(\{s\}_A^n) = p(\{s\}_B^{N-n}) = 1$. When account is taken of the multiplicity of the terms in the Taylor Series, the contribution is

$$E(\langle \{\mathbf{s}\}_A^n, \{\{\mathbf{s}\}_B^{N-n} \rangle = \left[\prod_{i=1}^3 n_{A,i}! \right]^{-1} \left[\prod_{i=1}^3 n_{B,i}! \right]^{-1} \sum_{\tau} (-1)^{n\tau} \times \sum_{\{\nu\}} \sigma(\{\mathbf{s}_k\}, \nu) K_T^N(\nu, [\mathbf{r}/r_0]) \quad (45)$$

$\tau(\{\mathbf{s}\}_A^n, \{\mathbf{s}\}_B^{N-n})$: the set of interactions with $\{\mathbf{s}\}_A^n$ at \mathbf{r} and $\{\mathbf{s}\}_B^{N-n}$ at the sites of T or vice versa.

$\{\mathbf{s}\}$: the characteristic directions of $\{\mathbf{s}\}_A^n$ and $\{\mathbf{s}\}_B^{N-n}$ expressed in the coordinate system used for the lattice.

Then the assumption about the quantitative charge distribution enters the N th order interaction energy only in the comparatively short sum:

$$E(\langle T_A, T_B \rangle) = \sum_{\{\{\mathbf{s}\}_A^n, \{\mathbf{s}\}_B^{N-n}\}} p(\{\mathbf{s}\}_A^n) \times p(\{\mathbf{s}\}_B^{N-n}) E(\langle \{\mathbf{s}\}_A^n, \{\mathbf{s}\}_B^{N-n} \rangle). \quad (46)$$

4. CONCLUSIONS

The use of a multipole expansion permitted the calculation to be split into two stages:

Stage I. A calculation which depends solely on the crystal geometry and on the symmetry of the molecule.

Stage II. A comparatively very small part of the calculation which uses the multipole moments, and, therefore, requires a quantitative knowledge of the charge distribution.

The proposed method of evaluating the lattice sum is based on an extension of EWALD's Formulae⁽⁵⁾ for the optical and electrostatic properties of ionic lattices. This has two general advantages.

(1) *Convenient error check.* One of the most important criteria of evaluating a machine method is the existence of a means to test for errors in input, algebra; or programs. The functions $U'_{T,1}$ and $U_{T,2}$ (and their derivatives) depend upon the arbitrary parameter ϵ , but their sum, U'_T (and its derivatives) does not. Experience has shown that the repetition of the calculation for two different values of ϵ has provided a means of detecting some errors in input and any errors in algebra or programming. Other common methods lack such a simple error check. It is imperative to note that approximate agreement is meaningless. Two values for a given $U'_T(\mathbf{r}, 0)$ which agreed to a few per cent were found to be in error by one hundred per cent.

(2) *Rapidity of convergence.* In general, the series given by the extended Ewald method should converge more rapidly than those given by the original Taylor Series (*vide infra* for a comparison of economy of the two). Since a decrease [increase] in ϵ will cause $U'_{T,1}(\mathbf{r}, 0, \epsilon)[U'_{T,2}(\mathbf{r}, 0, \epsilon)]$ to converge more rapidly, values should be chosen in a range to minimize the total work. KORNFELD⁽⁶⁾ was the first to propose the extension of EWALD's Formulae⁽⁵⁾ and gave equations for $N = 2$ and one special case for $N = 4$. The present paper has both generalized his work and developed forms adapted to machine calculations.

More recently, DEWETTE and NIJBOER⁽⁷⁾ published an alternative set of equations in the notation of spherical harmonics, derived as a special case of their very valuable general approach to the transformation of series into more rapidly convergent forms. Their work had a different primary purpose than the present study has. Their equations were designed to facilitate the calculation at a set of nonlattice points, while the equations of this paper are designed for convenience and economy of calculation at lattice points or a single non-lattice point. Consequently, they carried out an added expansion which is vital for their purpose but is not useful for the problem considered here. For the latter type of calculation the equations proposed here have the advantages: (a) they have been cast in forms which are simpler for coding the machine program; (b) the resulting programs can be expected to be more economical in machine time for the following reason: since they are based on Cartesian systems, they make more use of algebraic functions and less use of transcendental functions which require much more computer time.

Specific results in this paper can be summarized as follows. Section 3.12 develops general recursion relations which permit the deduction of the general equations for the self-energy and the self-potential in Section 3.1.3 and Appendix A. Section 3.1.2 casts the general equations for the directional derivatives defining the interaction energy in forms adapted to calculations for a sufficiently small number of molecular orientations for any particular fixed point in the crystal. Section 3.2 decomposes Stage I to give equations valid in general Cartesian systems and then special forms for orthogonal systems which will generally be more economical to use even if the unit cell axes are not orthogonal. For the latter case, the steps in the calculation can be summarized as follows:

Stage Ia: Use solely crystal geometry to compute the dimensionless crystal constants

For each order N , and each translation lattice T , follow the steps outlined in Appendix B.1 to compute

$$K_T^N(\nu, [\mathbf{r}/r_0]) = r_0^{N+1} K_T^N(\nu, \mathbf{r}) \quad (47)$$

Stage Ib: Use molecular symmetry plus crystal geometry

Follow Appendix B.2 to calculate the relative energies defined by equation (45).

Stage II. Use the multipole moments and, therefore, the quantitative charge distribution

Combine the relative energies from Stage Ib with the multipole moments to compute the N th order interaction energies of equation (46). Then sum over N in equation (1). Appendix B summarizes various subprograms and procedures which calculations on the ice lattice have shown to be convenient. A few results of this study will illustrate how important this 'convenience' is. First, depending upon the orientation assumed, the following ratios were found to cover the ranges

$$0.303 \leq \left| \frac{\text{Dipole - Dipole Energy}}{\text{Total Multipole Energy}} \right| \leq 0.525$$
$$0.117 \leq \left| \frac{\text{Nearest Neighbor Dipole - Dipole Energy}}{\text{Total Lattice Dipole - Dipole Energy}} \right| \leq 1.025.$$

In the actual study, it turned out to be desirable to include interactions for orders $\leq 8^*$. Thus it is necessary to have a method which can handle higher order multipole interactions and can make lattice sums including interactions between more distant neighbors. Tests showed that for an eighth order interaction, a next nearest neighbor calculation based on the original multipole expansion would require over two and one-half times as much computation as the accurate calculation following the proposed procedure for eight orientations. The ratio would become even larger if the number of orientations were increased.

The detailed results of the ice study are analyzed in terms of their implications for the theory of the hydrogen-bond and the structure of ice in a following paper.

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* In view of our ignorance of the actual charge distribution, this is only meaningful because the proposed method separates the calculation into such stages that the computations involving more than molecular symmetry are sufficiently short to permit the study of many different models.

APPENDIX

(A) *Derivation of equations required for the calculation of the ‘self-potential’ and ‘self-energy’*

Without loss in generality, in the calculation of the ‘self-energy’ or the ‘self-potential’ of a lattice $T = T_0$, the origin of the coordinate system is chosen so that

$$\mathbf{r}_{T_0} = \mathbf{0} \quad (A.1)$$

According to equation (19) the desired lattice sum is to be determined by the limiting process:

$$\left\{ \sum'_{\{L\}} \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) \|\mathbf{r} - \mathbf{r}_L\| \right\}_{\mathbf{r}=\mathbf{0}} = \lim_{\mathbf{r} \rightarrow \mathbf{0}} \left[\prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) \right] [U'_{T_0,1}(\mathbf{r}, 0, \epsilon) + U_{T_0,2}(\mathbf{r}, 0, \epsilon) - r^{-1}]. \quad (A.2)$$

$\sum'_{\{L\}}$: summation over $L \neq \langle 0, 0, 0 \rangle$.

It follows at once from equation (16) that the limit of the first term exists and equals

$$\begin{aligned} \lim_{\mathbf{r} \rightarrow \mathbf{0}} \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) U'_{T_0,1}(\mathbf{r}, 0, \epsilon) &= \left\{ \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) U'_{T_0,1}(\mathbf{r}, 0, \epsilon) \right\}_{\mathbf{r}=\mathbf{0}} \\ &= \begin{cases} N \text{ odd :} & \text{zero} \\ N \text{ even :} & \frac{4\pi(-1)^{N/2}}{(\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3)} \sum'_{\{L\}} q_L^{-2} \prod_{j=1}^N (\mathbf{q} \cdot \mathbf{s}_j) \times \exp[-q_L^2/4\epsilon^2]. \end{cases} \end{aligned} \quad (A.3)$$

The remaining two terms both diverge and it is only their difference which possesses a finite limit. Inspection of equations (15, 4, 11, 13) shows that the only divergent term in the series for $U_{T_0,2}$ is the term for $\mathbf{r}_L = \mathbf{0}$. Therefore, it is convenient to define

$$\prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) U'_{T_0,2}(\mathbf{r}, 0, \epsilon) = \sum_{j=q}^N \sum'_{\{L\}} a_j^N(\{\mathbf{s}_j\}, R_{L,T_0}) F_j(g_{L,T_0}). \quad (A.4)$$

Then

$$\lim_{\mathbf{r} \rightarrow \mathbf{0}} \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) [U_{T_0,2}(\mathbf{r}, 0, \epsilon) - r^{-1}] = \left[\prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) U_{T_0,2}(\mathbf{r}, 0, \epsilon) \right]_{\mathbf{r}=\mathbf{0}} + \quad (A.5a)$$

$$\lim_{\mathbf{r} \rightarrow \mathbf{0}} \sum_{j=q}^N a_j^N(\{\mathbf{s}_k\}, \mathbf{r}) [F_j(g[\epsilon\mathbf{r}]) - F_j(r^{-1})]$$

$$F_j(g), F_j(r^{-1}) \text{ cf. equations (13, 14)} \quad (A.5b)$$

$$g : \text{cf. equation (12)}. \quad (A.5c)$$

To evaluate the remaining limit in equation (A.5a), the various $F_j(g[\epsilon\mathbf{r}])$ and $F_j(r^{-1})$ are rewritten in terms of $F_q(g[\epsilon\mathbf{r}])$ and $F_q(r^{-1})$ respectively (q is defined in equation (10)). For the $F_j(r^{-1})$ equation (14) gives:

$$F_j(r^{-1}) = F_q(r) \left\{ \prod_{k=q+1}^j [-(2k-1)]/r^{2|j-q|} \right\}. \quad (A.6)$$

The following general relation between $F_s(g[\epsilon r])$ and

$F_j(g[\epsilon r])$ holds for $q \leq s \leq (j-1)$. It can be verified directly from equation (13d) for $s = j-1$ and established in general by finite induction:

$$F_j(g[\epsilon r]) = \left\{ \prod_{k=s+1}^j [-(2k-1)]/r^{2|j-s|} \right\} F_s(g[\epsilon r]) + \sum_{k=s+1}^j \left\{ \frac{(-2)^k \epsilon^{(2k-1)} e^{-\epsilon^2 r^2}}{\pi^{1/2} r^{2(j+1-k)}} \right\} \times \left\{ \delta_k^j + (1 - \delta_k^j) \prod_{p=k+1}^j [-(2p-1)] \right\}. \quad (A.7)$$

Then substitution of both (A.6) and (A.7) [for $s = q$] into the second term on the right hand side of (A.5a) gives:

$$\sum_{j=q}^N a_j^N(\{\mathbf{s}_k\}, \mathbf{r}) [F_j(g[\epsilon r]) - F_j(r^{-1})] \equiv S_1 + S_2 \quad (A8.a)$$

$$S_1 \equiv \{F_q(g[\epsilon r]) - F_q(r^{-1})\} \times \left\{ a_q^N(\{\mathbf{s}_k\}, \mathbf{r}) + \sum_{j=q+1}^N \frac{a_j^N(\{\mathbf{s}_k\}, \mathbf{r}) \prod_{k=q+1}^j [-(2k-1)]}{r^{2|j-q|}} \right\} \quad (A.8b)$$

$$S_2 \equiv \sum_{j=q+1}^N a_j^N(\{\mathbf{s}_p\}, \mathbf{r}) \sum_{k=q+1}^j \left\{ \frac{(-2)^k \epsilon^{(2k-1)} e^{-\epsilon^2 r^2}}{\pi^{1/2} r^{2(j+1-k)}} \right\} \times \left\{ \delta_k^j + (1 - \delta_k^j) \prod_{p=k+1}^j [-(2p-1)] \right\}. \quad (A.8c)$$

When N is odd, the following observations show that both S_1 and S_2 have the limit zero as $\mathbf{r} \rightarrow \mathbf{0}$:

Observation (1). By equation (11e) each $a_j^N(\{\mathbf{s}_k\}, \mathbf{r})$ is a sum of products, $P(D_j^N, \{\mathbf{s}_k\}, \mathbf{r})$ and by (11d.2) each product of the sum has as factors $(2j - \dot{N})$ components of \mathbf{r} .

Observation (2). Consider now the exponent of r in the denominators. For S_2 , the maximum power occurs for the minimum $k = q+1$. Thus, the maximum power is $2(j+1-k) = 2(j-q)$. This is also the exponent of r in the denominator of S_1 . According to equation(10), $q = (N+1)/2$, when N is odd. Therefore, the maximum exponent of the denominator, $2(j-q) = 2j - N - 1 < 2j - N$. Thus, when N is odd, S_1 and S_2 have the limit zero.

Consider now the case when N is even. According to equation (10), $q = N/2$. S_1 is, in general, non-vanishing. Consider the summation over k in S_2 . The only term which has a non-zero limit is the term for which k has its minimum value, $q+1$. This is a consequence of the fact that for $k > q+1$, the exponent of $1/r$ is $2(j+1-k) < 2(j+1-[q+1]) = 2j - N$. Thus the limiting value of the sum $S_1 + S_2$ becomes

$$\lim_{\mathbf{r} \rightarrow \mathbf{0}} (S_1 + S_2) = \lim_{\mathbf{r} \rightarrow \mathbf{0}} \sum_{j=q}^N a_j^N(\{\mathbf{s}_j\}, \mathbf{r}) [F_j(g[\epsilon r]) - F_j(r^{-1})] = \begin{cases} N \text{ odd :} & \text{zero} \\ N \text{ even :} & \lim_{\mathbf{r} \rightarrow \mathbf{0}} S_1 + \lim_{\mathbf{r} \rightarrow \mathbf{0}} \left\{ \frac{(-2)^{q+1} \epsilon^{(2q+1)} \exp(-\epsilon^2 r^2)}{\pi^{1/2}} \right\} \times \left\{ \sum_{j=q+1}^N \frac{a_j^N(\{\mathbf{s}_p\}, \mathbf{r}) [\delta_{q+1}^j + (1 - \delta_{q+1}^j) \prod_{p=q+2}^j (-[2p-1])] }{r^{2|j-q|}} \right\}. \end{cases} \quad (A.9)$$

According to equation (10), when N is even $q = N/2$ and according to equation (11d.3), $a_{N/2}^N$ is independent of \mathbf{r} . Therefore, each neighborhood of $\mathbf{r} = \mathbf{0}$ contains an \mathbf{r} for which the multiplier of $[F_q(g[\epsilon r]) - F_q(r^{-1})]$ in S_1 vanishes. It can be rewritten as:

$$q = N/2 : a_q^N(\{\mathbf{s}_k\}) + [-(2q+1)] \sum_{j=q+1}^N \left\{ \frac{a_j^N(\{\mathbf{s}_k\}, \mathbf{r})}{r^{2|j-q|}} \right\} \times \left\{ \delta_{q+1}^j + (1 - \delta_{q+1}^j) \prod_{k=q+2}^j [-(2k-1)] \right\} = 0. \quad (\text{A.10})$$

For each such \mathbf{r} , $S_1 = 0$ and comparison shows that the summation of the $\{ \}$ of the second limit of (A.9) can be replaced by $a_q^N(\{\mathbf{s}_k\})/(2q+1)$ so that

$$\lim_{\mathbf{r} \rightarrow \mathbf{0}} \sum_{j=q}^N a_q^N(\{\mathbf{s}_k\}, \mathbf{r}) [F_j(g[\epsilon r]) - F_j(r^{-1})] = \begin{cases} N \text{ odd} : & \text{zero} \\ N \text{ even} : & \frac{(-2)^{q+1} \epsilon^{2q+1} a_q^N(\{\mathbf{s}_k\})}{(2q+1)\pi^{1/2}} \equiv R_{T_0,2}^N(\{\mathbf{s}_k\}, \epsilon). \end{cases} \quad (\text{A.11})$$

Substitution of (A.11) into (A.5) and combination with (A.2,3) gives the final equation for the self-energy or the self-potential:

$$\left\{ \sum_{\{L\}}' \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) \|\mathbf{r} - \mathbf{r}_L\| \right\}_{\mathbf{r}=\mathbf{0}} = \left\{ \prod_{j=1}^N (\mathbf{s}_j \cdot \nabla_{\mathbf{r}}) [U'_{T_0,1}(\mathbf{r}, 0, \epsilon) + U'_{T_0,2}(\mathbf{r}, 0, \epsilon)] \right\}_{\mathbf{r}=\mathbf{0}} + R_{T_0,2}^N(\mathbf{s}_k, \epsilon). \quad (\text{A.12})$$

(B) *Steps in the procedure for the machine calculation* For clarity and convenience the steps in the machine calculation for stages Ia,b and II will be summarized for the case-generally the most economical in computer time-when an orthogonal Cartesian axis is used.

B.1. *Stage Ia. Calculation of the crystal constants.* According to equation (40), the crystal constants vanish for the self-potential or the self-energy (i.e., $T = T_0$) whenever N is odd. In all other cases the following procedure applies.

1. Generate vectors and calculate functions of vector magnitudes.

(i) Generate the dimensionless vectors, $r_0 \mathbf{q}_L$ (*cf.* equation (4)), order them into classes of non-vanishing magnitudes, M_i . For two values of the dimensionless arbitrary parameter, $\epsilon_0 = \epsilon r_0$, compute the exponentials of equation (16).

(ii) For each T , generate the dimensionless vectors $\mathbf{R}_{L,T}/r_0$ [*cf.* equation (4)], order them in classes of non-vanishing magnitudes, \mathcal{M}_i , and compute the $F_N(g[\epsilon, \mathcal{M}_i])$ [*cf.* equation (13)] for each of two values of the arbitrary dimensionless parameter, ϵ_0 .

2. For each order N generate the ν which satisfy equation (23b).

3. For each order N , complete the calculation of the dimensionless $K_{T,1}^N(\nu, [\mathbf{r}/r_0], \epsilon_0)$ following equation (25).

4. For each order N , and for each T complete the calculation of the $K_{T,2}^N(\nu, [r/r_0], \epsilon_0)$ in the following steps.

(i) For each $j, q \leq j \leq N$ [*cf.* equation (10)] generate the \mathbf{h} of $H(\langle j, N, \nu \rangle)$ defined by equations (28d, 36). For each $\langle \nu, \mathbf{h} \rangle$ calculate the symmetry numbers $I(\nu, \mathbf{h})$ of equation (37b). For convenience the allowed $\langle \nu, \mathbf{h} \rangle$ and the symmetry numbers are listed in Table 1 for $N \leq 5$.

(ii) For each such j, \mathbf{h} , calculate the

$$K_{T,2}^N(j, bf\nu, [\mathbf{r}/r_0], \mathcal{M}_i, \mathbf{h})$$

defined by equation (39a.4) for each class, $\mathcal{C}(\mathcal{M}_i)$.

(iii) Calculate $K_{T,2}^N(j, \nu, [\mathbf{r}/r_0], \mathcal{M}_i)$ of equation (39a.3) by summing over $H((j, N, \nu))$.

(iv) For each j and ν , use the results of steps (1.ii) and (4.iii) to compute

$$K_{T,2}^N(j, \nu, [\mathbf{r}/r_0], \epsilon_0)$$

by equation (39a.2)

(v) Following equation (39a.1), sum the results of step (4.iv) over j to obtain

$$K_{T,2}^N(\nu, [\mathbf{r}/r_0], \epsilon_0).$$

5. For each order N calculate the dimensionless crystal constants using the results of steps 3 and 4.

$$(i) T \neq T_0 : K_T^N(\nu, [\mathbf{r}/r_0]) = K_{T,1}^N(\nu, [\mathbf{r}/r_0], \epsilon_0) + K_{T,2}^N(\nu, [\mathbf{r}/r_0], \epsilon_0)$$

(ii) $T = T_0$: When N is even, compute the $R_{T_0,2}^N(\{\mathbf{s}_k\}, \epsilon_0)$ of equation (A.11). Then calculate

$$K_{T_0}^N(\nu, \mathbf{0}) = K_{T_0,1}^N(\nu, \mathbf{0}, \epsilon_0) + K_{T_0,2}^N(\nu, \mathbf{0}, \epsilon_0) + R_{T_0,2}^N(\{\mathbf{s}_k\}, \epsilon_0).$$

6. Reorder the allowed sequence of ν to eliminate any ν for which the crystal constant vanishes.

B.2. Stage Ib. Calculation of the sums of components of characteristic directions and of relative energies

Consider an interaction of order $N = N_0$ corresponding to the characteristic directions $\mathbf{s}_1, \dots, \mathbf{s}_{N_0}$. The first step in Stage Ib is to evaluate the $\sigma(\{\mathbf{s}_k\}, \nu)$ of equation (23c). Although it seems more straightforward to construct the permutations allowed by equation (22) and then to determine the ν for each permutation, since the crystal constants vanish for some ν , it is better to use an array of the ν for which $K_T^N(\nu, [\mathbf{r}/r_0]) \neq 0$ and for each ν of the array to construct the products of the sum $\sigma(\{\mathbf{s}_k\}, \nu)$ using a nested sequence of loops to select the components of the characteristic directions.

Frequently the calculations at order N_0 can be shortened by using results from lower orders. Suppose that the sequence of characteristic directions $\mathbf{s}_1, \dots, \mathbf{s}_{N_0}$ has d distinct elements which form the sequence

$$\mathbf{s}_1, \dots, \mathbf{s}_{i_d} \tag{B.1}$$

and that

$$N_j \equiv \text{number of } \mathbf{s}_k \text{ of the } j\text{th type, } 1 \leq j \leq d. \tag{B.2}$$

The calculation can be shortened whenever $N_j > 1$ for some j . This will commonly be the case since the reduction of the sum of all the N th order multipoles in the Taylor Series to a single multipole requires quantitative knowledge of the charge distribution, and in lieu of such knowledge, frequently the best that can be done is to use molecular symmetry in the selection of three axes to minimize the number of N th order terms in the Taylor Series with non-vanishing moments. This, of course, leads to $N_j > 1$. Let:

$$\nu_{N_0} : \text{an arbitrary } \nu \text{ for any particular } N = N_0 \tag{B.3}$$

$$\{\langle \nu_{N_1}, \dots, \nu_{N_d} \rangle\} : \text{the set of all } d\text{-tuples such that } \sum_{j=1}^d \nu_{N_j} = \nu_{N_0} \quad (B.4)$$

Then, provided there is sufficient machine storage available to preserve the results from lower orders, $\sigma(\{\mathbf{s}_j\}, \nu_{N_0})$ can be computed most economically as

$$\sigma(\{\mathbf{s}_j\}, \nu_{N_0}) = \sum_{\{\langle \nu_{N_1}, \dots, \nu_{N_d} \rangle\}} \prod_{j=1}^d \sigma(\{\mathbf{s}_{i_j}\}, \nu_{N_j}). \quad (B.5)$$

After the $\sigma(\{\mathbf{s}_j\}, \nu)$ have been computed, then the relative energies $E(\langle \{\mathbf{s}\}_A^n, \{\mathbf{s}\}_B^{N-n} \rangle)$ are computed by the summation of equation (45).

Table 1. Values of ν , \mathbf{h} and $I(\langle \nu, \mathbf{h} \rangle)$, $N \leq 5$

N	j	ν_r	ν_s	ν_t	h_r	h_s	h_t	$I(\langle \nu, \mathbf{h} \rangle)$	
2	1	2	0	0	0	0	0	1	
3	2	3	0	0	1	0	0	3	
		2	1	0	0	1	0	1	
4	3	4	0	0	2	0	0	6	
		3	1	0	1	1	0	3	
		2	2	0	2	0	0	1	
4	2				0	2	0	1	
		2	1	1	0	1	1	1	
		4	0	0	0	0	0	0	3
		2	2	0	0	0	0	0	1
5	4	5	0	0	3	0	0	10	
		4	1	0	2	1	0	6	
		3	2	0	1	2	0	3	
					3	0	0	1	
		3	1	1	1	1	1	1	3
		2	2	1	0	2	2	1	3
5	3				2	0	1	1	
		5	0	0	1	0	0	0	15
		4	1	0	0	1	1	0	3
		3	2	0	1	0	0	0	3
			2	1	0	1	1		

The columns headed by ν_r, ν_s, ν_t are to be any permutation of ν_1, ν_2, ν_3 , The columns headed by h_r, h_s, h_t give the allowed values of the corresponding components of the vector, \mathbf{h} . Whenever $j = N, \mathbf{h} = \nu$ and $I(\langle \nu, \mathbf{h} \rangle) = 1$.