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Note

Computer Algorithms and Programs for Permanent Multipole and Induced Dipole Interaction Energies and Dipole Vectors in Crystals*

1. INTRODUCTION

The purpose of this note is to report tested procedures and programs in CDC FORTRAN for calculating permanent multipole lattice energies with an option for induced dipole energies and vectors for perfect crystals. The programs can be supplied upon request. In addition, modifications, which have been shown useful for similar calculations on orientationally disordered crystals, are described. The programs have been extensively tested in calculations of the lattice energy of three forms of ice as well as other quantities of current interest [1], such as the total molecular dipole vector and, therefore, could be used to calculate the Kirkwood g-factor. According to dimensions now assigned, the programs are limited to the interactions of all multipoles of orders $\leqslant N$ where $N \leqslant 14$. A separate program can supplement the electrostatic part of the energy with inverse power terms, r^{-m}, which are not restricted to lattice sites. In the present version, m must be a positive integer $\leqslant 12$. It can be trivially extended for nonintegral exponents. Although the partial sums for $m \leqslant 3$ diverge, they have already proved their usefulness in check calculations on finite lattices as in Section 4.

The region of useful convergence of finite multipole approximations to the first-order Coulomb energy for molecular charge distributions is, of course, dependent upon the system. Pack *et al.* [2] have proven their utility for some approximate wavefunctions for larger molecules even at distances corresponding to condensed phases. Campbell and Mezei [3, 4] have established the useful convergence of three-center expansions for water for such distances and van Hemert and Mulder [5] are making comparisons with direct integral evaluation. Kin-Chue, *et al.* [6, 7] have compared results from integral evaluations with those from multipole expansions for four different simple molecules as types to aid in predicting when the approximations will and will not be useful.

2. THE PERMANENT MULTIPOLE CALCULATIONS

The calculation is based upon the multipole representation in the Maxwell Invariant Form in which an Nth-order multipole is characterized by N unit vectors, called characteristic directions and a scalar multipole moment,

$$\mathbf{s}_1, \ldots, \mathbf{s}_n, p^{(n)}. \tag{1}$$

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An algorithm for the determination of the $\mathbf{s}_i$ and $p^{(n)}$ has been published and programs are available on request [3, 8].[1] The programs reported here use an extension of the Ewald–Kornfeld method for lattices of dipoles and zonal quadrupoles to permanent multipoles of arbitrary order [9] and a subsequent extension of the formalism for permanent multipole lattices to induced dipoles [10]. The procedure has been generalized to induced multipoles of arbitrary order [11]. In this procedure, the sites of the crystal lattice are written as the union,

$$\bigcup_j T_j\,,\ T_j \equiv \text{the set of sites of the } j\text{th simple translation lattice.} \tag{2}$$

The permanent multipole energy, U_{P}, is given as a sum of contributions from each center in the unit cell, $\mathbf{X}_{\mathrm{c}}$, and each T_j :

$$U_{\mathrm{P}} = \tfrac{1}{2} \sum_{\{\mathbf{X}_{\mathrm{c}}\}} \sum_{\{T_j\}} U_{\mathrm{P}}(\mathbf{X}_{\mathrm{c}}, T_j); \tag{3a}$$

$U_{\mathrm{P}}(\mathbf{X}_{\mathrm{c}}, T_j)$: the interaction energy of a central site, $\mathbf{X}_{\mathrm{c}}$, with all sites belonging to the simple translation lattice, T_j. (3b)

Each $U_{\mathrm{P}}(\mathbf{X}_{\mathrm{c}}, T_j)$ is obtained from a truncation of the multipole sum over the multipole tensors of order $N(\mathbf{X}_{\mathrm{c}})$ at $\mathbf{X}_{\mathrm{c}}$ and $N(T_j)$ at the sites belonging to T_j. The programs make use of a technique developed for use when calculations are repeated for a large number of sets of different orientations at the lattice sites [9], which has recently been shown to be more efficient even for a single set when multipole interactions of order $N(\mathbf{X}_{\mathrm{c}}) + N(T_j) > {\sim}5$ are included [12]. In this procedure, $U_p(\mathbf{X}_{\mathrm{c}}, T_j, \langle N(\mathbf{X}_{\mathrm{c}}), N(T_j)\rangle)$ is written as a sum of products of K-functions, which depend only on the crystal geometry, by σ functions, which are determined by the charge densities:

$$\begin{aligned} &U_{\mathrm{P}}(\mathbf{X}_{\mathrm{c}}, T_j, \langle N(\mathbf{X}_{\mathrm{c}}), N(T_j)\rangle) \\ &\quad = \frac{p^{(N(\mathbf{X}_{\mathrm{c}}))}\,p^{(N(T_j))}}{N(\mathbf{X}_{\mathrm{c}})!\,N(T_j)!} \sum_{\{\boldsymbol{\nu}\}} K(\boldsymbol{\nu}, \mathbf{X}_{\mathrm{c}} - \mathbf{X}_j, \langle N(\mathbf{X}_{\mathrm{c}}), N(T_j)\rangle)\,\sigma(\mathscr{S}(\mathbf{X}_{\mathrm{c}}), \mathscr{S}(T_j), \boldsymbol{\nu}); \end{aligned} \tag{4a}$$

$\boldsymbol{\nu} = \langle \nu_1, \nu_2, \nu_3\rangle$; $\nu_1 + \nu_2 + \nu_3 = N(\mathbf{X}_{\mathrm{c}}) + N(T_j)$; each

ν_i is a positive integer or zero; (4b)

$\mathbf{X}_j$: an arbitrary site belonging to T_j ; (4c)

$\mathscr{S}(\mathbf{X}_{\mathrm{c}})[\mathscr{S}(T_j)]$: the set of the $N(\mathbf{X}_{\mathrm{c}})[N(T_j)]$ characteristic directions; (4d)

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[1] One stage of the current programs assumes one electron orbitals constructed from a linear combination of Gaussians. Only this stage must be modified for other forms.

$$P^{(M)}\text{: the scalar multipole moment of order } M; \tag{4e}$$

$$K(\mathbf{v}, \mathbf{X}_{\mathrm{c}} - \mathbf{X}_j, \langle N(\mathbf{X}_{\mathrm{c}}), N(T_j)\rangle) \quad \text{(cf. [9, Eqs. (4), (24), (25), (28), (37), (39), (40)]);}^{2} \tag{4f}$$

$$\sigma(\mathscr{S}(\mathbf{X}_{\mathrm{c}}), \mathscr{S}(T_j), \mathbf{v}) \qquad \text{(cf. [9, Eqs. (22), (23)]).} \tag{4g}$$

The specific equations and the method used to construct the K's have been published [9a]. The σ's are constructed by a new efficient recursion analogous to that of [12, Eq. (9)] to reduce the increase of operations with the order N from $O(3^N)$ for direct evaluation to $O(N^3)$.

The extended Ewald–Kornfeld technique has the advantage of a simple check on the calculation of the lattice sums giving the K's. Each K is given as a sum of two series, one over the lattice and the other over the reciprocal lattice. Although each of the two series is a function of an arbitrary parameter, ϵ, their sum is not. Comparison of calculations using two different values of ϵ has been found useful for the detection of programmatic and other errors [9b] and has been used as a basis for an estimate of the error introduced by the truncation of the lattice sums.

The input consists essentially of the following: (i) indices determining the type and orientation of the charge distribution at each site, $\mathbf{X}$; (ii) the components of the sites $\mathbf{X}_{\mathrm{c}}$ and $\mathbf{X}(T_j)$ and of the unit cell basis vectors relative to a common orthogonal Cartesian frame for the crystal; (iii) the components of the characteristic directions relative to an intrinsic orthogonal Cartesian frame assigned to each type; (iv) the elements of rotation matrices defining the transformation from the intrinsic frame for each distribution to the common crystal frame. The number of redundant calculations can be reduced in three different ways: (i) the program automatically uses some aspects of the general symmetry of multipole sums; (ii) additional optional input can further use this general symmetry, (iii). Further identities for other $\langle \mathbf{X}_{\mathrm{c}}, T_j\rangle$ and $\langle \mathbf{X}'_{\mathrm{c}}, T'_j\rangle$ determined by the symmetry of the particular cyrstal can be specified. Our work on the rotationally disordered ice Ih suggests a way of locating such identities as a possible alternative to a symmetry analysis for the different $\langle \mathbf{X}_{\mathrm{c}}, T_j\rangle$ pairs. If for all orders

$$N(\mathbf{X}_{\mathrm{c}}) + N(T_j) \leqslant N_0, \tag{5a}$$

$$U_{\mathrm{P}}(\mathbf{X}_{\mathrm{c}}, T_j, \langle N(\mathbf{X}_{\mathrm{c}}), N(T_j)\rangle) = U_{\mathrm{P}}(\mathbf{X}'_{\mathrm{c}}, T'_j, \langle N(\mathbf{X}'_{\mathrm{c}}), N(T'_j)\rangle), \tag{5b}$$

and if N_0 is sufficiently high, then our work suggests the assumption that the equality holds for higher orders as well. In the case of ice Ih, $N_0 = 5$ was the minimum value such that the identities of Eq. (5b) implied equalities which were verified for all orders $N(\mathbf{X}_{\mathrm{c}}) + N(T_j) \leqslant 14$.

The basic program can be extended to the case of rotationally disordered crystals in the following crystal analog of calculations on translationally and rotationally disordered fluids. (i) The rotationally disordered lattice is replaced by a rotationally ordered lattice with a larger unit cell. Define an allowed configuration as any set of orientations consistent with constraints on allowed mutual orientations at nearest-neighbor lattice sites and with the assumed unit cell. Generate all allowed configura-

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[2] A clearly recognizable error in Eq. (40) is corrected in the documentation and will be submitted as an erratum to the original Journal.

tions. For example, Campbell *et al.* [13] have shown that for ice Ih it sufficed to replace the unit cell for 0 sites, which contains four water molecules, with a unit cell containing 16 molecules and have described a routine for configuration generation (cf. [13, Appendix A]). (ii) Replace the costly calculations of the energy for each configuration by the generation of lattice sums for each $\langle \mathbf{X}_c, T_j \rangle$ pair, after identities have been eliminated as described above. The sum over $\langle \mathbf{X}_c, T_j \rangle$ for any allowed configuration is then computed simply as a sum of entries in the tabulated array.

3. The Induced Moment Option

The present program is limited to the approximation in which the components of the induced dipole vector at any site $\mathbf{X}_0$ are given by

$$I^i(\mathbf{X}_0) = \alpha^{ij} E_j(\mathbf{X}_0); \tag{6a}$$

α^{ij}: the (i, j) component of the ordinary dipole polarizability tensor; (6b)

$E_j(\mathbf{X}_0)$: the jth component of the electric field
defined at $\mathbf{X}_0$ by the induced dipoles and permanent multipoles (6c)
of all orders located at other sites.

Thus it neglects the contributions to $I^i(\mathbf{X}_0)$ arising from higher powers in the $E_j(\mathbf{X}_0)$ as well as from the first and higher powers of the derivatives in the field components, which are included in a general procedure which has been developed [11]. Campbell [10] has shown that in the approximation of Eq. (6) the $I^i(\mathbf{X}_c)$ for all N_{cell} sites, $\mathbf{X}_c$, in the unit cell are obtained as the solution of a set of at most 3 N_{cell} simultaneous linear equations. The present program solves for all components in a single crystal-based reference frame rather than in different intrinsic reference frames for each $\mathbf{X}_c$. In contrast to implications of the earlier article, in the approximation of Eq. (6) the general frame turns out to be more convenient. The additional contribution to the lattice energy arising from the interaction of each $I^i(\mathbf{X}_c)$ with the permanent multipoles of other sites is then computed by a generalization of the procedure of Mandel and Mazur [14] for a finite set of polarizable dipoles.

4. Tests of Programs

The programs have been subjected to the following tests. (i) When the fifth-order contribution to the interaction energy was computed by the present program and by a lattice sum using the untransformed multipole equations of Campbell [9, Eqs. (1), (2)] the results agreed within the estimated error from the truncation of the lattice sum, 0.021 %. (ii) The results for the U_p were compared with Gelernter's [15] calculations based on somewhat different algorithms. They agreed for orders $n \leqslant 4$. Discrepancies for some orientations, which appeared at $n = 5$, were interpreted in terms of special coding for $n = 5$ in the earlier work, in contrast with the cyclic coding of the present program. This interpretation was supported by the fact that the difference between Gelernter's value and the value given by the untransformed lattice sum was 11-fold larger than the difference in test (i). (iii) The induced moment option has been subjected to a consistency test. A program written for equations which use components for each induced dipole vector relative to an intrinsic molecular coordinate system at the lattice site gave the same lattice energy as the present program written for equations which use components for each induced dipole vector relative to a single crystal based coordinate system for all sites. (iv) The program for inverse power potentials has been checked in two ways. (a) The lattice sums for face centered lattices agreed with the 6 and 7 digit values quoted by Hirschfelder *et al.* [16]. (b) A multipole expansion for the interaction energy defined by two finite lattices of unit positive charges contained within nonoverlapping spheres was constructed. The distance between the expansion centers was chosen to be sufficiently great to give reasonably rapid convergence. This value agreed with the potential calculated by a simple Coulomb sum using the inverse power program to within the estimated convergence error of the multipole expansion: exactly through five decimal digits.

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