Computation of Lattice Sums: Generalization of the Ewald Method II

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Our method of computing lattice sums[1] is carried through the final stage of numerical computation. We calculate the expansion coefficients of the crystal potential, evaluated at each inequivalent site of a number of cubic structures. Some of the structures chosen are simple, to afford comparison with previous calculations. Many, however, are too complex to be amenable to other methods, and our results are the first reported. The sequence of computer programs, timing, and accuracy are discussed.

In a previous paper[1] concerning lattice sums we discussed summation methods which hinge on two facts: First, many lattices can be decomposed into so-called "primitive" lattices. Second, a wide class of summation procedures is feasible for such primitive lattices, which are impossible or impractical for arbitrary lattices. In particular, we developed an extension of the Ewald method, following the general philosophy of Nijboer and DeWette,[2] Adler,[3] and Barlow and Macdonald.[4] The conditions under which a given lattice can be decomposed into primitive lattices, and the algorithm accomplishing this, have been discussed with full generality and rigor by Graham.[5]

In this paper we present a sample of numerical results obtained by our method, together with some discussion of computational techniques and computational efficiency. We have evaluated the coefficients, up to order six, for the spherical harmonic expansion of the potential due to a lattice of point charges. We have done this for every inequivalent site in a number of cubic lattices. Some of the lattices were chosen to provide comparison with other calculations; some, on the contrary, were chosen because their complexity puts them beyond the reach of other methods; others still because cubic lattices without an inversion center are interesting in a number of other connections.

We define terms and display the relevant equations, as briefly as possible. For a fuller exposition we refer to Refs. 1 and 5.

A lattice is primitive if it consists of a set of points of position $\mathbf{r}_n$ and charge q_n such that

$$\mathbf{r}_n = \sum_{i=1}^{3} n_i \mathbf{b}_i , \qquad n_i = 0, \pm 1, \pm 2, \cdots \tag{1a}$$

$$q_n = q_0(-1)^{n_1+n_2+n_3}. \tag{1b}$$

For instance, NaCl is primitive, with $\mathbf{b}_1 = (\frac{1}{2},0,0)$, $\mathbf{b}_2 = (0,\frac{1}{2},0)$, and $\mathbf{b}_3$ $(0,0,\frac{1}{2})$, where the components of the b's are given along the cube axes in units of the cube dimensions. We call the vectors $\mathbf{b}_i$ the basis vectors of the primitive lattice. These should be distinguished from primitive translations $\mathbf{c}_i$, which are defined by the relation $q(\mathbf{r}) = q(\mathbf{r} + n_1\mathbf{c}_1 + n_2\mathbf{c}_2 + n_3\mathbf{c}_3)$, for all $\mathbf{r}$, and for all integers n_1, n_2, n_3.

An arbitrary three-dimensional lattice can be decomposed if it is of periodicity $2^N \times 2^N \times 2^N$. This condition can be loosened to periodicities $2^L \times 2^M \times 2^N$ with $L,M < N$, since by taking appropriate multiples in the direction in which the periodicity is 2^L or 2^M one can reduce this case to the previous one. The existence condition can be further loosened to include lattices composed of "interlocking" sublattices of periodicity $2^L \times 2^M \times 2^N$, provided each such sublattice is separately electrically neutral.

We consider, then, an array of periodicity $2^N \times 2^N \times 2^N$, and primitive translations $\mathbf{c}_1$, $\mathbf{c}_2$, $\mathbf{c}_3$. This array can be decomposed into 2^{3N-1} primitive lattices. These component lattices will be grouped into $3N$ sets. All lattices within one set will be defined by the same basis vectors, but will differ in choice of origin. With respect to the origin in the original lattice, the position of the origin of a component lattice is denoted by $\mathbf{R}$. We define auxiliary vectors $\mathbf{a}_i = \mathbf{c}_i/2^N$. We wish to express the basis vectors $\mathbf{b}_i$ of the primitive component lattices, as well as the origin positions $\mathbf{R}$, in terms of the $\mathbf{a}_i$. Let the columns of the matrix $\mathbf{A}$ denote the components of $\mathbf{a}_i$, and likewise for $\mathbf{B}$ and $\mathbf{b}_i$. Superscripts will denote sets of primitive component lattices, subscripts denote lattices within a given set. Then the required relations are

$$\mathbf{B}^{(1)} = \begin{bmatrix} 1 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \mathbf{A} \tag{2a}$$

$$\mathbf{B}^{(2)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & 1 & 1 \end{bmatrix} \mathbf{A} \tag{2b}$$

$$\mathbf{B}^{(3)} = \begin{bmatrix} 1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{bmatrix} \mathbf{A} \tag{2c}$$

$$\mathbf{B}^{(n+3)} = 2\mathbf{B}^{(n)} \tag{2d}$$

$$\{\mathbf{R}^{(1)}\} = (0,0,0) \tag{3a}$$

$$\{\mathbf{R}^{(n+1)}\} = \{\mathbf{R}^{(n)}\} + \{\mathbf{R}^{(n)} + \mathbf{B}_1{}^{(n)}\} \tag{3b}$$

$$q^{(1)} = 2^{-3N/2} \tag{4a}$$

$$q^{(n+1)} = q^{(n)}\sqrt{2}. \tag{4b}$$

These definitions differ from those given in Refs. 1 and 5 by relabeling some of the indices, which has the effect that all the **b** vectors now define right-handed bases. The primitive lattices so defined are orthonormal in the sense that

$$\sum_n q_\alpha{}^{(i)}(\mathbf{r}_n) q_\beta{}^{(j)}(\mathbf{r}_n) = \delta_{ij}\delta_{\alpha\beta} \tag{5}$$

where n runs over the sites in a unit cell, the superscript i or j denotes a set of primitive lattices, and the subscript α or β denotes a particular lattice belonging to that set. The primitive lattices do not necessarily correspond to physically real structures. If we take $\mathbf{A} = \mathbf{1}$, representative lattices belonging to the first three sets are shown in Fig. 1. There is one member in set 1, two in set 2, four in set 3. For every set we show only the lattice with origin at $\mathbf{R} = 0$. Only set 3 has a physical counterpart, and will be recognized as the CsCl structure. Further examples may be found in Ref. 5.

We now consider the expansion coefficients of the crystal potential. Just as the physical lattice is represented as the sum of primitive lattices, so a given expansion coefficient is computed as the sum of the corresponding coefficients proper to the primitive lattices. As suggested in the previous paper,[1] the coefficients arising from primitive component lattices can be computed once and for all, so that the problem for a real physical lattice, no matter how complicated, is reduced to the

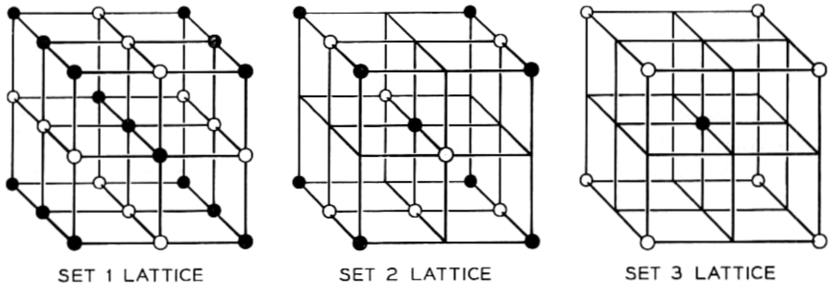

Fig. 1 — Conventional unit cell representation of primitive lattices, sets 1, 2, and 3 (Translation $R = 0,0,0$).

decomposition of that lattice into primitive components. If the potential is given, as usual, by

$$V(\mathbf{x}) = \sum_{l=0} \sum_{m=-l}^{l} C_{lm} \mid \mathbf{x} \mid^{l} Y_{l,-m}(\theta_{\mathbf{x}}, \varphi_{\mathbf{x}}) \tag{6}$$

then the expansion coefficients may be represented as

$$C_{lm} = \sum_{\text{sets } (i)} \sum_{\text{translations } (\alpha)} C_{lm}(\mathbf{b}^{(i)} - \mathbf{R}_{\alpha}{}^{(i)}) \tag{7}$$

where the notation is consistent with that of (2) through (5). Shortening the argument of the primitive lattice C_{lm} to ρ, ($\rho = \mathbf{b}^{(i)} - \mathbf{R}_{\alpha}{}^{(i)}$), we have, for each primitive lattice,

$$C_{lm} = \frac{4\pi}{2l+1} \sum_{n} q_n \mid \boldsymbol{\varrho}_n \mid^{-l-1} Y_{l,m}(\theta_{\boldsymbol{\varrho}_n}, \varphi_{\boldsymbol{\varrho}_n}) \tag{8}$$

where n runs over the sites of that particular lattice. The spherical harmonics are defined as usual:

$$Y_{l,m}(\theta,\varphi) = \left[\frac{2l+1}{4\pi} \cdot \frac{(l - \mid m \mid)!}{(l + \mid m \mid)!}\right]^{\frac{1}{2}} e^{im\varphi} P_{lm}(\theta). \tag{9}$$

For small l, the summation in (8) converges poorly or not at all. By means of the formalism discussed in Ref. 1, (8) can be transformed into the following, which converges rapidly for all l:

$$\begin{aligned} C_{lm} = \frac{4\pi}{2l+1} \cdot \frac{1}{\Gamma(l+\frac{1}{2})} \\ \cdot \Big\{ \sum_{n} \mid \boldsymbol{\varrho}_n \mid^{l-1} \Gamma(l + \tfrac{1}{2}, \pi\alpha^2 \mid \boldsymbol{\varrho}_n \mid^2) \\ \cdot Y_{lm}(\theta_{\boldsymbol{\varrho}_n}, \varphi_{\boldsymbol{\varrho}_n}) (-1)^{n_1+n_2+n_3} \\ + i^l \pi^{l-\frac{1}{2}} v_c^{-1} \sum_{n} \exp\,(i2\pi \mathbf{n}_n \cdot \mathbf{R}_j{}^{(i)}) \mid \mathbf{n}_n \mid^{l-2} \\ \cdot \Gamma(1, \pi\alpha^{-2} \mid \mathbf{n}_n \mid^2) \cdot Y_{lm}(\theta_{\mathbf{n}_n}, \varphi_{\mathbf{n}_n}) - \alpha \delta_l \delta_{\boldsymbol{\varrho}_n} \Big\}. \end{aligned} \tag{10}$$

Here, Γ is the incomplete Gamma function, and v_c is the cell volume $\mathbf{b}_1 \cdot \mathbf{b}_2 \times \mathbf{b}_3$. The vector $\mathfrak{n}$ in reciprocal space is defined by

$$\mathfrak{n}_n = \mathbf{h}_n^{(i)} - \tfrac{1}{2}(\mathbf{h}_1^{(i)} + \mathbf{h}_2^{(i)} + \mathbf{h}_3^{(i)}) \tag{11}$$

where the $\mathbf{h}$'s are basis vectors in the reciprocal lattice,

$$\mathbf{h}_1^{(i)} = \frac{1}{v_c} (\mathbf{b}_2^{(i)} \times \mathbf{b}_3^{(i)}), \tag{12}$$

and $\mathbf{h}_n$ is a lattice vector of the reciprocal lattice. The sums on n are to be understood as triple sums on n_1, n_2, n_3. The scale factor α is given by

$$\alpha = v_c^{-\frac{1}{3}} \tag{13}$$

and makes the rate of convergence equal in both coordinate and reciprocal space, regardless of choice of units or size of cell. The result of the summation is independent of the choice of α, but the correct choice is crucial in practice since it can affect computation time by orders of magnitude. The last term in (10) exhibits explicitly the correction discussed in Ref. 1 for the case $\rho = 0$.

In practice, there are four computational processes, performing the following functions: (*i*) We generate all the primitive component lattices of periodicity $2^N \times 2^N \times 2^N$. We did this for $N = 1,2,3$, requiring respectively 7, 63, and 511 lattices. (*ii*) For each component lattice, we calculate the C_{lm}, both real and imaginary parts, with $0 \leqq l \leqq 6$, $0 \leqq m \leqq l$. (*iii*) We decompose a given lattice, by taking appropriate dot-products (see (5)). (*iv*) We reconstitute the C_{lm}'s for the given lattice by combining the results of steps (*ii*) and (*iii*). Parts (*i*) and (*ii*) are done once only for a given type of geometrical grid. Parts (*iii*) and (*iv*) are done for each charge configuration that can be placed on that grid.

The computing time is spent almost entirely on Part (*ii*). About an hour on the IBM 7094 was required to calculate all the C_{lm}'s for all the primitive lattices. To compensate, the application of these results to 32 physical configurations, for all 56 coefficients, took about twelve seconds.

The computation for Part (*ii*) is done shell-wise. By the kth shell we mean here a set of points $\mathbf{r}_n = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3$ such that at least one n_i is equal to k in absolute value, but no n_i is greater than k in absolute value. The number of points in the kth shell is $(24k^2 + 2)$, and the number of points in all shells up to and including the kth is $(2k + 1)^3$. These shells differ from "Evjen" shells, which, unlike ours, use fractional charges, and preserve crystal symmetry and electrical neutrality for every shell. The kth shell defined above contains an excess charge of $2q(-1)^k$, if the charge $q(-1)^{n_1+n_2+n_3}$ is associated with each site. Since the excess charge alternates in sign, and the fractional excess decreases as k^2, convergence is not affected adversely. Summation was stopped when the contribution of a shell was less than 10^{-6} of the aggregate sum. This required, on the average, about 4 shells. Allowing for normal round-off errors, we expect an accuracy, in final results, of five significant figures.

The computed expansion coefficients are exhibited in Tables I through XIII. These tables are reproductions of computer output. Each table is headed by the chemical formula, and by the length of the unit cell, in angstroms. Next follows a list of all atomic positions in the unit cell. The crystallographic data is taken from Wyckoff.[6] Next follows a tabular listing of the expansion coefficients, i.e., the C_{lm} of (6). Due to evolution in notation, these coefficients are called ALM in Tables I–XIII. Both the real and imaginary parts are given for positive m; our definition of the spherical harmonics requires $C_{l,-m} = C_{l,m}^*$. The coefficients are listed for the expansion of the potential at every inequivalent site. For purposes of this computation, sites whose environment differs only by rotations and/or reflections are considered equivalent. All the structures are cubic, except SnF_4. This substance in tetragonal, with $c = 7.93$ Å, $a = 4.048$ Å. Since c is so nearly twice a, we have cheated a little by stacking together four of the tetragonal cells to make an almost cubic

TABLE I

NA-CL A=5.640

NA	0.	0.	0.	0.500	0.500	0.	0.500	0.	0.500	0.	0.500	0.50
CL	0.500	0.500	0.500	0.	0.	0.500	0.500	0.	0.	0.	0.500	0.

ØRIGIN NA

L	M	ALM REAL	ALM IMAG
0	0	-2.19679242	0.
1	0	0.	0.
1	1	0.	0.
2	0	0.	0.
2	1	0.	0.
2	2	0.	0.
3	0	0.	0.
3	1	0.	0.
3	2	0.	0.
3	3	0.	0.
4	0	-0.02371096	0.
4	1	0.	0.
4	2	0.	0.
4	3	0.	0.
4	4	-0.01417001	0.
5	0	0.	0.
5	1	0.	0.
5	2	0.	0.
5	3	0.	0.
5	4	0.	0.
5	5	0.	0.
6	0	-0.00068597	0.
6	1	0.	0.
6	2	0.	0.
6	3	0.	0.
6	4	0.00128333	0.
6	5	0.	0.
6	6	0.	0.

Table II

CS-CL A=4.123

CS	0.	0.	0.
CL	0.500	0.500	0.500

L	M	ØRIGIN ALM REAL	CS ALM IMAG
0	0	-1.74998032	0.
1	0	0.	0.
1	1	0.	0.
2	0	0.	0.
2	1	0.	0.
2	2	0.	0.
3	0	0.	0.
3	1	0.	0.
3	2	0.	0.
3	3	0.	0.
4	0	0.00924632	0.
4	1	0.	0.
4	2	0.	0.
4	3	0.	0.
4	4	0.00552573	0.
5	0	0.	0.
5	1	0.	0.
5	2	0.	0.
5	3	0.	0.
5	4	0.	0.
5	5	0.	0.
6	0	-0.00020874	0.
6	1	0.	0.
6	2	0.	0.
6	3	0.	0.
6	4	0.00039051	0.
6	5	0.	0.
6	6	0.	0.

Table III

ZN-S A=5.409

ZN	0.	0.	0.	0.500	0.	0.500	0.500	0.500	0.	0.	0.500	0.500
S	0.250	0.250	0.250	0.250	0.750	0.750	0.750	0.250	0.750	0.750	0.750	0.250

M	ØRIGIN ALM REAL	ZN ALM IMAG
0	-4.95817298	0.
0	0.	0.
1	0.	0.
0	0.	0.
1	0.	0.
2	0.	0.
0	0.	0.
1	0.	0.
2	0.	0.17556879
3	0.	0.
0	0.04689946	0.
1	0.	0.
2	0.	0.
3	0.	0.
4	0.02802778	0.
0	0.	0.
1	0.	0.
2	0.	0.02525550
3	0.	0.
4	0.	0.
5	0.	0.
0	-0.00491204	0.
1	0.	0.
2	0.	0.
3	0.	0.
4	0.00918959	0.
5	0.	0.
6	0.	0.

Table IV

CAF2 A=5.463

CA	0.	0.	0.	0.	0.500	0.500	0.500	0.	0.500	0.500	0.500	0.
F	0.250	0.250	0.250	0.250	0.250	0.750	0.250	0.750	0.250	0.250	0.750	0.750
	0.750	0.250	0.250	0.750	0.250	0.750	0.750	0.750	0.250	0.750	0.750	0.750

L	M	ØRIGIN CA ALM REAL	ALM IMAG	ØRIGIN F ALM REAL	ALM IMAG
0	0	-4.90943545	0.	2.64146748	0.
1	0	0.	0.	0.	0.
1	1	0.	0.	0.	0.
2	0	0.	0.	0.	0.
2	1	0.	0.	0.	0.
2	2	0.	0.	0.	0.
3	0	0.	0.	0.	0.
3	1	0.	0.	0.	0.
3	2	0.	0.	0.	0.16876671
3	3	0.	0.	0.	0.
4	0	0.04463929	0.	-0.07244851	0.
4	1	0.	0.	0.	0.
4	2	0.	0.	0.	0.
4	3	0.	0.	0.	0.
4	4	0.02667707	0.	-0.04329626	0.
5	0	0.	0.	0.	0.
5	1	0.	0.	0.	0.
5	2	0.	0.	0.	0.02380209
5	3	0.	0.	0.	0.
5	4	0.	0.	0.	0.
5	5	0.	0.	0.	0.
6	0	-0.00458386	0.	0.00372635	0.
6	1	0.	0.	0.	0.
6	2	0.	0.	0.	0.
6	3	0.	0.	0.	0.
6	4	0.00857561	0.	-0.00697135	0.
6	5	0.	0.	0.	0.
6	6	0.	0.	0.	0.

Table V

CU2-Ø A=4.270

CU	0.250	0.250	0.250	0.250	0.750	0.750	0.750	0.250	0.750	0.750	0.750	0.250
Ø	0.	0.	0.	0.500	0.500	0.500						

L	M	ØRIGIN CU ALM REAL	ALM IMAG	ØRIGIN Ø ALM REAL	ALM IMAG
0	0	-3.14083827	0.	5.37724918	0.
1	0	0.	0.	0.	0.
1	1	0.	0.	0.	0.
2	0	0.	0.	0.	0.
2	1	-0.35325349	-0.35325350	0.	0.
2	2	0.	-0.35325350	0.	0.
3	0	0.	0.	0.	0.
3	1	0.	0.	0.	0.
3	2	0.	0.	0.	-0.22616888
3	3	0.	0.	0.	0.
4	0	0.07654336	0.	-0.07763660	0.
4	1	0.02818000	0.02818003	0.	0.
4	2	0.	-0.07970510	0.	0.
4	3	0.07455729	-0.07455732	0.	0.
4	4	0.04574336	0.	-0.04639675	0.
5	0	0.	0.	0.	0.
5	1	0.	0.	0.	0.
5	2	0.	0.	0.	-0.05222149
5	3	0.	0.	0.	0.
5	4	0.	0.	0.	0.
5	5	0.	0.	0.	0.
6	0	-0.01286795	0.	0.01144142	0.
6	1	0.00987714	0.00987714	0.	0.
6	2	0.	0.01481423	0.	0.
6	3	0.00467044	-0.00467045	0.	0.
6	4	0.02407371	0.	-0.02140493	0.
6	5	0.01274865	0.01274866	0.	0.
6	6	0.	0.00790175	0.	0.

Table VI

K-TA-Ø3   A=3.988

TA	0.	0.	0.						
Ø	0.500	0.	0.	0.	0.500	0.	0.	0.	0.500
K	0.500	0.500	0.500						

	ØRIGIN	TA	ØRIGIN	Ø	ØRIGIN	K
M	ALM REAL	ALM IMAG	ALM REAL	ALM IMAG	ALM REAL	ALM IMAG
0	-12.80986524	0.	6.17036784	0.	-2.97906271	0.
0	0.	0.	0.	0.	0.	0.
1	0.	0.	0.	0.	0.	0.
0	0.	0.	-0.77709828	0.	0.	0.
1	0.	0.	0.	0.	0.	0.
2	0.	0.	0.95174713	0.	0.	0.
0	0.	0.	0.	0.	0.	0.
1	0.	0.	0.	0.	0.	0.
2	0.	0.	0.	0.	0.	0.
3	0.	0.	0.	0.	0.	0.
0	-0.25413066	0.	0.13074156	0.	-0.00784040	0.
1	0.	0.	0.	0.	0.	0.
2	0.	0.	-0.18082657	0.	0.	0.
3	0.	0.	0.	0.	0.	0.
4	-0.15187213	0.	0.21482505	0.	-0.00468555	0.
0	0.	0.	0.	0.	0.	0.
1	0.	0.	0.	0.	0.	0.
2	0.	0.	0.	0.	0.	0.
3	0.	0.	0.	0.	0.	0.
4	0.	0.	0.	0.	0.	0.
5	0.	0.	0.	0.	0.	0.
0	-0.01117794	0.	-0.02269032	0.	0.00485897	0.
1	0.	0.	0.	0.	0.	0.
2	0.	0.	0.02488248	0.	0.	0.
3	0.	0.	0.	0.	0.	0.
4	0.02091200	0.	-0.03023670	0.	-0.00909032	0.
5	0.	0.	0.	0.	0.	0.
6	0.	0.	0.03690669	0.	0.	0.

Table VII

SR-TI-Ø3   A=3.905

TI	0.	0.	0.						
Ø	0.500	0.	0.	0.	0.500	0.	0.	0.	0.500
SR	0.500	0.500	0.500						

	ØRIGIN	TI	ØRIGIN	Ø	ØRIGIN	SR
M	ALM REAL	ALM IMAG	ALM REAL	ALM IMAG	ALM REAL	ALM IMAG
0	-11.23581445	0.	5.86043859	0.	-4.89031279	0.
0	0.	0.	0.	0.	0.	0.
1	0.	0.	0.	0.	0.	0.
0	0.	0.	-0.57006907	0.	0.	0.
1	0.	0.	0.	0.	0.	0.
2	0.	0.	0.69818916	0.	0.	0.
0	0.	0.	0.	0.	0.	0.
1	0.	0.	0.	0.	0.	0.
2	0.	0.	0.	0.	0.	0.
3	0.	0.	0.	0.	0.	0.
0	-0.29458212	0.	0.10063877	0.	0.00341623	0.
1	0.	0.	0.	0.	0.	0.
2	0.	0.	-0.18383221	0.	0.	0.
3	0.	0.	0.	0.	0.	0.
4	-0.17604650	0.	0.19910725	0.	0.00204157	0.
0	0.	0.	0.	0.	0.	0.
1	0.	0.	0.	0.	0.	0.
2	0.	0.	0.	0.	0.	0.
3	0.	0.	0.	0.	0.	0.
4	0.	0.	0.	0.	0.	0.
5	0.	0.	0.	0.	0.	0.
0	-0.01265471	0.	-0.02098419	0.	0.00532835	0.
1	0.	0.	0.	0.	0.	0.
2	0.	0.	0.02283370	0.	0.	0.
3	0.	0.	0.	0.	0.	0.
4	0.02367478	0.	-0.02744369	0.	-0.00996845	0.
5	0.	0.	0.	0.	0.	0.
6	0.	0.	0.03386784	0.	0.	0.

Table VIII

AG2-Ø3 A=4.940

AG	0.250	0.250	0.250	0.250	0.750	0.750	0.750	0.250	0.750	0.750	0.750	0.250
Ø	0.500	0.500	0.	0.500	0.	0.	0.	0.	0.500	0.	0.500	0.
	0.	0.500	0.500	0.500	0.	0.500						

L	M	ØRIGIN AG ALM REAL	ALM IMAG	ØRIGIN Ø ALM REAL	ALM IMAG
0	0	-8.14379931	0.	5.44399786	0.
1	0	0.	0.	0.	0.
1	1	0.	0.	0.	0.
2	0	0.	0.	0.28160676	0.
2	1	0.22806948	0.22806949	0.	0.
2	2	0.	0.22806947	0.	0.
3	0	0.	0.	0.	0.
3	1	0.	0.	0.	0.
3	2	0.	0.	0.	-0.37861259
3	3	0.	0.	0.	0.
4	0	0.11074642	0.	-0.14234010	0.
4	1	-0.01359074	-0.01359070	0.	0.
4	2	0.	0.03844038	0.	0.
4	3	-0.03595767	0.03595764	0.	0.
4	4	0.06618364	0.	-0.12796166	0.
5	0	0.	0.	0.	0.
5	1	0.	0.	0.	0.
5	2	0.	0.	0.	-0.06530282
5	3	0.	0.	0.	0.
5	4	0.	0.	0.	0.
5	5	0.	0.	0.	0.
6	0	-0.01390760	0.	0.01744156	0.
6	1	-0.00355838	-0.00355838	0.	0.
6	2	0.	-0.00533705	0.	0.
6	3	-0.00168260	0.00168259	0.	0.
6	4	0.02601873	0.	-0.01976332	0.
6	5	-0.00459289	-0.00459289	0.	0.
6	6	0.	-0.00284672	0.	0.

Table IX

NA-PT3-Ø A=5.689

NA	0.	0.	0.	0.500	0.500	0.500						
PT	0.250	0.	0.500	0.500	0.250	0.	0.	0.500	0.250	0.750	0.	0.500
	0.500	0.750	0.	0.	0.500	0.750						
Ø	0.250	0.250	0.250	0.250	0.750	0.750	0.750	0.250	0.750	0.750	0.750	0.250
	0.750	0.750	0.750	0.750	0.250	0.250	0.250	0.750	0.250	0.250	0.250	0.750

L	M	ØRIGIN NA ALM REAL	ALM IMAG	ØRIGIN PT ALM REAL	ALM IMAG	ØRIGIN Ø ALM REAL	ALM IMAG
0	0	-3.35616586	0.	-6.34012449	0.	5.55158836	0.
1	0	0.	0.	0.	0.	0.	0.
1	1	0.	0.	0.	0.	0.	0.
2	0	0.	0.	-0.36297223	0.	0.	0.
2	1	0.	0.	0.	0.	-0.20518058	-0.20518055
2	2	0.	0.	0.44454841	0.	0.	-0.20518056
3	0	0.	0.	0.	0.	0.	0.
3	1	0.	0.	-0.01247910	0.	-0.13190589	0.13190588
3	2	0.	0.	0.	0.	0.16684922	0.
3	3	0.	0.	-0.00966616	0.	-0.10217387	-0.10217386
4	0	0.08977990	0.	0.12715140	0.	-0.08866502	0.
4	1	0.	0.	0.	0.	-0.01313988	-0.01313991
4	2	0.	0.	0.13210720	0.	0.	0.03716524
4	3	0.	0.	0.	0.	-0.03476488	0.03476491
4	4	0.05365372	0.	-0.02387614	0.	-0.05298738	0.
5	0	0.	0.	0.	0.	0.	0.
5	1	0.	0.	-0.00066188	0.	0.01643208	-0.01643208
5	2	0.	0.	0.	0.	0.05803908	0.
5	3	0.	0.	0.	0.	-0.01777077	-0.01777077
5	4	0.	0.	0.	0.	0.	0.
5	5	0.	0.	0.00068512	0.	-0.01700882	0.01700882
6	0	-0.00708890	0.	0.00653744	0.	-0.01030961	0.
6	1	0.	0.	0.	0.	0.00545928	0.00545928
6	2	0.00276061	0.	0.00421905	0.	0.	-0.00679379
6	3	0.	0.	0.	0.	-0.00740649	0.00740649
6	4	0.01326215	0.	-0.02455502	0.	0.01928758	0.
6	5	0.	0.	0.	0.	-0.00461697	-0.00461697
6	6	-0.00186120	0.	0.00625787	0.	0.	0.00773438

Table X

K-FE-Ø2 A=7.960

E	0.	0.	0.	0.	0.500	0.500	0.250	0.250	0.250	0.250	0.750	0.750
	0.500	0.	0.500	0.500	0.500	0.	0.750	0.250	0.750	0.750	0.750	0.250
	0.	0.	0.500	0.	0.500	0.	0.250	0.250	0.750	0.250	0.750	0.250
	0.500	0.	0.	0.500	0.500	0.500	0.750	0.250	0.250	0.750	0.750	0.750
	0.125	0.125	0.125	0.125	0.375	0.375	0.125	0.625	0.625	0.125	0.875	0.875
	0.375	0.125	0.375	0.375	0.375	0.125	0.375	0.625	0.875	0.375	0.875	0.625
	0.625	0.125	0.625	0.625	0.375	0.875	0.625	0.625	0.125	0.625	0.875	0.375
	0.875	0.125	0.875	0.875	0.375	0.625	0.875	0.625	0.375	0.875	0.875	0.125

	ØRIGIN	FE	ØRIGIN	K	ØRIGIN	Ø
M	ALM REAL	ALM IMAG	ALM REAL	ALM IMAG	ALM REAL	ALM IMAG
0	-9.58162487	0.	-1.95541081	0.	6.05419123	0.
0	0.	0.	0.	0.	0.	0.
1	0.	0.	0.	0.	0.	0.
0	0.	0.	0.	0.	0.	0.
1	0.	0.	0.	0.	0.57498499	0.57498499
2	0.	0.	0.	0.	0.	0.57498500
0	0.	0.	0.	0.	0.	0.
1	0.	0.	0.	0.	0.	0.
2	0.	0.62112275	0.	-0.02205049	0.	0.
3	0.	0.	0.	0.	0.	0.
0	0.23410912	0.	-0.01350321	0.	-0.16853560	0.
1	0.	0.	0.	0.	-0.06204139	-0.06204142
2	0.	0.	0.	0.	0.	0.17547956
3	0.	0.	0.	0.	-0.16414609	0.16414613
4	0.13990695	0.	-0.00806973	0.	-0.10071925	0.
0	0.	0.	0.	0.	0.	0.
1	0.	0.	0.	0.	0.	0.
2	0.	0.16091968	0.	-0.00173405	0.	0.
3	0.	0.	0.	0.	0.	0.
4	0.	0.	0.	0.	0.	0.
5	0.	0.	0.	0.	0.	0.
0	-0.03802649	0.	0.00061209	0.	0.03073002	0.
1	0.	0.	0.	0.	-0.02280463	-0.02280463
2	0.	0.	0.	0.	0.	-0.03775779
3	0.	0.	0.	0.	-0.01315276	0.01315277
4	0.07114104	0.	-0.00114511	0.	-0.05749060	0.
5	0.	0.	0.	0.	-0.03220146	-0.03220146
6	0.	0.	0.	0.	0.	-0.01744504

Table XI

SI-Ø2 A=7.160

I	0.	0.	0.	0.	0.500	0.500	0.250	0.250	0.250	0.250	0.750	0.750
	0.500	0.	0.500	0.500	0.500	0.	0.750	0.250	0.750	0.750	0.750	0.250
	0.125	0.125	0.125	0.125	0.375	0.375	0.125	0.625	0.625	0.125	0.875	0.875
	0.375	0.125	0.375	0.375	0.375	0.125	0.375	0.625	0.875	0.375	0.875	0.625
	0.625	0.125	0.625	0.625	0.375	0.875	0.625	0.625	0.125	0.625	0.875	0.375
	0.875	0.125	0.875	0.875	0.375	0.625	0.875	0.625	0.375	0.875	0.875	0.125

	ØRIGIN	SI	ØRIGIN	Ø
M	ALM REAL	ALM IMAG	ALM REAL	ALM IMAG
0	-12.38263190	0.	7.98499638	0.
0	0.	0.	0.	0.
1	0.	0.	0.	0.
0	0.	0.	0.	0.
1	0.	0.	1.18484712	1.18484712
2	0.	0.	0.	1.18484716
0	0.	0.	0.	0.
1	0.	0.	0.	0.
2	0.	0.89161128	0.	0.
3	0.	0.	0.	0.
0	0.39038371	0.	-0.39493667	0.
1	0.	0.	-0.13557618	-0.13557624
2	0.	0.	0.	0.38346738
3	0.	0.	-0.35870086	0.35870098
4	0.23329886	0.	-0.23601974	0.
0	0.	0.	0.	0.
1	0.	0.	0.	0.
2	0.	0.29911921	0.	0.
3	0.	0.	0.	0.
4	0.	0.	0.	0.
5	0.	0.	0.	0.
0	-0.07994447	0.	0.08471100	0.
1	0.	0.	-0.06395741	-0.06395740
2	0.	0.	0.	-0.10588079
3	0.	0.	-0.03687867	0.03687868
4	0.14956238	0.	-0.15847975	0.
5	0.	0.	-0.09030070	-0.09030071
6	0.	0.	0.	-0.04892916

TABLE XII

AL2-MG-Ø4 A=8.059

AL	0.625	0.625	0.625	0.625	0.875	0.875	0.875	0.625	0.875	0.875	0.875	0.625
	0.625	0.125	0.125	0.625	0.375	0.375	0.875	0.125	0.375	0.875	0.375	0.125
	0.125	0.625	0.125	0.125	0.875	0.375	0.375	0.625	0.375	0.375	0.875	0.125
	0.125	0.125	0.625	0.125	0.375	0.875	0.375	0.125	0.875	0.375	0.375	0.625
MG	0.	0.	0.	0.	0.500	0.500	0.500	0.	0.500	0.500	0.500	0.
	0.250	0.250	0.250	0.250	0.750	0.750	0.750	0.250	0.750	0.750	0.750	0.250
Ø	0.375	0.375	0.375	0.375	0.625	0.625	0.625	0.375	0.625	0.625	0.625	0.375
	0.875	0.875	0.875	0.875	0.625	0.625	0.625	0.875	0.625	0.625	0.625	0.875
	0.375	0.875	0.875	0.375	0.125	0.125	0.625	0.875	0.125	0.625	0.125	0.875
	0.875	0.375	0.375	0.875	0.125	0.125	0.625	0.375	0.125	0.625	0.125	0.375
	0.875	0.375	0.875	0.875	0.625	0.125	0.125	0.375	0.125	0.125	0.625	0.875
	0.375	0.875	0.375	0.375	0.625	0.125	0.125	0.875	0.125	0.125	0.625	0.375
	0.875	0.875	0.375	0.875	0.125	0.625	0.125	0.875	0.625	0.125	0.125	0.375
	0.375	0.375	0.875	0.375	0.125	0.625	0.125	0.375	0.625	0.125	0.125	0.875

		ØRIGIN	AL	ØRIGIN	MG	ØRIGIN	Ø
L	M	ALM REAL	ALM IMAG	ALM REAL	ALM IMAG	ALM REAL	ALM IMAG
0	0	-7.90614063	0.	-7.72952527	0.	6.27619386	0.
1	0	0.	0.	0.	0.	-0.48349914	0.
1	1	0.	0.	0.	0.	-0.34188542	-0.3418855
2	0	0.	0.	0.	0.	0.	0.
2	1	0.14782479	0.14782480	0.	0.	0.21011862	0.2101186
2	2	0.	0.14782477	0.	0.	0.	0.2101186
3	0	0.	0.	0.	0.	-0.34034213	0.
3	1	0.	0.	0.	0.	0.14737244	0.1473722
3	2	0.	0.	0.	-0.52087519	0.	0.1174009
3	3	0.	0.	0.	0.	-0.19025676	0.1902568
4	0	-0.25165626	0.	0.22841588	0.	0.13994851	0.
4	1	0.00384695	0.00384693	0.	0.	-0.01881876	-0.0188187
4	2	0.	-0.01088079	0.	0.	0.	0.0532275
4	3	0.01017814	-0.01017799	0.	0.	-0.04978986	0.0497897
4	4	-0.15039334	0.	0.13650463	0.	0.08363526	0.
5	0	0.	0.	0.	0.	-0.05583144	0.
5	1	0.	0.	0.	0.	-0.03652287	-0.0365228
5	2	0.	0.	0.	-0.14423722	0.	0.0354473
5	3	0.	0.	0.	0.	-0.02353180	0.0235318
5	4	0.	0.	0.	0.	-0.03039386	0.
5	5	0.	0.	0.	0.	-0.03370390	-0.0337039
6	0	-0.01370632	0.	-0.03512712	0.	0.02047696	0.
6	1	-0.00176585	-0.00176584	0.	0.	-0.00740547	-0.0074054
6	2	0.	0.00169610	0.	0.	0.	-0.0111071
6	3	0.00206141	-0.00206143	0.	0.	-0.00350171	0.0035017
6	4	0.02564218	0.	0.06571680	0.	-0.03830889	0.
6	5	0.00110306	0.00110306	0.	0.	-0.00955843	-0.0095584
6	6	0.	-0.00238906	0.	0.	0.	-0.0059244

cell of average dimension 8 Å. We have included SnF_4 mainly as an illustration of a case where the actual periodicity is not the same in all dimensions.

For purposes of checking, there exist simple relations between the Madelung constant and our coefficients C_{00}. The Madelung constants for NaCl, CsCl, ZnS, CaF_2, Cu_2O hark back to an extensive tabulation by J. Sherman.[7] (Sherman's number for Cu_2O, quoted throughout the literature, e.g., by Born and Huang,[8] is in error. The correct value has been given by Hund.[9] Very accurate computations for some cubic crystals have been made by Benson and Zeggeren.[10] For MX compounds, the Madelung constant is related to our C_{00} by a simple multiplicative factor. This factor is $(4\pi)^{\frac{1}{2}}$ times the ionic charge divided by the length of the unit cell. For compounds like CaF_2 and Cu_2O, the Madelung constant is related in the same fashion to the average of the absolute values of the C_{00}'s for the various sites. For Cu_2O, the potential at each site separately has more recently been computed by Dahl.[11] Madelung calculations for the perovskites have been considered by Templeton,[12] Fumi and Tosi,[13] and Cowley.[14] Cowley has calculated numerically the

TABLE XIII

SN-F4 A=8.000

N	0.	0.	0.	0.250	0.250	0.500	0.500	0.	0.	0.750	0.	0.
	0.	0.500	0.	0.250	0.750	0.	0.500	0.500	0.	0.750	0.500	0.
1	0.	0.250	0.	0.250	0.	0.	0.250	0.	0.500	0.	0.250	0.500
	0.500	0.250	0.	0.750	0.	0.	0.750	0.	0.500	0.500	0.250	0.500
	0.	0.750	0.	0.250	0.500	0.	0.250	0.500	0.500	0.	0.750	0.500
	0.500	0.750	0.	0.750	0.500	0.	0.750	0.500	0.500	0.500	0.750	0.500
2	0.	0.	0.250	0.	0.	0.750	0.250	0.250	0.750	0.250	0.250	0.250
	0.500	0.	0.250	0.500	0.	0.750	0.750	0.250	0.750	0.750	0.250	0.250
	0.	0.500	0.250	0.	0.500	0.750	0.250	0.750	0.750	0.250	0.750	0.250
	0.500	0.500	0.250	0.500	0.500	0.750	0.750	0.750	0.750	0.750	0.750	0.250

	ØRIGIN	SN	ØRIGIN	F1	ØRIGIN	F2
M	ALM REAL	ALM IMAG	ALM REAL	ALM IMAG	ALM REAL	ALM IMAG
0	-6.58065987	0.	5.55493051	0.	2.55387265	0.
0	0.	0.	0.	0.	2.36476621	0.
1	-0.52353968	0.33058744	-0.27535433	0.	-0.42667971	0.
0	-0.34731891	0.	-0.93092058	0.	0.74515594	0.
1	0.	0.	0.	0.	0.	0.10740093
2	0.	-0.14623467	-0.92373976	0.	0.	0.
0	0.	0.	0.	0.	0.29895561	0.
1	0.01702513	-0.03159145	-0.01105826	0.	-0.01496998	0.
2	0.	0.	0.	0.	0.	-0.03669877
3	0.03774419	0.03278823	0.01427609	0.	0.01932615	0.
0	-0.09091583	0.	0.14195608	0.	0.16193924	0.
1	0.	0.	0.	0.	0.	-0.00244038
2	0.	0.01162022	0.11792579	0.	0.	0.
3	0.	0.	0.	0.	0.	0.00645663
4	-0.07077464	0.	0.16640348	0.	0.01216549	0.
0	0.	0.	0.	0.	0.06735962	0.
1	-0.00211426	0.00191500	-0.00070479	0.	0.00125949	0.
2	0.	0.	0.	0.	0.	-0.00241358
3	-0.00041911	-0.00083644	-0.00031195	0.	0.00196165	0.
4	0.	0.	0.	0.	0.00081620	0.
5	0.00288825	-0.00288930	-0.00042522	0.	0.00057840	0.
0	-0.00668188	0.	-0.01733700	0.	0.03332756	0.
1	0.	0.	0.	0.	0.	-0.00024364
2	0.	-0.00081959	-0.01953730	0.	0.	0.
3	0.	0.	0.	0.	0.	0.00011520
4	0.01081367	0.	-0.02548826	0.	-0.00445095	0.
5	0.	0.	0.	0.	0.	-0.00031447
6	0.	0.00129473	-0.02929148	0.	0.	0.

"partial Madelung coefficients" as defined by Templeton, and Fumi and Tosi have shown how the potential at any site of an arbitrary perovskite structure can be obtained by linear combinations of these partial Madelung coefficients. Our numerical comparison for the perovskite C_{00}'s is therefore, essentially with Cowley's calculation. Comparison of our C_{00}'s

TABLE XIV—COMPARISON BETWEEN PRESENT COMPUTATION AND PREVIOUS WORK FOR THE COEFFICIENTS C_{00}

Substance	Site	Present Result	Previous Result	Source for Previous Result
NaCl	either	2.19679	2.1968	Sherman
CsCl	either	1.74998	1.75003	Benson, Zeggeren
ZnS	either	4.95817	4.95845	Benson, Zeggeren
CaF_2	$\|Ca\| + \|F\|$	7.55090	7.55090	Benson, Zeggeren
Cu_2O	$\|Cu\| + \|O\|$	8.51809	8.5172	Hund
Cu_2O	Cu	3.14084	3.1406	Dahl
Cu_2O	O	5.37725	5.3768	Dahl
$KTaO_3$	K	2.97906	2.9765	Cowley
$KTaO_3$	Ta	12.80987	12.8115	Cowley
$KTaO_3$	O	6.17037	6.1711	Cowley
$SrTiO_3$	Sr	4.89031	4.8905	Cowley
$SrTiO_3$	Ti	11.2358	11.2362	Cowley
$SrTiO_3$	O	5.86044	5.8606	Cowley

with previous work is made in Table XIV. In general, some divergence appears in the fifth significant figure.

We have ourselves checked a portion of our results by using the Evjen summation method. This method is particularly useful for coefficients with higher l-values, but converges quite slowly for C_{00}. Only for CsCl and NaCl were we able, in reasonable computing time, to carry the summation to a sufficient degree of convergence for C_{00}. The Evjen results confirm our Ewald results for these substances, for all the coefficients. For the perovskites, we pushed the summation at the Ta site as far as the ninth Evjen shell (24,564 neighbors), but for C_{00} shell-to-shell fluctuations were still in the fourth significant figure. For higher l-values, the Evjen summation was able to confirm our Ewald results for all coefficients, for all sites, for both perovskites. The same is true for Cu_2O. It should be pointed out that the computation of the coefficients (exclusive of C_{00}) takes about ten minutes of 7094 time per crystal if the Evjen method is used. We attempted a check on one site of Al_2MgO_4. The computer was stopped after 20 minutes, at which time usefully convergent results were obtained only for coefficients with $l \geqq 3$.

We note that the appearance of coefficients of odd l, at any site, is associated with lack of inversion symmetry.

We believe that the computations we have discussed show that in certain applications our method of doing crystal sums offers definite advantages, both in accuracy and in time. Suitable applications are those where a number of structures must be considered that can be described by basically the same coordinate grid, especially if the number of ions per unit cell is large.

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