vector approximation. Because the momentum transferred in the plane of the slab is small, we need not take the wave vector into account for the components of the dynamical matrix of nonzero reciprocal-lattice vector. These components, independent of the transfer wave vector, have been summed and appear as the Lorentz-local-field correction which is contained in the dielectric function used. See Ref. 1.

[10] See Eq. (12) of Ref. 2.

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[14] $K=430$ is equivalent to a scattering angle of $(10)^{-4}$ rad.

[15] Recently Lucas and Kartheuser [Phys. Rev. B **1,** 3588 (1970)] have developed a single slab nonretarded theory for $\langle \Delta U(\Omega) \rangle$ which gives results comparable to those of FO except in the frequency range near $\Omega=\Omega_l$. Lucas and Kartheuser neglected the interaction between the bulk modes and the surface modes and this interaction gives rise to significant effects near $\Omega=\Omega_l$.

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[17] For details of the Al loss distribution see Ref. 2.

[18] See also the first paper of Ref. 1, p. A2084.

[19] The plasma energy chosen is the lowest energy at which the real part of the dielectric function of graphite has a zero according to the data of H. R. Philipp [*Optical Properties and Electronic Structure of Metals and Alloys* (North-Holland, Amsterdam, 1966), p. 408]. We calculated the relaxation time using the carbon conductivity at zero frequency given in the *Handbook of Chemistry and Physics*, 48th ed. (Chemical Rubber Publishing Co., Akron, 1968) p. f-132.

[20] H. Boersch, J. Geiger, and W. Stickel [Z. Physik **212,** 130 (1968)] show theoretical energy-loss curves which clearly include both angular- and energy-resolution functions. Their Figs. 5 and 6 are much like our Figs. 7 and 6. However, this paper of Boersch, Geiger, and Stickel contains almost no details concerning their treatment.

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Electronic-Structure Studies of Solids. I. Fourier Representation Method for Madelung Sums*

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By use of Fourier-integral representations and lattice orthogonality relations, Madelung sums are cast in a form which explicitly separates contributions due to crystal symmetry from those due to the detailed arrangement of neighboring ions. The usefulness and mathematical soundness of the method are demonstrated by verifying known Madelung constants and by obtaining more accurate values for the electrostatic energies of low-density plasma models. The method is also easily applied to the study of ionic displacements or crystal defects.

I. INTRODUCTION

In connection with electronic-structure calculations of crystalline solids, we found it convenient to introduce a Fourier-integral representation for the electrostatic potential energy. The various contributions of opposite sign exhibit cancellations and limiting properties also manifested by classical electrostatic interactions as encountered in the evaluation of Madelung constants. We therefore found it profitable to reinvestigate the Madelung problem to establish the correctness of the mathematical steps, and to determine highly accurate values of numerical constants entering the electronic-structure studies.

The classical methods for the evaluation of Madelung sums are those of Evjen[1] and Ewald.[2] These sums, which are conditionally (and slowly) convergent, are in Evjen's method analyzed by grouping contributions into shells with vanishing low-order multiple moments. Ewald introduces an integral transformation which is then broken into two parts, each of which is more rapidly convergent than the original sum. However, neither of these methods has really made the evaluation of Madelung sums as simple as might be desired. Refinements and modifications of the Evjen and Ewald procedures have therefore been investigated; of note are the contributions of Emersleben[3] and of Bertaut.[4]

The explicit use of Fourier transforms in lattice-sum evaluations has been considered before,[5] and in fact a treatment containing some of the features of that described here is to be found in the work of Nijboer and De Wette.[6] However, the previous use of Fourier methods has been such as to avoid the mathematical difficulties associated with arrays of point charges, and the finally resulting formulations are not optimal for the application we contemplate to quantum mechanics. In contrast, we find that passage to the point-charge limit leads to simple and useful final formulas.

Our final formulas in effect calculate the electrostatic energy as a deviation from a limiting case in which ions of one sign are immersed in a uniform background of opposite charge. This limiting case, familiar in plasma physics, is treated with the aid of the Euler-Maclaurin summation formula. The notion of a point-charge array and compensating uniform background has also entered previous discussions of Madelung energies. For example, Tosi[7] reviews methods whereby this idea can be used to relate Madelung constants of different structures of the same lattice symmetry. The resulting formulas are similar to those presented here. The most

TABLE I. Values of lattice structure constants C [Eq. (7)] and quantities $F(\alpha)$ (see Appendix B).

Symmetry	$b/a=\alpha$	c/a	$F(\alpha)_{n=4}$	$F(\alpha)_{n=5}$	C (units $2\pi/a$)
Cubic	1	1	−0.975 066 171	−0.975 066 212	−8.913 633
Tetragonal	1	2			−5.673 219
Orthorhombic	$\sqrt{\frac{8}{3}}$	$\sqrt{3}$	−0.731 669 897	−0.731 669 901	−5.688 760
Orthorhombic	$\sqrt{3}$	$\sqrt{\frac{8}{3}}$	−0.702 237 143	−0.702 237 095	−5.688 760
Orthorhombic	$\sqrt{3}$	$\sqrt{6}$			−4.170 255
Hexagonal	1	$\sqrt{\frac{8}{3}}$			−7.033 153

significant practical point of departure from earlier work is that we give a direct method for evaluating the energetic contribution for the array plus background, while previous authors deduced this quantity from conventionally calculated Madelung constants.

After describing our methods, we verify the analysis by reproducing known Madelung constants and plasma-energy limits, and we indicate how one may treat deviations from perfect lattice structures.

II. METHOD

Consider an infinite periodic lattice each cell of which is electrically neutral and contains an identical distribution of charge. Let $\mathbf{r}_i$ denote the position of the origin of cell i, and let $\mathbf{s}_m$, $m=1, 2, \ldots, d$, denote the respective locations, relative to the cell origin, of charges q_m in each cell. If there is a charge at the cell origin, we assign it the symbol q_0. Then the electrostatic potential at $\mathbf{r}_i$ due to ions at all other points in the lattice may be expressed as the sum

$$V(\mathbf{r}_i)=q_0\sum_{j\neq i}|\,\mathbf{r}_j-\mathbf{r}_i\,|^{-1}+\sum_j\sum_{m=1}^{d}q_m\,|\,\mathbf{r}_j-\mathbf{r}_i+\mathbf{s}_m\,|^{-1}. \tag{1}$$

In this and all equations to follow, sums over lattice cells will include all cells except as explicitly indicated otherwise. As written, the j summations in Eq. (1) are individually divergent, but it is to be understood that the two summations are to be combined to produce a convergent result.

We proceed by introducing Fourier-integral representations for the summands of Eq. (1), in the form

$$|\,\mathbf{r}\,|^{-1}=(1/2\pi^2)\int(d\mathbf{k}/k^2)\,\exp(-i\mathbf{k}\cdot\mathbf{r}), \tag{2}$$

thereby obtaining

$$V(\mathbf{r}_i)=(q_0/2\pi^2)\sum_{j\neq i}\int(d\mathbf{k}/k^2)\,\exp[-i\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_i)]$$
$$+\sum_{m=1}^{d}(q_m/2\pi^2)\sum_j\int(d\mathbf{k}/k^2)\,\exp[-i\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_i+\mathbf{s}_m)]. \tag{3}$$

We intend now to interchange the order of the summation and integration in Eq. (3), but we note that the necessary uniform-convergence criteria cannot be fulfilled in the neighborhood of $\mathbf{k}=0$. We therefore divide the $\mathbf{k}$ integrations into two regions, the first of which is a sphere of radius ϵ about $\mathbf{k}=0$, the second region being the remainder of $\mathbf{k}$ space. Appropriate conditions determining ϵ are examined in Appendix A, as is a discussion of the first integration region. It is shown there that the first integration region makes no contribution to $V(\mathbf{r}_i)$. In the second integration region, we interchange summation and integration, reaching

$$V(\mathbf{r}_i)=\frac{1}{2\pi^2}\int'\frac{d\mathbf{k}}{k^2}\{\sum_j\exp[-i\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_i)]$$
$$\times[q_0+\sum_{m=1}^{d}q_m\exp(-i\mathbf{k}\cdot\mathbf{s}_m)]-q_0\}. \tag{4}$$

The prime indicates the exclusion of the sphere about $\mathbf{k}=0$. In writing Eq. (4), we have added the term $j=i$ to the summation involving q_0 and then explicitly subtracted it again.

Next, we recognize that the sum over j can be identified in terms of δ functions for points $\mathbf{k}_\mu$ of the reciprocal lattice[6]:

$$\sum_j\exp[-i\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_i)]=(8\pi^3/v_0)\sum_{\mathbf{k}_\mu}\delta(\mathbf{k}-\mathbf{k}_\mu), \tag{5}$$

where v_0 is the cell volume (in ordinary space). Introducing Eq. (5), two of the terms in the $\mathbf{k}$ integration of Eq. (4) reduce to reciprocal-lattice sums, and

$$V(\mathbf{r}_i)=\frac{q_0}{2\pi^2}\left[\frac{8\pi^3}{v_0}\sum_{\mathbf{k}_\mu\neq0}k_\mu^{-2}-\int'k^{-2}d\mathbf{k}\right]$$
$$+(4\pi/v_0)\sum_{m=1}^{d}q_m\sum_{\mathbf{k}_\mu\neq0}k_\mu^{-2}\exp(-i\mathbf{k}_\mu\cdot\mathbf{s}_m). \tag{6}$$

The portion of Eq. (6) in square brackets consists of two individually divergent terms; by examining the manner in which Eq. (6) was derived from Eq. (4), it is clear that the square bracket is to be interpreted as the limit reached when the integration and summation are extended infinitely over identical regions of $\mathbf{k}$ space. This limit, to which we assign the symbol C, depends upon the lattice structure. It is clear that C need not be zero, as it is a close three-dimensional analog of the one-dimensional limit leading to Euler's constant. The evaluation of C and some mathematical questions associated therewith are discussed in Appendix B, and values of C for some common lattice systems are listed in Table I. Equation (6) therefore

becomes our final form

$$V(\mathbf{r}_i)=(q_0C/2\pi^2)+(4\pi/v_0)\sum_{m=1}^{d} q_m \sum_{\mathbf{k}_\mu\neq 0} k_\mu^{-2} \times \exp(-i\mathbf{k}_\mu\cdot\mathbf{s}_m). \quad (7)$$

Equation (7) may be interpreted as the sum of two contributions, of which the first depends only upon the lattice structure, while the second depends also upon the distribution of charge within each unit cell. A fuller interpretation follows if we consider the result of distributing the charges q_m uniformly over the unit cell. This corresponds to averaging $\exp(-i\mathbf{k}_\mu\cdot\mathbf{s}_m)$ with respect to $\mathbf{s}_m$ and leads to the vanishing of the second term of Eq. (7). The quantity C is therefore a measure of the potential at a lattice point when a unit positive charge is placed at each other lattice point and balancing negative charge is distributed uniformly throughout all space. The second term of Eq. (7) therefore represents the effect of replacing a uniform background of charge $-q_0$ per cell by the actual localized charges $q_1, q_2, \ldots, q_m$.

Turning now to the localization-dependent term of Eq. (7), we note that the complex exponential provides an oscillatory factor which accelerates convergence. Because $V(\mathbf{r}_i)$ is real, we may make the oscillatory nature explicit by replacing $\exp(-i\mathbf{k}_\mu\cdot\mathbf{s}_m)$ by $\cos(\mathbf{k}_\mu\cdot\mathbf{s}_m)$, or, for orthorhombic systems, by cosines produced by a component expansion: $\cos(k_{\mu x}x_m)\times\cos(k_{\mu y}y_m)\cos(k_{\mu z}z_m)$, where $\mathbf{s}_m=(x_m, y_m, z_m)$ and $\mathbf{k}_\mu=(k_{\mu x}, k_{\mu y}, k_{\mu z})$. The oscillations and concomitant convergence will be most rapid when $\mathbf{s}_m$ is near the center of the unit cell.

If one or more of the lattice axial directions is orthogonal to the others, the sum of Eq. (7) can be reduced analytically to two dimensions through use of the relations[8]

$$\sum_{w=1}^{\infty}(\cos\gamma w/w^2)=\tfrac{1}{6}\pi^2-\tfrac{1}{2}\pi\gamma+\tfrac{1}{4}\gamma^2, \quad (8)$$

$$\sum_{w=-\infty}^{\infty}\frac{\cos\gamma w}{w^2+\alpha^2}=\frac{\pi\cosh\alpha(\pi-\gamma)}{\alpha\sinh\alpha\pi} \quad (\alpha\neq 0). \quad (9)$$

We illustrate for an orthorhombic lattice of cell dimensions a, b, c, for which $\mathbf{k}_\mu=(2\pi u/a, 2\pi v/b, 2\pi w/c)$, for integer or zero u, v, w. Then

$$V(\mathbf{r}_i)=(q_0C/2\pi^2)+(1/\pi abc)\sum_{m=1}^{d} q_m \times \sum_{uvw\neq 000}\frac{\cos(u\pi x_m/a)\cos(v\pi y_m/b)\cos(w\pi z_m/c)}{(u/a)^2+(v/b)^2+(w/c)^2}. \quad (10)$$

At least one of x_m, y_m, z_m will be nonzero. Assuming $z_m\neq 0$ for all m, we apply Eqs. (8) and (9) to the sum over w, obtaining

$$V(\mathbf{r}_i)=\frac{q_0C}{2\pi^2}+\frac{c\pi}{ab}\sum_{m=1}^{d} q_m \times\left[\frac{1}{3}-\frac{z_m}{c}+\frac{z_m^2}{2c^2}+\sum_{uv\neq 00}\cos\left(\frac{u\pi x_m}{a}\right)\cos\left(\frac{u\pi y_m}{b}\right)\frac{\cosh\{R_{uv}(1-z_m/c)\}}{R_{uv}\sinh R_{uv}}\right], \quad (11)$$

where

$$R_{uv}=\pi[(cu/a)^2+(cv/b)^2]^{1/2}.$$

III. DISCUSSION

Our first concern might well be an explicit verification of the mathematical arguments by reproduction of some established Madelung constants. We also wish to see what computational effort is needed to obtain reasonable accuracy. We look first at a cubic CsCl structure of cell dimension a, with a unit positive charge at each cell origin and a unit negative charge at the midpoint of each cell $(\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a)$. We find the correct value of $V(\mathbf{r}_i)$ already given to four significant figures when the summation of Eq. (11) only contains the five distinct terms with $u^2+v^2<3$; extension to $u^2+v^2<5$ yields from 12 distinct terms the six-significant-figure result $V=-1.762\,675/s$, where s, the nearest-neighbor separation, is $(\sqrt{\frac{3}{4}})a$. The established value[9] of this Madelung constant is $-1.762\,670/s$. The calculation just described takes 5 or 10 min on a good desk calculator and obviously does not involve the use of tables of error functions. Comparable results are obtained for the NaCl structure, calculated as a cubic lattice of cell dimension a with unit positive charges at $(0, 0, 0)$, $(\frac{1}{2}a, 0, \frac{1}{2}a)$, $(0, \frac{1}{2}a, \frac{1}{2}a)$, and $(\frac{1}{2}a, \frac{1}{2}a, 0)$ and unit negative charges at $(\frac{1}{2}a, 0, 0)$, $(0, \frac{1}{2}a, 0)$, $(0, 0, \frac{1}{2}a)$, and $(\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a)$. Our six-figure result is $-1.747\,563/s$, $(s=\frac{1}{2}a)$, while the established value[9] is $-1.747\,558/s$.

We next look more closely at the relation between our present calculations and those of low-density limits for the energy of a plasma. The usual low-density plasma model[10] consists of a lattice of point electrons in

TABLE II. Energy (Hartrees) per particle for unit charges in various space lattices with uniform background of neutralizing charge. The quantity r_s (Bohrs) is the radius of the sphere containing the volume per particle.

Lattice	Energy: This research	Energy: Previous work (Refs. 11–13)
Simple cubic	$-0.880\,059\,r_s^{-1}$	$-0.880\,r_s^{-1}$
Face-centered cubic	$-0.895\,874\,r_s^{-1}$	$-0.895\,86\,r_s^{-1}$
Body-centered cubic	$-0.895\,929\,r_s^{-1}$	$-0.895\,93\,r_s^{-1}$
Hexagonal close-packed	$-0.895\,838\,r_s^{-1}$	$-0.895\,84\,r_s^{-1}$

a uniform background of positive charge, and therefore has an energy closely related to the constant we denote by C. These plasma energies have been previously calculated by Ewald-type methods for simple cubic,[11] body- and face-centered cubic,[12] and hexagonal close-packed[13] lattices. For primitive Bravais lattices (e.g., simple cubic), our C values are directly identifiable as electrostatic potentials at lattice sites. For nonprimitive lattices, additional face- or body-centered charges can be treated by explicitly including them in the summation of Eq. (7). This idea is used in Appendix B to derive C values for hexagonal lattices.

In line with the preceding discussion, we have calculated the potential at lattice points of face- and body-centered cubic lattices and of the hexagonal close-packed lattice. Our results, shown in Table II, agree with the less accurate previously reported values to within the error limits of the latter.

Finally, we consider the application of our method to calculations involving deviations from perfect crystalline symmetry. For such calculations we may need the electrostatic potential at an arbitrary point of the crystal. To make such a calculation, all we need do is to define that point as a lattice point, making suitable assignments of the locations of all charges. If no charge is at a lattice point, we simply have $q_0=0$ and no term involving C occurs. Thus an interstitial defect can be handled simply by evaluating the potential at its location, while the displacement of an atom can be treated by deducting from the potential calculated for its displaced position the effect of the missing charge at its original position.

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APPENDIX A: BEHAVIOR AT $\mathbf{k}=0$

In order to carry out the analysis leading from Eq. (4) to Eq. (6), it is necessary that the region excluded at $\mathbf{k}=0$ be sufficiently large that no residual contributions are produced from the presence of $\delta(\mathbf{k}-\mathbf{k}_\mu)$ with $\mathbf{k}_\mu=0$. What this statement really implies is that as we proceed to the limit of an infinite lattice, the value assigned to ϵ must tend to zero more slowly than the width of the function whose limit is $\delta(\mathbf{k})$. An explicit examination of Eq. (5) indicates that the width of $\delta(\mathbf{k})$ approaches zero as $N^{-1/3}$, where N is the number of lattice cells. Therefore ϵ cannot be assumed to go to zero more rapidly than $N^{-1/3}$. This dependence for ϵ is such that the contribution to Eq. (3) near $\mathbf{k}=0$ requires delicate analysis. We proceed accordingly, but without great rigor.

Introducing spherical wave expansions for the exponentials in Eq. (3), and discarding the terms which vanish upon angular integration, we find that the contribution to Eq. (3) from $k<\epsilon$ is proportional to

$$\Gamma=q_0\sum_{j\neq i}\int_0^\epsilon dk\,\frac{\sin k\,|\,\mathbf{r}_j-\mathbf{r}_i\,|}{k\,|\,\mathbf{r}_j-\mathbf{r}_i\,|}+\sum_{m=1}^{d}q_m \times\sum_j\int_0^\epsilon dk\,\frac{\sin k\,|\,\mathbf{r}_j-\mathbf{r}_i+\mathbf{s}_m\,|}{k\,|\,\mathbf{r}_j-\mathbf{r}_i+\mathbf{s}_m\,|}. \quad \text{(A1)}$$

We rewrite Γ in the form

$$\Gamma=q_0\sum_{j\neq i}|\,\mathbf{r}_j-\mathbf{r}_i\,|^{-1}\int_0^{\epsilon|\mathbf{r}_j-\mathbf{r}_i|}t^{-1}\sin t\,dt + \sum_{m=1}^{d}q_m\sum_j|\,\mathbf{r}_j-\mathbf{r}_i+\mathbf{s}_m\,|^{-1}\int_0^{\epsilon|\mathbf{r}_j-\mathbf{r}_i|}t^{-1}\sin t\,dt + \sum_{m=1}^{d}q_m\sum_j|\,\mathbf{r}_j-\mathbf{r}_i+\mathbf{s}_m\,|^{-1}\int_{\epsilon|\mathbf{r}_j-\mathbf{r}_i|}^{\epsilon|\mathbf{r}_j-\mathbf{r}_i+\mathbf{s}_m|}t^{-1}\sin t\,dt \quad \text{(A2)}$$

and approximate the last integral by

$$\int_{\epsilon|\mathbf{r}_j-\mathbf{r}_i|}^{\epsilon|\mathbf{r}_j-\mathbf{r}_i+\mathbf{s}_m|}t^{-1}\sin t\,dt=(\epsilon\,|\,\mathbf{r}_j-\mathbf{r}_i+\mathbf{s}_m\,|-\epsilon\,|\,\mathbf{r}_j-\mathbf{r}_i\,|)\times\frac{\sin\epsilon\,|\,\mathbf{r}_j-\mathbf{r}_i\,|}{\epsilon\,|\,\mathbf{r}_j-\mathbf{r}_i\,|}. \quad \text{(A3)}$$

The result is that the third term of Eq. (A2) becomes

$$-q_0\sum_{j\neq i}|\,\mathbf{r}_j-\mathbf{r}_i\,|^{-1}\sin\epsilon\,|\,\mathbf{r}_j-\mathbf{r}_i\,| - \sum_{m=1}^{d}q_m\sum_j|\,\mathbf{r}_j-\mathbf{r}_i+\mathbf{s}_m\,|^{-1}\sin\epsilon\,|\,\mathbf{r}_j-\mathbf{r}_i\,|+\cdots.$$

In obtaining this result we removed the term $j=i$ from the first summation because it vanishes proportionally to ϵ. We also used the fact that

$$\sum_{m=1}^{d}q_m=-q_0.$$

We are now ready to argue that $\Gamma\to0$ as $N\to\infty$, even though (i) $\epsilon\sim N^{-1/3}$, (ii) the maximum values of $|\,\mathbf{r}_j-\mathbf{r}_i\,|$ and $|\,\mathbf{r}_j-\mathbf{r}_i+\mathbf{s}_m\,|$ both increase proportionally to $N^{1/3}$, and (iii) there are N terms in the summations over j. To start, we remember that the sums over j are to be carried out in a way leading to the convergence of Eq. (1). One way to do this is to sum successively over spherical shells whose boundaries are chosen to make them have vanishing moments at least through order 2. Looking now at the expression for Γ, we see that, because $\epsilon\to0$, all the terms from a single shell of j values will have nearly the same values of

$$\int_0^{\epsilon|\mathbf{r}_j-\mathbf{r}_i|}t^{-1}\sin t\,dt$$

and of $\sin\epsilon\,|\,\mathbf{r}_j-\mathbf{r}_i\,|$, and that for such a shell the net contribution to Γ will be proportional to the contribution of that shell to $V(\mathbf{r}_i)$. Since the sum for $V(\mathbf{r}_i)$ converges, we conclude there will be no significant contribution to Γ for j-value shells of radii greater than some R_0 which is independent of N. Finally, we cause

the j values inside the radius R_0 to have a negligible contribution to Γ by increasing N and thereby decreasing ϵ. Since R_0 does not depend on N, this can certainly be done.

An argument such as we have just given is necessary because a straightforward expansion of $|\mathbf{r}_j-\mathbf{r}_i+\mathbf{s}_m|^{-1}$ does not lead directly to cancellations of sufficiently high order. The difficulty is related to that which would arise if an attempt were made to evaluate Eq. (1) by grouping terms of equal j from the two sums. This would result in charge arrays which, even in the limit $N\to\infty$, would have nonvanishing dipole moments and therewith divergent long-range contributions.

APPENDIX B: LATTICE-STRUCTURE CONSTANTS

As indicated in the text, the electrostatic potential at a point of a periodic lattice may include a constant C whose value depends only upon the lattice structure. In particular,

$$C=\lim[(8\pi^3/v_0)\sum_{\mathbf{k}_\mu\neq 0}k_\mu^{-2}-\int k^{-2}d\mathbf{k}], \qquad \text{(B1)}$$

where the limit is that reached as the included region of $\mathbf{k}$ space is extended infinitely. We no longer indicate the exclusion from the integration of a small sphere about $\mathbf{k}=0$ as it does not affect the value of the integral in Eq. (B1).

The limiting process of Eq. (B1) has not been precisely defined, but a satisfactory way to complete the definition is to extend the included region to infinity in one lattice direction and to take successive regular two-dimensional arrays of lattice cells in the remaining directions. This will result in sets of points $\mathbf{k}_\mu$ on the boundary; it is clear from the way Eq. (B1) was obtained that such points are to be given half-weight (or quarter-weight if on a corner). If Eq. (B1) is evaluated as just indicated, consistency requires a similar treatment (such as that given in the main text) for the remaining conditionally convergent summation of Eq. (7).

We have evaluated C for the general orthorhombic lattice, thereby obtaining also as special cases the tetragonal and cubic lattices. We have in addition obtained C for the hexagonal lattice. Particular examples of the other lattice systems can be investigated by the same methods, but the lower symmetry then makes a completely general algebraic treatment less attractive.

We discuss first an orthorhombic lattice of cell dimensions a, b, and c. Then $v_0=abc$, and $k_\mu^2=4\pi^2[(u/a)^2+(v/b)^2+(w/c)^2]$, where the lattice point $\mathbf{k}_\mu$ is removed from $\mathbf{k}=0$ by u, v, and w lattice steps, respectively, in the $+a$, $+b$, and $+c$ directions. In accordance with our earlier discussion, we take the limit C by making evaluations over regions in space R_N bounded in the a and b directions by the planes $\pm 2\pi N/a$ and $\pm 2\pi N/b$ (corresponding to $u=\pm N$, $v=\pm N$), where N is an integer which will be increased to infinity. We have proceeded directly to $\pm\infty$ in the c direction. Our expression for C may then be written

$$C=\lim_{N\to\infty}\left[(2\pi c/ab)\sum_{uvw\in R_N}[(cu/a)^2+(cv/b)^2+w^2]^{-1}-\int_{R_N}k^{-2}d\mathbf{k}\right] \qquad \text{(B2)}$$

with the convention that the summation over R_N excludes $u=v=w=0$ and is with appropriate fractional weights for the boundary points.

We begin the evaluation by summing and integrating to $\pm\infty$ in the c direction. The w summation is performed using Eqs. (8) and (9), and the integration over the corresponding Cartesian coordinate is elementary. The result is, after some rearrangement,

$$\begin{aligned}C=(2\pi c/ab)&[(\pi^2/3)+\pi\sum_{uv\neq 00}[(cu/a)^2+(cv/b)^2]^{-1/2}\\&\times(\coth\pi[(cu/a)^2+(cv/b)^2]^{1/2}-1)]\\&+\frac{2\pi^2}{ab}\lim_{N\to\infty}\Bigg(\sum_{uv\in R_N}\left[\left(\frac{u}{a}\right)^2+\left(\frac{v}{b}\right)^2\right]^{-1/2}\\&-\int_{-N}^{N}du\int_{-N}^{N}dv\left[\left(\frac{u}{a}\right)^2+\left(\frac{v}{b}\right)^2\right]^{-1/2}\Bigg).\end{aligned} \qquad \text{(B3)}$$

The terms of Eq. (B3) are grouped as shown to make explicit the fact that the limit is still of the difference between the summation and integration of the same arguments. The first sum, indicated as for u, $v\neq 0$, 0, need not be limited to R_N because it converges exponentially.

We next evaluate the limit, which is now in two dimensions, by applying the Euler-Maclaurin sum formula. We apply that formula to rectangular two-dimensional regions in the form

$$\begin{aligned}\sum_{u=u_1}^{u_2}\sum_{v=v_1}^{v_2}f(u,v)-\int_{u_1}^{u_2}du\int_{v_1}^{v_2}dv\,f(u,v)&\\\approx\sum_i d_i\int_{u_1}^{u_2}du[f^{(0i)}(u,v_2)-f^{(0i)}(u,v_1)]&\\+\sum_j d_i\int_{v_1}^{v_2}dv[f^{(i0)}(u_2,v)-f^{(i0)}(u_1,v)]&\\+\sum_{ij}d_id_j[f^{(ij)}(u_2,v_2)-f^{(ij)}(u_1,v_2)&\\-f^{(ij)}(u_2,v_1)+f^{(ij)}(u_1,v_1)],&\end{aligned} \qquad \text{(B4)}$$

where $f^{(ij)}$ means $(\partial/\partial u)^i(\partial/\partial v)^j f(u,v)$, boundary terms in the sums on the left-hand side are to given half-weight (quarter weight for corner points), and the sums on the right-hand side are over the first few odd positive integers, with $d_1=1/12$, $d_3=-1/720$, $d_5=1/302\,40$, $d_7=-1/120\,960\,0$, ...

The Euler-Maclaurin formula cannot be applied here to any region too close to $u=v=0$ because the remainder terms are then too large. We accordingly evaluate the

limit of Eq. (B3) by explicitly summing and integrating out to $|u|=n$, $|v|=n$, and then using Euler-Maclaurin formulas for the several rectangles comprising the remainder of R_N. For the calculations we have made, seven-significant-figure limits were obtained when the n value defining the lower limits of the Euler-Maclaurin formulas was as small as 4 or 5.

Proceeding as outlined in the foregoing paragraph, and letting $f(u,v)$ denote $[(u/a)^2+(v/b)^2]^{-1/2}$, we find

$$\lim_{N\to\infty}\left[\sum_{uv\epsilon R_N} f(u,v)-\int_{-N}^{N}du\int_{-N}^{N}dv\,f(u,v)\right]$$

$$\approx\sum_{uv\epsilon R_n} f(u,v)-\int_{-n}^{n}du\int_{-n}^{n}dv\,f(u,v)$$

$$-4\sum_i d_i\int_0^n du\,f^{(0i)}(u,n)$$

$$-4\sum_i d_i\int_0^n dv\,f^{(i0)}(n,v)-4\sum_{ij}d_id_jf^{(ij)}(n,n). \quad \text{(B5)}$$

In Eq. (B5), all terms containing vanishing derivatives have been dropped, and the notation $uv\epsilon R_n$ has been introduced to indicate that after setting up the Euler-Maclaurin formulas the terms on the boundaries $|u|=n$, $|v|=n$, remain for explicit summation with just the partial weights appropriate to that notation.

We complete the processing of Eq. (B5) by taking the derivatives and integrals indicated on its right-hand side. The double integral is most easily evaluated in circular coordinates. The final results obtained after some algebraic manipulations are

$$C=(2\pi c/ab)\left[(\pi^2/3)+\pi\sum_{uv\neq 00}[(cu/a)^2+(cv/b)^2]^{-1/2}\right.$$

$$\left.\times\{\coth\pi[(cu/a)^2+(cv/b)^2]^{1/2}-1\}+(\pi b/c)F\left(\frac{b}{a}\right)\right], \quad \text{(B6)}$$

with

$$F(\alpha)=\sum_{uv\epsilon R_n}(\alpha^2u^2+v^2)^{-1/2}-4n\ln\left(\frac{1+(\alpha^2+1)^{1/2}}{\alpha}\right)$$

$$-\frac{4n}{\alpha}\ln[\alpha+(\alpha^2+1)^{1/2}]+\frac{2}{3n(\alpha^2+1)^{1/2}}$$

$$-\frac{8\alpha^4+25\alpha^2+8}{180n^3(\alpha^2+1)^{5/2}}+\frac{48\alpha^8+146\alpha^6+21\alpha^4+146\alpha^2+48}{2520n^5(\alpha^2+1)^{9/2}}$$

$$-\cdots. \quad \text{(B7)}$$

We have evaluated Eqs. (B6) and (B7) numerically for some cases of particular interest. Values of C and $F(\alpha)$ are presented in Table I. We give $F(\alpha)$ for $n=4$ and $n=5$, to indicate the degree to which the Euler-Maclaurin formulas have converged. The C values are believed accurate to seven significant figures.

The method just described for the orthorhombic lattice could with obvious modifications be applied to the hexagonal lattice. However, there is available a simpler alternative procedure based on the fact that a hexagonal lattice can be described as an orthorhombic system with additional face-centered points. In particular, an orthorhombic lattice with $b=\sqrt{3}a$ and with additional points centered in the a-b face of each unit cell is exactly equivalent to a hexagonal lattice whose unit cell has two dimensions of length a. The value of C for such a lattice will clearly be equal to C for the orthorhombic lattice plus the contribution of the face-centered points to the potential at an orthorhombic lattice point. The contribution of the face-centered points to the potential is carried out as described in Sec. II of the main text. A C value has been obtained in this way for a hexagonal lattice whose c dimension is appropriate to closest packing of spheres. This value is included in Table I.

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