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The Evaluation of Lattice Sums for Cubic Crystals

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A method is presented of evaluating the sums which arise in calculating the total long-range interaction energy between a semi-infinite crystal and a particle placed above its surface. For example, if the particle is an ion and the crystal is polarizable, this method facilitates the calculation of the polarization and Van der Waal's energies. It is pointed out that many calculations within a solid can be reduced to a combination of cases each of which is of the above type. As an illustration, we obtain the total interaction at an interior lattice point for a simple-cubic structure with an individual atom-pair interaction of λr^{-n}.

I. INTRODUCTION

IN many problems which occur in the physics of solids, it is necessary to perform sums over the lattice sites of long-range central force interactions. One such problem is that of calculating the binding energy per ion pair of an ionic crystal, which can be assumed to be three-dimensionally infinite. In this case, the point at which the interaction energy is desired is located at a lattice site and the procedure is somewhat simplified. These sums have been worked out by Madelung and Ewald[1] for the Coulomb interaction energy using a potential method and by Jones and Ingham[2] for any interactions which can be represented by inverse powers (greater than 3) of the center distance. It is of some interest to note from the results of Jones and Ingham that a direct summation over the lattice sites becomes very inconvenient if good accuracy is desired. For example, for an inverse power of 4, a direct summation over the nearest 500 atom sites is in error by about 25 percent, while an error of 6 percent or less requires a sum over at least 4000 of the nearest atom sites.

If the point at which the interaction energy is to be evaluated is not a lattice site, the evaluation of such sums does not appear to have been so thoughly treated, except for the Coulomb potential. These calculations within a solid can be reduced to a combination of cases for each of which the point where the interaction energy is desired is an arbitrary distance above a principal surface of a semi-infinite crystal, so we shall discuss this latter problem, which is, of course, interesting in its own right. The Coulomb interaction between an ion above the (100) surface of an ionic crystal was first evaluated by Lennard-Jones and Dent,[3] using the potential method of Madelung. However, interactions involving higher inverse powers of the distance seem to have been evaluated by direct summation over a large number of sites and integration over the remainder of the crystal, a rather tedious and often unsatisfactory method. Since such interactions are frequently quite important, especially for highly polarizable materials, it appears that a better method of treating these sums would be useful.

In this note, the authors propose to outline a rather simple transformation whereby series of λr^{-n} (and other central force) interactions can usually be made to converge more rapidly. For illustration of the application of our method some of the results of Jones and Ingham[2] are obtained.

II. SUMMING METHOD

We consider a semi-infinite perfect single crystal and, although we will soon specialize to a cubic crystal, we will be more general at first. We define the crystal space vectors as

$$\mathbf{r}=x_1\mathbf{a}_1+x_2\mathbf{a}_2+x_3\mathbf{a}_3=\mathbf{y}+x_3\mathbf{a}_3,$$

where $\mathbf{y}$ is in the plane of the surface and $\mathbf{a}_3$ pointing inward (not necessarily normal to the surface plane). The position vector of any unit cell is

$$\mathbf{r}_l=l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3=\mathbf{y}_\lambda+l_3\mathbf{a}_3,$$

where $l_1l_2l_3$ are integers, and the position vector of an atom within the unit cell is

$$\mathbf{r}_s=x_1{}^s\mathbf{a}_1+x_2{}^s\mathbf{a}_2+x_3{}^s\mathbf{a}_3=\mathbf{y}_\sigma+x_3{}^s\mathbf{a}_3.$$

The crystal space vector of the kth atom is thus $\mathbf{r}_k=\mathbf{r}_l+\mathbf{r}_s$.

We also define the general reciprocal space vector as

$$\mathbf{h}=p_1\mathbf{b}_1+p_2\mathbf{b}_2+p_3\mathbf{b}_3=\mathbf{p}+p_3\mathbf{b}_3,$$

and the reciprocal lattice vector as

$$\mathbf{h}_m=m_1\mathbf{b}_1+m_2\mathbf{b}_2+m_3\mathbf{b}_3=\mathbf{p}_\mu+m_3\mathbf{b}_3,$$

where $m_1m_2m_3$ are integers. From its definition, $\mathbf{b}_3$ is normal to the crystal surface, but the plane formed by $\mathbf{b}_1$ and $\mathbf{b}_2$ is, in general, inclined to the crystal surface.

Let the interaction energy between a particle at the position $\mathbf{r}$ (above the surface) and the kth atom at $\mathbf{r}_k$ in a crystal be $\epsilon(|\mathbf{r}-\mathbf{r}_k|)$, i.e., an arbitrary function but with no angular dependence. The total interaction

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[1] E. Madelung, Physik. Z. Sowjetunion **19**, 524 (1918); P. P. Ewald, Ann. Physik **64**, 253 (1921). For a review see, for example, M. Born and M. Göppert-Mayer, *Handbuch der Physik* (Verlag. Julius Springer, Berlin, 1933), Vol. 24, p. 623.

[2] J. E. Jones and A. E. Ingham, Proc. Roy. Soc. (London) **A107**, 636 (1925).

[3] J. E. Lennard-Jones and B. M. Dent, Trans. Faraday Soc. **24**, 92 (1928).

energy between this atom and the crystal is then

$$\phi(\mathbf{r})=\textstyle\sum_k \epsilon(|\mathbf{r}-\mathbf{r}_k|)=\sum_l \sum_s \epsilon(|\mathbf{r}-\mathbf{r}_l-\mathbf{r}_s|). \quad (1)$$

The sum over l means all values of l_1 and l_2 but only $l_3 \geqslant 0$. Thus $\phi(r)$ is periodic in x_1 and x_2 with period unity and may be expanded in the double Fourier series

$$\phi(\mathbf{r})=\sigma_A^{-1} \textstyle\sum_\mu \psi_{\mathbf{p}_\mu}(x_3) \exp(2\pi i \mathbf{p}_\mu \cdot \mathbf{y}), \quad (2)$$

where σ_A is the unit cell surface area $|\mathbf{a}_1 \times \mathbf{a}_2|$ in a plane $x_3=$constant. Then

$$\psi_{\mathbf{p}_\mu}(x_3)=\int_{\sigma A} d_2\mathbf{y}\phi(\mathbf{r}) \exp(-2\pi i \mathbf{p}_\mu \cdot \mathbf{y}), \quad (3)$$

where $d_2\mathbf{y}=|\mathbf{a}_1 \times \mathbf{a}_2| dx_1 dx_2$ is the element of surface area. Substituting from (1),

$$\begin{aligned}\psi_{\mathbf{p}_\mu}(x_3)&=\sum_{\lambda,l_3} \sum_s \int_{\sigma A} d_2\mathbf{y}[\exp(-2\pi i \mathbf{p}_\mu \cdot \mathbf{y})] \\ &\qquad \times \epsilon\{|\mathbf{y}-\mathbf{y}_\lambda-\mathbf{y}_\sigma+\mathbf{a}_3(x_3-l_3-x_3^s)|\} \\ &=\sum_{l_3} \sum_s \sum_\lambda \{\exp[-2\pi i \mathbf{p}_\mu \cdot (\mathbf{y}_\lambda+\mathbf{y}_\sigma)]\} \\ &\quad \times \int_{\sigma A} d_2\mathbf{y}\{\exp[-2\pi i \mathbf{p}_\mu \cdot (\mathbf{y}-\mathbf{y}_\lambda-\mathbf{y}_\sigma)]\} \\ &\qquad \times \epsilon\{|\mathbf{y}-\mathbf{y}_\lambda-\mathbf{y}_\sigma+\mathbf{a}_3(x_3-l_3-x_3^s)|\}.\end{aligned}$$

Noting that $\exp(-2\pi i \mathbf{p}_\mu \cdot \mathbf{y}_\lambda)=1$ and that summing over λ is then equivalent to extending the integration over the entire surface $x_3=$constant, we finally obtain

$$\begin{aligned}\phi(\mathbf{r})&=\sigma_A^{-1} \sum_\mu [\exp(2\pi i \mathbf{p}_\mu \cdot \mathbf{y})] \sum_{l_3} \sum_s [\exp(-2\pi i \mathbf{p}_\mu \cdot \mathbf{y}_\sigma)] \\ &\quad \times \int_A d_2\mathbf{t}\epsilon\{|\mathbf{t}+\mathbf{a}_3(x_3-l_3-x_3^s)|\} \exp(-2\pi i \mathbf{p}_\mu \cdot \mathbf{t}), \quad (4)\end{aligned}$$

where $\mathbf{t}=\mathbf{a}_1\xi_1+\mathbf{a}_2\xi_2$ is a dummy variable and the integration is over the entire surface A. In the particular case of the Coulomb potential, the ψ_{00} term diverges and must be considered separately by a limiting technique such as that of Ewald and Juretschke.[4] This term is the average Coulomb potential and is zero in a neutral cubic structure. It may be noted in passing that the above is a logical extension to two dimensions of the usual Poisson sum formula.[5]

For cubic lattices with $|\mathbf{a}_1|=|\mathbf{a}_2|=|\mathbf{a}_3|=a$ and with a (100) surface, we obtain (where μ stands for the pair of integers m_1m_2), for a simple cubic,

$$\phi(\mathbf{r})=\sum_\mu \{\exp[2\pi i(m_1x_1+m_2x_2)]\} \sum_{l_3=0}^{\infty} E_{\mu,\,l_3}(0); \quad (5)$$

and for a face-centered cubic with basis

$$\left[000;\ \frac{a}{2}\frac{a}{2}0;\ \frac{a}{2}0\frac{a}{2};\ 0\frac{a}{2}\frac{a}{2}\right],$$

we obtain

$$\begin{aligned}\phi(\mathbf{r})=2\sum_{l_3=0}^{\infty}\Bigg\{&\sum_{\substack{m_1m_2\\ \text{even}}} \{\exp[2\pi i(m_1x_1+m_2x_2)]\} \\ &\qquad \times [E_{\mu,\,l_3}(0)+E_{\mu,\,l_3}(\tfrac{1}{2})] \\ &+\sum_{\substack{m_1m_2\\ \text{odd}}} \{\exp[2\pi i(m_1x_1+m_2x_2)]\} \\ &\qquad \times [E_{\mu,l_3}(0)-E_{\mu,l_3}(\tfrac{1}{2})]\Bigg\}, \quad (6)\end{aligned}$$

where

$$\begin{aligned}E_{\mu,\,l_3}(x_3^s)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} & d\xi_1 d\xi_2 \epsilon\{a[\xi_1^2+\xi_2^2+(z+l_3+x_3^s)^2]^{\frac{1}{2}}\} \\ &\times \exp[-2\pi i(m_1\xi_1+m_2\xi_2)].\end{aligned}$$

Here $z=-x_3$ is the normal distance of the particle above the surface and this is valid only for $z \geqslant 0$. Note that $E_{\mu,\,0}(0)$ is the double Fourier transform of the individual energy and can frequently be obtained from tables such as those of Foster and Campbell.[6] An important case is that in which $\epsilon=\lambda r^{-n}$ with n integral. For convenience we shall list in Table I some values of $E_{\mu,\,0}(0)$ for such cases. To get $E_{\mu,l_3}(x_3^s)$ from these, one merely replaces z by $(z+l_3+x_3^s)$.

In Table I, K_ν is the Bessel function of the second kind for imaginary argument. For large z, K_ν is exponentially decreasing, so that the leading term in the series is the term which falls off algebraically. When z is replaced by $(z+l_3+x_3^s)$ and the sum over l_3 performed (these sums are generalized Riemann zeta functions and

TABLE I. The double Fourier transform, $E_{\mu,\,0}(1)$, for an individual interaction energy $\epsilon=\lambda r^{-n}$.

n	$E_{000}(0)$	$E_{\mu,0}(0)$
4	$\lambda a^{-4}\pi z^{-2}$	$\lambda a^{-4}2\pi^2(m_1^2+m_2^2)^{\frac{1}{2}}z^{-1}K_1[2\pi z(m_1^2+m_2^2)^{\frac{1}{2}}]$
5	$\lambda a^{-5}\frac{2}{3}\pi z^{-3}$	$\lambda a^{-5}\frac{2}{3}\pi z^{-3}[1+2\pi z(m_1^2+m_2^2)^{\frac{1}{2}}] \times\exp[-2\pi z(m_1^2+m_2^2)^{\frac{1}{2}}]$
6	$\lambda a^{-6}\frac{1}{2}\pi z^{-4}$	$\lambda a^{-6}\pi^3 z^{-2}(m_1^2+m_2^2)K_2[2\pi z(m_1^2+m_2^2)^{\frac{1}{2}}]$
7	$\lambda a^{-7}\frac{2}{5}\pi z^{-5}$	$\lambda a^{-7}\frac{2}{5}\pi z^{-5}[1+2\pi z(m_1^2+m_2^2)^{\frac{1}{2}} + (4/3)\pi^2 z^2(m_1^2+m_2^2)] \times\exp[-2\pi z(m_1^2+m_2^2)^{\frac{1}{2}}]$
8	$\lambda a^{-8}\frac{1}{3}\pi z^{-6}$	$\lambda a^{-8}\frac{1}{3}\pi^4 z^{-3}(m_1^2+m_2^2)^{\frac{3}{2}}K_3[2\pi z(m_1^2+m_2^2)^{\frac{1}{2}}]$

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[4] P. P. Ewald and H. Juretschke, paper presented at the National Research Council Conference on the Structure and Properties of Solid Surfaces, Lake Geneva, Wisconsin, September, 1952 (unpublished).

[5] The Poisson summation formula says that, for $f(x)$ a decent function,

$$\sum_{n=-\infty}^{\infty} f(x+n)=\sum_{m=-\infty}^{\infty}\int_{-\infty}^{\infty} f(y) \exp[2\pi i m(x-y)]dy.$$

By letting $f(x)=\exp(-\pi t x^2)$, the "Poisson identity" is obtained [see, for example, H. Bateman, *Partial Differential Equations* (Dover Publications, New York, 1944)]. It may be noted that the method presented here for a λr^{-n} interaction is analogous, in one-dimension, to Lerch's theorem given there (p. 405).

[6] G. A. Foster and R. M. Campbell, Bell Telephone System, Tech. Publs. (1942). Monograph B 584.

can be evaluated exactly; this is briefly discussed at the end of this section), this term is, of course, just the asymptotic value of ϕ for large z and essentially includes the contribution of a continuous distribution of force centers in the crystal. The advantage of the present formulation lies in the rapid decay of the coefficients E_μ with increasing μ; thus series of the form (5) and (6) converge rapidly, even if z is as small as half a lattice constant.

III. SUMMATION OVER A HALF-PLANE

In passing, we note that the same method can be applied to calculate the interaction energy at a point near the edge of a semi-infinite plane of atoms if this point is also in the plane. Consider a plane of atoms located at $x_2=0$ and extending from $x_3=0$ to infinity. In a similar fashion to the above treatment for a semi-infinite solid, we can find the interaction enery with an atom at the point x_1, $x_2=0$, $z=-x_3$. For a λr^{-n} interaction, the normal lattice sum for a square lattice with $|\mathbf{a}_1|=|\mathbf{a}_2|=a$ is

$$\phi_n(x_1, z)=\lambda a^{-n}\sum_{l=0}^{\infty}\sum_{k=-\infty}^{\infty}[(x_1-k)^2+(z+l)^2]^{-\frac{1}{2}n}, \quad (7)$$

and by the use of the present method, this may be expressed as

$$\phi_3(x_1, z)=\lambda a^{-3}\{2\sum_{l=0}^{\infty}(z+l)^{-2}+8\pi\sum_{l=0}^{\infty}\sum_{m=1}^{\infty}m(z+l)^{-1}$$
$$\times\cos(2\pi m x_1)K_1[2\pi m(z+l)]\}, \quad (8)$$

$$\phi_4(x_1, z)=\lambda a^{-4}\Bigg\{\frac{\pi}{2}\sum_{l=0}^{\infty}(z+l)^3$$
$$+\pi\sum_{l=0}^{\infty}\sum_{m=1}^{\infty}[1+2\pi m(z+l)](z+l)^{-3}$$
$$\times\cos(2\pi m x_1)\exp[-2\pi m(z+l)]\Bigg\}, \quad (9)$$

where z and x_1 are defined as before. Higher powers of n may be obtained as follows:

If we define $\phi_n{}^l$ such that

$$\phi_n(x_1, z)=\sum_{l=0}^{\infty}\phi_n{}^l,$$

we see from Eq. (7) that

$$\phi_{n+2}=-n^{-1}a^{-2}(z+l)^{-1}\partial\phi_n{}^l/\partial z,$$

and thus

$$\phi_{n+2}(x_1, z)=-n^{-1}a^{-2}\sum_{l=0}^{\infty}(z+l)^{-1}\partial\phi_n{}^l/\partial z.$$

The summation over m in (9) can be performed to give a closed form, but this is not usually convenient for computations. It should be noted that the first series in (8) and (9) are tabulated functions. The generalized Riemann zeta function

$$\zeta(z, n)=\sum_{l=0}^{\infty}(z+l)^{-n}$$

can be expressed in terms of the logarithmic derivative of the gamma function for non-negative integer values of n greater than unity.[6] Thus, if

$$\psi(z)=(d/dz)\ln\Gamma(z),$$

then

$$\zeta(z, n)=\frac{(-1)^n}{(n-1)!}\frac{d^{n-1}}{dz^{n-1}}\psi(z)$$

and the first few derivatives of ψ are tabulated.[7]

IV. EXAMPLES

1. The Coulomb interaction with a semi-infinite ionic crystal having the NaCl structure can be readily obtained from (6) since such a structure can be considered as two interlaced face-centered cubic lattices. The result is the same as that given in reference 3.

2. Lattice potentials at a lattice site in the interior of an infinite crystal.

Here we want to show briefly how sums of the type evaluated by Jones and Ingham[2] can be found by the above method. Principally this is intended to show the rate of convergence of the various series used above, since the numerical results of reference 2 are exact to within specified limits. We will consider, for simplicity, only the case of a simple cubic lattice and we want to sum terms like λr^{-n} over a three-dimensionally unbounded crystal to find the total interaction at a lattice point. For any value of n, this total interaction can be expressed as

$$\phi_n=a^{-n}A_n,$$

where A_n is a pure number. To use the above method, we break A_n up into two parts:

$$A_n=2B_n+C_n,$$

where B_n is the contribution of a semi-infinite crystal whose (100) face is a distance $z=1$ away from the lattice point in question, and C_n is the contribution from the 100 plane containing the lattice point. B_n is obtained from (5), and C_n is further broken up into

$$C_n=2D_n+F_n,$$

where D_n is from the semi-infinite plane a distance $z=1$ away [and obtained from Eqs. (7) or (8) or one of their derivatives] and F_n is from the (1,0) line contain-

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[7] See E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1945), and references therein, particularly H. T. Davis, *Tables of Higher Mathematical Functions* (Principia Press, Bloomington, 1935), Vol. 2. Note that Jahnke and Emde define ψ somewhat differently.

TABLE II. Terms in the evaluation of the total interaction at a lattice point inside an infinite crystal, for an individual interaction energy $\epsilon=\lambda r^{-n}$.

n	F_n	D_n	C_n	B_n	A_n	A_n (reference 2)
4	2.165	1.931	6.027	5.253	16.53	16.5323
5	2.074	1.510	5.094	2.643	10.38	10.3775
6	2.035	1.311	4.657	1.871	8.40	8.4019
7	2.017	1.203	4.422	1.420	7.46	7.4671
8	2.008	1.134	4.276	1.330	6.94	6.9458

ing the lattice point. F_n simply equals

$$F_n=2\sum_{s=1}^{\infty} s^{-n},$$

which is tabulated in Jahnke and Emde.[7] The results of the calculations are presented in Table II, which also includes the values given in reference 2.

All the values calculated above were obtained by using only the zero and first order terms of our series. The values given by Jahnke and Emde[7] for F_n are carried to three decimal places only. Since in addition the numerical work was done with a slide rule, the above calculated numbers are only good to two decimal places. To this accuracy, our values agree with the values of reference 2. It may be mentioned that the computations take little time to perform; for the above, the value for each n required about twenty minutes to obtain.

V. SUMMARY

A method of increasing the rate of convergence of sums of central-force interactions over a rigid cubic lattice is presented. We feel that the example considered in Sec. 3 shows that the method is convenient and practical to employ. Since the point at which the interaction energy is to be found need not necessarily be at a lattice point, it is possible, for example, to use this procedure conveniently to obtain the long-range contributions to the energy of an interstitial ion. Probably its greatest usefulness lies in the problem of evaluating the energy of atoms above the surfaces of solids, since the distance of the atom above the surface is usually great enough (about one lattice spacing) so that only the first periodic term in the series of Sec. 2 need be retained.