PHYSICAL REVIEW VOLUME 181, NUMBER 3 15 MAY 1969

Generalized Ewald Potential Problem*

WILLIAM E. RUDGE
IBM Research Laboratory, San Jose, California 95114
(Received 25 November 1968)

The Coulomb potential due to a periodic array of point multipoles is found and expressed, in terms of the multipole moments and dimensionless Ewald coefficients, in a form convenient for energy-band calculations by the augmented-plane-wave method. The formalism is then applied to an array of multipoles having the symmetry of the crystal lattice. Numerical values are given for the Ewald coefficients for a monatomic body-centered cubic crystal.

I. INTRODUCTION

FINDING the Coulomb potential due to a periodic array of point multipoles is a problem which arises, for example, in a self-consistent energy-band calculation, as part of the problem of finding the total potential due to a given crystalline charge density. The monopole problem (the potential due to an array of point charges) has been discussed by Ewald[1] and by Slater and DeCicco.[2] In the present paper the method of Ewald is generalized to include higher multipole moments. The potential so found is then recast into a form suitable for use in an augmented-plane-wave (APW) energy band calculation,[3] namely, into a dual representation: inside the APW spheres around the atomic sites the potential is expanded as a sum of radial functions multiplied by spherical harmonics; outside it is expanded in a Fourier series. This Fourier series is not unique, since it is not specified inside the spheres. Two useful forms of the series will be given. The first converges reasonably rapidly, and has no physical meaning inside the spheres. The second, denoted by subscript *s*, is a step function, identical to zero inside the spheres, and equal to the first series outside the spheres. The step function series, the form needed for an APW calculation, does not converge, but the finite number of basis functions used in such a calculation couples only with a reasonably small number of the Fourier coefficients, and these coefficients may be calculated as indicated below. A set of dimensionless "Ewald coefficients" depending only on the structure of the crystal is found, so that once the strengths of the multipole moments are known, the potential is easily found, either numerically, or analytically (in dual form). Finally, the solution is specialized to an array of multipoles having full crystalline symmetry. As an example, numerical values are given for the Ewald coefficients for the monatomic body centered cubic structure.

II. PROBLEM AND ITS FORMAL SOLUTION

The Coulomb potential $\Phi(\mathbf{r})$ due to a charge density $\rho(\mathbf{r})$ must be a solution to Poisson's equation

$$\nabla^2\Phi(\mathbf{r}) = -4\pi\alpha\rho(\mathbf{r}) , \qquad (1)$$

where α is a number which depends on the systems of units used. In particular, $\alpha=2$ for atomic units, in which energies are measured in Rydbergs and distances are measured in units of the Bohr radius.

A crystal lattice with *n* atoms per unit cell is introduced by the following definitions. Corresponding dimensionless quantities are defined simultaneously by introducing a scaling factor *a* with the dimension of length.

$\mathbf{R}=\frac{1}{2}a\mathbf{p}$	are the primitive vectors defining the Bravais lattice. The $\mathbf{p}$ determine the type of structure, while a determines the scale or size.
$\mathbf{r}_i=\frac{1}{2}a\mathbf{x}_i$	are the positions of the atoms in the zeroth unit cell. $i=1, \cdots, n$.
$\mathbf{r}=\frac{1}{2}a\mathbf{x}$	is any position in the crystal.
$\Omega=(\frac{1}{2}a)^3\omega$	is the volume of the unit cell.
$\mathbf{R}_{si}=\frac{1}{2}a\mathbf{x}_{si}$	are the radii of nonoverlapping spheres drawn about the atoms. The region in the crystal not in one of these spheres is referred to as the plane wave region.
$\mathbf{K}=\pi\mathbf{q}$	are the primitive vectors for the corresponding reciprocal lattice. $\mathbf{K}\cdot\mathbf{R}=\pi\mathbf{q}\cdot\mathbf{p}=2\pi N$, where N is an integer depending on $\mathbf{q}$ and $\mathbf{p}$.

An array consisting of one point multipole on the *i*th atomic site in each unit cell, with moment Q_{lmi}, may then be represented by the charge density

$$\rho_{lmi}(\mathbf{r})=\sum_{\mathbf{R}} \frac{\delta(|\mathbf{r}-\mathbf{r}_i-\mathbf{R}|)}{|\mathbf{r}-\mathbf{r}_i-\mathbf{R}|^{l+2}\sigma^2} Q_{lmi}Y_{lmi}(\mathbf{r}-\mathbf{r}_i-\mathbf{R}) -\delta_{l0}\frac{(4\pi)^{1/2}Q_{00i}}{\Omega\sigma}, \qquad (2)$$

where $Y_{lm}(\mathbf{r})$ is a spherical harmonic with arguments equal to the angular coordinates of the vector $\mathbf{r}$. For later convenience in introducing lattice harmonics, it is assumed that the spherical harmonics are normalized to σ^2, although σ is normally equal to unity. The

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* Based in part on a thesis submitted in partial fulfillment of the requirements for a Ph.D. degree from the Department of Physics at the Massachusetts Institute of Technology. Further details are given in an expanded version of this paper, IBM Research Report No. RJ 538 (unpublished), available from the author.

[1] P. P. Ewald, Ann. Physik **64**, 253 (1921); Nachr. Akad. Wiss. Göttingen, II. Math.-Physik. Kl., 55 (1938).

[2] J. C. Slater and P. D. DeCicco, Quarterly Progress Report of the Solid State and Molecular Theory Group, M. I. T., No. 50, p. 46, 1963 (unpublished).

[3] J. C. Slater, Phys. Rev. **51**, 846 (1937).

multipole moment of a charge distribution $\rho(\mathbf{r})$ is here taken to be

$$Q_{lm}=\int d\mathbf{r}\, r^l Y_{lm}^*(\mathbf{r})\rho(\mathbf{r}) \tag{3}$$

regardless of the value of σ. The constant term for the monopole case ($l=0$) has been added to the charge density to maintain charge neutrality in each unit cell.

The potential due to the periodic charge density $\rho_{lmi}(\mathbf{r})$ can be written as

$$\Phi_{lmi}(\mathbf{r})=(2/a)^{l+1}\alpha Q_{lmi}U(2\mathbf{r}/a)\,, \tag{4}$$

where $U(x)$, a dimensionless potential, is a solution of the dimensionless Poisson's equation

$$\nabla^2 U(\mathbf{x})=-4\pi\rho(\mathbf{x})\,, \tag{5}$$

where

$$\rho(\mathbf{x})=(\tfrac{1}{2}a)^{l+3}\rho_{lmi}(a\mathbf{x}/2)/Q_{lmi} \tag{6}$$

is a dimensionless charge density. For $\mathbf{x}$ inside the zeroth cell, $U(\mathbf{x}+\mathbf{p})=U(\mathbf{x})$ can be written in the dual form

$$\begin{aligned}U(\mathbf{x})=&\frac{4\pi\delta_{ii'}Y_{lm}(\mathbf{x}-\mathbf{x}_{i'})}{(2l+1)\,|\mathbf{x}-\mathbf{x}_{i'}|^{l+1}\sigma^2}\\&+\sum_{l'm'}A_{l'm'i'}{}^{lmi}|\mathbf{x}-\mathbf{x}_{i'}|^{l'}Y_{l'm'}(\mathbf{x}-\mathbf{x}_{i'})\\&+\delta_{l0}\frac{8\pi^2|\mathbf{x}-\mathbf{x}_{i'}|^2}{3\omega\sigma^2}Y_{00}(\mathbf{x}-\mathbf{x}_{i'})\end{aligned} \tag{7a}$$

within the sphere about the i'th atom, $|\mathbf{x}-\mathbf{x}_{i'}|\leq \mathbf{x}_{si'}$ and

$$U(\mathbf{x})=\sum_{\mathbf{q}}U_{\mathbf{q}}{}^{lmi}e^{i\pi\mathbf{q}\cdot\mathbf{x}}=\sum_{\mathbf{q}\neq0}U_{s\mathbf{q}}{}^{lmi}e^{i\pi\mathbf{q}\cdot\mathbf{x}} \tag{7b}$$

in the plane-wave region outside all spheres. Note that $U(\mathbf{x})$ and $\rho(\mathbf{x})$ depend on the indices lmi. To simplify the notation, the indices have been omitted, but are to be assumed wherever appropriate.

The term involving $\delta_{ii'}$ is a particular solution to Poisson's equation for the charge inside the i'th sphere. There is no charge in the i'th sphere when $i'\neq i$, for it has been assumed that the multipoles are placed only on the ith atomic sites. The term involving δ_{l0} is a particular solution for the constant charge density introduced to maintain charge neutrality in the monopole case. This accounts for all the charge in the i'th sphere. To these solutions, only solutions to Laplace's equation which are regular everywhere within the sphere can be added, namely, functions of the form $x^l Y_{lm}(\mathbf{x})$. The coefficients $A_{l'm'i'}{}^{lmi}$ are determined by the charges outside the sphere, or alternately, by the boundary conditions on the surface of the sphere. Note that an arbitrary constant added to the potential can be absorbed by the coefficients $A_{00i'}{}^{lmi}$.

In the plane-wave region, the Fourier series is clearly the most general form for the periodic potential. The first form, with coefficients $U_{\mathbf{q}}{}^{lmi}$, is a convergent series. The second series has been reanalyzed to be a step function at the surface of each sphere, with the property

$$\sum_{\mathbf{q}\neq0}U_{s\mathbf{q}}{}^{lmi}e^{i\pi\mathbf{q}\cdot\mathbf{x}}=0 \text{ (inside any sphere).} \tag{8}$$

The sum omits $\mathbf{q}=0$ since $U_{s\,\mathbf{q}=0}{}^{lmi}=0$. This follows from the choice of the zero of energy, which is chosen according to the traditional convention of the APW method so that the average value of $U(\mathbf{x})$ in the plane wave region is zero.

The total potential, due to multipoles of all orders on all atomic sites, is simply a superposition of potentials of the type described, namely,

$$\Phi_T(\mathbf{r})=\sum_i\sum_{lm}\Phi_{lmi}(\mathbf{r})\,. \tag{9}$$

The task remaining is to find the Ewald coefficients $A_{l'm'i'}{}^{lmi}$, $U_{\mathbf{q}}{}^{lmi}$, and $U_{s\mathbf{q}}{}^{lmi}$.

III. EWALD METHOD

The dimensionless potential $U(\mathbf{x})$ can easily be written as a direct lattice sum, but it is immediately found that for the cases $l=0$, 1, and 2, the infinite sum is at best conditionally convergent. In any case, the sum is not in a convenient form for direct comparison with (7) to find the Ewald coefficients. A Fourier series representation for the potential is also easily found, but this sum fails to converge for any l.

The result of the Ewald method is an expression for the potential which is the sum of a direct lattice sum and a Fourier series, where the rate of convergence of each of these sums is controlled by a parameter ϵ, which is otherwise arbitrary. The derivation follows closely, for example, that given by Born and Huang[4] for the monopole case. The angular dependence introduced by $l>0$ plays a largely passive role, and does not unduly complicate the method. By this procedure, it is found that

$$\begin{aligned}U(\mathbf{x})=&\frac{16(-i\pi)^l}{\sigma^2\omega(2l+1)!!}\sum_{\mathbf{q}\neq0}e^{i\pi\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}_i)}Y_{lm}(\mathbf{q})q^{l-2}\\&\times\exp\left(-\frac{\pi^2q^2}{4\epsilon^2}\right)+\frac{4\pi}{\sigma^2(2l+1)}\sum_{\mathbf{p}}Y_{lm}(\mathbf{x}-\mathbf{x}_i-\mathbf{p})\\&\times\frac{I_l(|\mathbf{x}-\mathbf{x}_i-\mathbf{p}|\,\epsilon)}{|\mathbf{x}-\mathbf{x}_i-\mathbf{p}|^{l+1}}-\delta_{l0}\frac{2\pi^{3/2}}{\sigma\omega\epsilon^2}+U_{\text{av}}\,,\end{aligned} \tag{10}$$

where U_{av} is the average value of the potential $U(\mathbf{x})$ over all space, and $I_l(x)$, related to the incomplete Γ

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[4] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, 1964), p. 248. Their method is actually to get a dipole sum from a monopole sum by differentiation, but the formal derivation has much in common.

function, is given by

$$I_l(x)=2\int_x^\infty dt\, t^{2l}e^{-t^2}/\Gamma(l+\tfrac{1}{2}) \tag{11a}$$

$$=\operatorname{erfc}(x)+e^{-x^2}\sum_{\nu=1}^{l} x^{2\nu-1}/\Gamma(\nu+\tfrac{1}{2}). \tag{11b}$$

The sum over ν is to be omitted if $l=0$.

It should be noted that in general U_{av} could be any solution to Laplace's equation. The present interest, however, is in the bulk properties of the crystal, and hence in a periodic potential. Since a constant is the only periodic solution to Laplace's equation, U_{av} has been so chosen, and thus $U(\mathbf{x})$ is the most general periodic solution.

IV. EWALD COEFFICIENTS

Since the expression (10) for $U(\mathbf{x})$ is independent ϵ, this parameter may be chosen sufficiently large so that the direct lattice sum is negligible everywhere in the plane wave region. Comparison of (10) to (7b) then immediately yields

$$\begin{aligned} U_{\mathbf{q}}{}^{lmi}&=U_{\mathrm{av}}-\delta_{l0}\frac{2\pi^{3/2}}{\sigma\omega\epsilon^2} &&\text{for}\quad \mathbf{q}=0,\\ &=\frac{16(-i\pi)^l}{\sigma^2\omega(2l+1)!!}e^{-\pi\mathbf{q}\cdot\mathbf{x}_i}Y_{lm}(\mathbf{q})q^{l-2}\\ &\quad\times\exp\left(-\frac{\pi^2q^2}{4\epsilon^2}\right) &&\text{for}\quad \mathbf{q}\neq 0. \end{aligned} \tag{12}$$

In a similar manner, ϵ may be chosen large enough so that the only significant contribution to the potential within the i'th sphere from the direct lattice sum is from that term with $\mathbf{p}=0$. All functions of $\mathbf{x}$ are then expanded in powers of $|\mathbf{x}-\mathbf{x}_{i'}|$, and a comparison is made with (7a). It is then found that

$$\begin{aligned} A_{l'm'i'}{}^{lmi}&=\frac{64i^{l'-l}\pi^{l+l'+1}}{\sigma^4\omega(2l+1)!!(2l'+1)!!}\sum_{\mathbf{q}\neq 0}e^{i\pi\mathbf{q}\cdot(\mathbf{x}_{i'}-\mathbf{x}_i)}\\ &\quad\times\exp\left(-\frac{\pi^2q^2}{4\epsilon^2}\right)Y_{l'm'}{}^*(\mathbf{q})Y_{lm}(\mathbf{q})q^{l+l'-2}\\ &\quad-\delta_{ll'}\delta_{mm'}\left[\delta_{ii'}\frac{2^{l+3}\pi^{1/2}\epsilon^{2l+1}}{\sigma^2(2l+1)(2l+1)!!}+\delta_{l0}\frac{4\pi^2}{\sigma^2\omega\epsilon^2}\right]\\ &\quad+\delta_{l'0}(4\pi)^{1/2}U_{\mathrm{av}}/\sigma. \end{aligned} \tag{13}$$

The terms from (10) which have no counterpart in (7a) can be shown to approach zero as ϵ becomes large. Further, $A_{l'm'i'}{}^{lmi}$ becomes independent of ϵ in the limit $\epsilon\to\infty$.

If it is required that the average value of the potential over the plane wave region be zero, the U_{av} must be chosen to be

$$U_{\mathrm{av}}=G(\mathbf{q}=0)+2\pi^{3/2}\delta_{l0}/(\sigma\omega\epsilon^2), \tag{14}$$

where

$$G(\mathbf{q}=0)=-\sum_{\mathbf{q}'\neq 0}G(\mathbf{q}')\Delta(-\mathbf{q}')/\Delta(0), \tag{15a}$$

$$G(\mathbf{q})=U_{\mathbf{q}}{}^{lmi},\quad\text{for}\quad \mathbf{q}\neq 0 \tag{15b}$$

and

$$\Delta(\mathbf{q})=\int_{\mathrm{PW}}d\mathbf{x}\, e^{-i\pi\mathbf{q}\cdot\mathbf{x}}/\omega, \tag{16a}$$

$$=\delta_{q0}-\sum_i 4x_{si}{}^2e^{-i\pi\mathbf{q}\cdot\mathbf{x}_i}j_1(\pi q x_{si})/(q\omega). \tag{16b}$$

Finally, the step function coefficients are

$$U_{s\mathbf{q}}{}^{lmi}=\sum_{\mathbf{q}'}G(\mathbf{q}')\Delta(\mathbf{q}-\mathbf{q}'). \tag{17}$$

V. CRYSTALLINE SYMMETRY

It is useful to consider the special case when all the point multipoles have the symmetry of the crystal lattice in which they are located. Any function with such symmetry can be expanded about the ith atomic site in terms of a sum over radial functions multiplied by lattice harmonics,[5] which are simply suitable linear combinations of spherical harmonics:

$$W_{L\nu i}(\mathbf{r})=\sum_m C_{Lm\nu i}Y_{Lm}(\mathbf{r}), \tag{18}$$

where the coefficients $C_{Lm\nu i}$ are determined by the symmetry about the ith site. The index ν runs over all the possible independent combinations of the spherical harmonics for a given L. The advantage of introducing the lattice harmonics is that in general there are significantly fewer values of ν for a given L than there are values of m, so that numerical work is vastly simplified.

If the harmonics are orthonormalized to σ^2 so that

$$\int_{4\pi}d\Omega W_{L'\nu'i}{}^*(\mathbf{r})W_{L\nu i}(\mathbf{r})=\sigma^2\delta_{L'L}\delta_{\nu'\nu} \tag{19}$$

it is possible to go back to the beginning of this paper and make the substitutions $Y_{lm}(\mathbf{r})\to W_{L\nu i}(\mathbf{r})$ within the ith sphere, $l\to L$, $m\to\nu$, and all the expressions given remain valid. Note that l is replaced by L only for mnemonic reasons; in fact the two have precisely the same significance. It would be possible to replace the simple exponential $e^{i\pi\mathbf{q}\cdot\mathbf{x}}$ by a symmeterized exponential, but this does not seem to be particularly advantageous.

VI. NUMERICAL RESULTS FOR A MONATOMIC BODY CENTERED CUBIC STRUCTURE

The Ewald coefficients have been calculated for the body centered cubic structure with one atom per unit

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[5] D. G. Bell, Rev. Mod. Phys. 26, 311 (1954).

TABLE I. Ewald coefficients $A_L{}^{L'}$ for monatomic body-centered cubic structure and maximum sphere radius.

	$L=0$	$L=4$	$L=6$
$L'=0$	−1.504750155	−0.132471807	0.104369269
$L'=4$	−0.042367827	0.132784561	−0.131952123
$L'=6$	0.033379926	−0.131952123	0.157486296

cell. The scaling factor a is chosen to be the lattice constant, that is, equal to the distance along one cube edge. For this choice the components of the vectors $\mathbf{q}$ and $\mathbf{p}$ are integers.

The largest possible sphere radius is then $x_s=\frac{1}{2}\sqrt{3}$. In this case the spheres are tangent to one another and to the surface of the Wigner-Seitz unit cells at the L points (in the $\langle 1,1,1\rangle$ directions). The volume of the unit cell is $\Omega=\frac{1}{2}a^3$, so that $\omega=4$. The origin is placed at an atomic site, so that $x_i=0$. Since $i=i'=1$ for one atom, i can be dropped from the notation. The coefficients $C_{Lm\nu}$ have been discussed for the cubic case.[5,6] $C_{Lm\nu}=0$ unless $L=0, 4, 6, 8, \cdots$, and for $L<12$, ν takes on just one value. Assuming that the interest is in small L, the index ν is also dropped from the notation. The cubic harmonics are normalized so that $\sigma^2=4\pi$.

TABLE II. Ewald coefficients $U_{s\mathbf{q}}{}^L$ for monatomic body-centered cubic structure and maximum sphere radius.

$\mathbf{q}$	$L=0$	$L=4$	$L=6$
(0 0 0)	0.0	0.0	0.0
(1 1 0)	0.0005416870	−0.0032529063	0.0005432944
(2 0 0)	−0.0026460662	0.0223914757	0.0016733617
(2 1 1)	0.0000086981	−0.0055765699	−0.0043464848
(2 2 0)	0.0002166606	0.0076716496	0.0108606447
(3 1 0)	0.0012079119	−0.0072346557	−0.0004018551
(2 2 2)	0.0005834899	0.0056430467	0.0027581433
(3 2 1)	−0.0005977479	0.0020274549	−0.0013950515
(4 0 0)	−0.0014744587	0.0061950817	−0.0001347041
(3 3 0)	−0.0000762771	−0.0036068060	−0.0065981030
(4 1 1)	−0.0005744615	0.0037050944	0.0012440220
(4 2 0)	0.0001905379	−0.0005591625	0.0009995303
(3 3 2)	0.0002571742	−0.0042307754	0.0015130121
(4 2 2)	0.0002760030	−0.0005704390	−0.0010789687
(4 3 1)	0.0003554952	−0.0001601095	0.0017783182
(5 1 0)	0.0005710762	−0.0016667357	−0.0007014597
(5 2 1)	0.0000831868	−0.0009119892	−0.0002660176
(4 4 0)	−0.0002747543	0.0027274541	0.0020461388
(4 3 3)	−0.0003233022	0.0033426048	−0.0021105218
(5 3 0)	−0.0003479692	0.0011229409	0.0001198405
(4 4 2)	−0.0002529031	0.0016243754	−0.0000716619
(6 0 0)	−0.0001474853	−0.0017810185	0.0009625362
(5 3 2)	−0.0001800681	0.0002290063	0.0000836403
(6 1 1)	−0.0002877577	0.0000998761	0.0001657651
(6 2 0)	−0.0003028214	0.0010839216	−0.0008026855
(5 4 1)	−0.0000622982	−0.0007462787	−0.0015553375
(6 2 2)	0.0000133636	0.0001522324	0.0008850772
(6 3 1)	0.0000981623	−0.0000715873	−0.0003007473
(4 4 4)	0.0003528538	−0.0030195845	0.0024593024

TABLE III. Ewald coefficients $U_{\mathbf{q}}{}^L$ for monatomic body-centered cubic structure and maximum sphere radius.

$\mathbf{q}$	$L=0$ $\epsilon=3.50$	$L=4$ $\epsilon=3.68$	$L=6$ $\epsilon=3.48$
(0 0 0)	0.2507592050	−0.0900009516	0.0687998522
(1 1 0)	0.1063820880	−0.0261103148	0.0124839844
(2 0 0)	0.0355538710	0.1450930920	−0.0204452067
(2 1 1)	0.0158432404	−0.0377939814	−0.0157280512
(2 2 0)	0.0079424347	−0.0350030609	0.0588258466
(3 1 0)	0.0042470954	0.0668626152	−0.0020698039
(2 2 2)	0.0023656972	−0.0675546578	−0.0640970638
(3 2 1)	0.0013553790	−0.0205294823	0.0035815275
(4 0 0)	0.0007927152	0.0651890387	−0.0283727518
(3 3 0)	0.0004709915	−0.0127353754	0.0388232180
(4 1 1)	0.0004709915	0.0249990702	−0.0059113542
(4 2 0)	0.0002833374	0.0078632823	0.0133442362
(3 3 2)	0.0001721708	−0.0174410312	−0.0188825151
(4 2 2)	0.0001054920	−0.0056909453	−0.0064280589
(4 3 1)	0.0000650887	−0.0042824387	0.0066290377
(5 1 0)	0.0000650887	0.0139622707	−0.0059744140
(5 2 1)	0.0000252031	0.0027020041	0.0004444961
(4 4 0)	0.0000157933	−0.0017664515	0.0070805682
(4 3 3)	0.0000099356	−0.0031081121	−0.0047677260
(5 3 0)	0.0000099356	0.0001398425	0.0034156532
(4 4 2)	0.0000062722	−0.0018466437	−0.0010346991
(6 0 0)	0.0000062722	0.0038353368	−0.0024410862
(5 3 2)	0.0000039718	−0.0007030226	−0.0004875159
(6 1 1)	0.0000039718	0.0021012779	−0.0009861454
(6 2 0)	0.0000025221	0.0011308708	−0.0000733709
(5 4 1)	0.0000016055	−0.0003749076	0.0009799112
(6 2 2)	0.0000010244	0.0002344878	−0.0000944811
(6 3 1)	0.0000006549	0.0001014929	0.0002320375
(4 4 4)	0.0000004195	−0.0003829295	−0.0006691570

For purposes of calculating, tabulating, and using these coefficients, several interrelationships are of interest:

$$A_{L'}{}^{L}=A_L{}^{L'}+(\delta_{L'0}-\delta_{L0})U_{\mathrm{av}} \tag{20}$$

and

$$U_{sR\mathbf{q}}{}^{L}=U_{s\mathbf{q}}{}^{L}, \tag{21}$$

where the rotation R is any operation in the cubic group, so that $R\mathbf{q}$ is any vector in the star of $\mathbf{q}$.

Also, it is noted that while U_{av}, $U_{\mathbf{q}=0}{}^{L}$, and $U_{s\mathbf{q}}{}^{L}$ depend on the sphere radius x_s, $(A_{L'}{}^{L}-\delta_{L'0}U_{\mathrm{av}})$, and $U_{\mathbf{q}\neq 0}{}^{L}$ do not depend on this parameter.

The coefficients were calculated using FORTRAN IV programs on an IBM System/360 Model 65 computer. Double-precision arithmetic (approximately 15 decimal places) was used throughout.

First the quantities $(A_{L'}{}^{L}-\delta_{L'0}U_{\mathrm{av}})$ are found, using $\epsilon=6$, which is large enough so that results do not depend on ϵ to the number of figures given. The sum over $\mathbf{q}$ in (13) was carried out over 1250 stars, or about 50 000 vectors in reciprocal space to insure convergence. The magnitude of the largest vector used is $28.8(2\pi/a)$. The only numerical problem is with the diagonal coefficients $A_L{}^L$, where there is a difference between two nearly equal quantities, namely, the sum over $\mathbf{q}$ and the $\delta_{LL'}$ term. For $A_4{}^4$, the first five decimal places cancel, while for $A_6{}^6$, six places cancel. This leaves a maximum of $15-6=9$ decimal place accuracy in the difference. The number of decimal places lost in the difference increases with ϵ.

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[6] F. C. Von der Lage and H. A. Bethe, Phys. Rev. **71**, 612 (1947); P. D. DeCicco and A. Kitz, Quarterly Progress Report of the Solid State and Molecular Theory Group, M. I. T., No. 59, p. 34, 1966 (unpublished).

A second program introduces the sphere radius x_s, and using the quantities $(A_{L'}{}^{L}-\delta_{L'0}U_{\text{av}})$ calculates the Ewald coefficients, which are tabulated in Tables I–III. For U_{av} and $U_{\text{sq}}{}^{L}$, $\epsilon=8$ was used, again so that the results are independent of ϵ. To insure convergence, these sums were carried over 1800 stars, or about 73 000 vectors, up to a magnitude of $32.7(2\pi/a)$. The coefficients are all accurate to the number of decimal places given in the tables.

The coefficients $U_{\text{q}}{}^{L}$ are a slightly different case, since they depend heavily on ϵ. The particular ϵ's chosen, $\epsilon=3.50$, 3.68, and 3.48 for $L=0$, 4, and 6, were picked so that reasonable convergence is achieved in the first 29 stars, so that the series may be truncated after the vector $(4,4,4)(2\pi/a)$. Further, with an application to lithium in mind,[7] the $L=4$ and $L=6$ series need not converge as much as the dominant $L=0$ series, owing to the small multipole moments for higher L in lithium. In short, the ϵ's can be chosen for each L to suit a given application. For lithium, the coefficients in Table III give the potential to an accuracy of about three significant figures, or within 0.00005 Ry in the plane-wave region.

Note added in proof: The author has recently become aware of a very similar approach to this potential problem. See B. R. A. Nijboer and F. W. DeWette, Physica **23**, 309 (1957); **24**, 1105 (1958).

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[7] W. E. Rudge, Phys. Rev., second following paper, 181, 1033 (1969).

PHYSICAL REVIEW VOLUME 181, NUMBER 3 15 MAY 1969

Self-Consistent Augmented-Plane-Wave Method*

William E. Rudge
IBM Research Laboratory, San Jose, California 95114

(Received 25 November 1968)

The augmented-plane-wave method for energy-band calculations is presented in a form which handles a general one-electron crystalline potential, rather than the restricted "muffin-tin" potential which has traditionally been used. From the wave functions resulting from the band calculation, the total crystalline charge density is found, and from this, a new potential is found, making an iterative self-consistent calculation possible. As an example, the method has been applied to body-centered cubic (bcc) lithium. The results of two energy-band calculations are reported. One used the average free-electron-exchange approximation suggested by Slater. The second used two-thirds of this exchange.

I. INTRODUCTION

The augmented-plane-wave (APW) method, originally proposed by Slater,[1–3] solves the energy-band problem by dividing a crystal into several parts. A sphere is constructed about each atomic site. The wave function is then expanded inside each APW sphere in terms of radial functions multiplied by spherical harmonics; in the region between the spheres, the plane-wave region, the wave function is expanded in a Fourier series of plane waves. Wood[4] has discussed the method for a monatomic crystal, using group-theoretical methods to reduce the size of the secular equation. Ern and Switendick[5] have generalized the method to any number of atoms per unit cell. Traditionally, the model for the one-electron potential energy has been limited to a muffin-tin form, in which the potential is assumed to be spherically symmetric within each APW sphere, and constant in the plane-wave region. The method is not limited to this model. Marcus[6] has considered the non-muffin-tin contributions to the matrix elements which enter into the eigenvalue problem, and DeCicco[7] included a nonconstant potential in the plane wave region in his calculation of energy bands in KCl. The first aim of the present paper is to present the more general APW method for any crystal with a symmorphic space group, allowing the use of an arbitrary potential, limited only by the assumption that it have the full symmetry of the crystal, and using the symmetry of the crystal to reduce the size of the secular determinant and to simplify the matrix elements as much as possible for use in numerical calculations. Section II presents a set of basis functions useful in this connection.

Section IV gives an expression for the electron density found in the energy-band calculation, and also considers the normalization of the one-electron wave functions. From this, the Coulomb potential energy is found. The average free-electron-exchange approximation is

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* Based in part on a thesis submitted in partial fulfillment of the requirements for a Ph.D. degree from the Department of Physics at the Massachusetts Institute of Technology. Further details are given in an expanded version of this paper, IBM Research Report No. RJ 540 (unpublished), available from the author.

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