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Solution of Poisson's equation for arbitrarily shaped overlapping or nonoverlapping charge densities in terms of multipole moments

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The solution of Poisson's equation in terms of a Green's function expanded in spherical harmonics is presented. No restrictions are imposed on the charge density. An angular-momentum representation for the potential is obtained ready for application in self-consistent full-potential band-structure methods, which are based on a multicenter expansion of the one-electron Green's function into spherical harmonics.

I. INTRODUCTION

Electrostatic interactions are quite important in many areas of condensed-matter theory. Poisson's equation describes these interactions by relating a charge distribution to the potential function contingent upon certain boundary conditions. The general solution can be found in terms of the Green's function (see Jackson[1]).

In condensed-matter theory Madelung[2] calculated the energy of point charges distributed on a regular lattice; Ewald[3] generalized the problem to a charge distribution of nonoverlapping spheres each centered at a lattice site and obtained the corresponding potential function. These methods and derivatives of them have been applied quite successfully in various areas of condensed-matter theory, but always assuming certain geometrical restrictions on the charge density. Removing these restrictions of nonoverlapping spheres poses certain difficulties.

Especially in band-structure calculations, which use the local-density approximation (LDA) of the density-functional theory, Poisson's equation plays a central role. The solution of the effective one-electron Schrödinger equation provides a charge density of the crystal, which in turn is related to the solution of the Poisson equation—the crystal potential. In the LDA the ground state of the system is found if the crystal charge density, obtained from the solution of Schrödinger's equation for the crystal potential, has as a solution of Poisson's equation the same crystal potential (self-consistency). Approximating the cells of a crystal by muffin-tin spheres makes the numerical solution of these two differential equations easier. But in order to describe the crystal more realistically these geometrical restrictions have to be abandoned, posing mathematical difficulties for a correct numerical solution of the effective Schrödinger equation and the Poisson equation. In this paper a solution for the latter one will be presented.

Considering space-filling nonoverlapping Wigner-Seitz (WS) cells (Voronoi polyhedra), Morgan[4] tried to derive a solution of Poisson's equation using only angular-momentum basis functions. But this result is valid only for limited domains of space and is incomplete. A different approach was used by Weinert.[5] He divided each cell into a sphere plus the remainder. Using different representations of the charge density, namely spherical harmonics within the sphere and plane waves outside, he obtained the solution of Poisson's equation in each region in the corresponding representation. At the sphere boundary one has to match these two different representations. To obtain a smooth potential function one has to use a sufficient number of plane waves and of spherical harmonics. This makes the problem numerically more involved. In order to reduce the number of basis functions, it is well known[6] that the angular-momentum representation has a very compact basis, namely the spherical harmonics. Only a small number of these functions has to be taken into account to obtain convergence in numerical calculations.

The aim of this paper is to present a method that gives the crystal potential as an expansion into spherical harmonics. The expansion coefficients are given in terms of multipole moments of cell charge densities contained in a cell centered at different sites. The equations are valid in all space and for any geometrical arrangement of the cells. The usefulness of the derived equations will be demonstrated by applying the method to a nonspherical charge density for which the corresponding potential is known.

II. SOLUTION OF POISSON'S EQUATION FOR ARBITRAILY SHAPED OVERLAPPING OR NONOVERLAPPING CHARGE DENSITIES

The general solution for the Coulomb potential due to a charge distribution in a crystal in terms of a Green's function is given by

$$V(\mathbf{r}_1) = 2\int_{\infty} \frac{\rho(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_1|} d\mathbf{r}_2 \, . \tag{2.1}$$

Assuming that the charge density can be represented as a sum over cellular charge densities

$$\rho(\mathbf{r}_2) = \sum_{\mu} \rho^{\mu}(\mathbf{r}_2 - \mathbf{R}_{\mu}) \, , \tag{2.2}$$

where ρ^{μ} represents the true charge density when $\mathbf{r}_2$ is contained in the WS cell Ω_{μ} and vanishes everywhere else, one can rewrite[4] Eq. (2.1),

$$\sum_{\mu} V(\mathbf{r}_1 + \mathbf{R}_{\mu}) = \sum_{\mu} V_1^{\mu}(\mathbf{r}_1) + V_2^{\mu}(\mathbf{r}_1) \, , \tag{2.3}$$

by making use of the translational invariance of a crystal (this is a convenient but not a necessary assumption for the following). $\mathbf{R}_\mu$ denotes a real-space lattice vector. The potential due to the charge distribution within the central cell is given by[1]

$$V_1^\mu(\mathbf{r}) = 8\pi \sum_L (2l+1)^{-1} Y_L(\hat{r})[r^l P_L^\mu(r) + r^{-l-1} Q_L^\mu(r)] , \tag{2.4}$$

where

$$Q_L^\mu(r) = \int d\Omega \int_0^r r_1^2 dr_1 r_1^l \rho^\mu(\mathbf{r}_1) Y_L^*(\hat{r}_1)\sigma(\mathbf{r}_1) \tag{2.5}$$

is the $L = (l, m)$th multipolelike expansion term of the charge density contained in a sphere with radius r, while

$$P_L^\mu(r) = \int d\Omega \int_r^{r_c} r_1^2 dr_1 r_1^{-l-1} \rho^\mu(\mathbf{r}_1) Y_L^*(\hat{r}_1)\sigma(\mathbf{r}_1) , \tag{2.6}$$

where r_c is the radius of a sphere which circumscribes the cell. The shape function $\sigma(\mathbf{r})$, as discussed in the Appendix, assures that the integration is performed only over the WS cell [$\sigma(\mathbf{r})$ is one if $\mathbf{r}$ is contained in the cell and zero otherwise].

The contribution to the potential from all the other, external cells is given by

$$V_2^\mu(\mathbf{r}_1) = 2 {\sum_\nu}' \int_{\Omega_\nu} \frac{\rho^\nu(\mathbf{r}_2) d\mathbf{r}_2}{|\mathbf{r}_2 - \mathbf{r}_1 + \mathbf{R}_{\mu\nu}|} . \tag{2.7}$$

To expand the Green's function $|\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{R}_{\mu\nu}|^{-1}$ ($\mathbf{r}_1 \in \Omega_\mu, \mathbf{r}_2 \in \Omega_\nu, \mathbf{R}_{\mu\nu} = \mathbf{R}_\nu - \mathbf{R}_\mu$) into spherical harmonics several different geometrical cases must be considered. According to Sack[7] one has to distinguish four different regions for the bipolar expansion of the Green's function

$$\begin{aligned} &S_0 : |\mathbf{r}_1 - \mathbf{r}_2| \le R_{\mu\nu} \le |\mathbf{r}_1 + \mathbf{r}_2| , \\ &S_1 : r_1 \ge |\mathbf{r}_2 + \mathbf{R}_{\mu\nu}| , \\ &S_2 : r_2 \ge |\mathbf{r}_1 + \mathbf{R}_{\mu\nu}| , \\ &S_3 : R_{\mu\nu} \ge |\mathbf{r}_1 + \mathbf{r}_2| , \end{aligned} \tag{2.8}$$

using the same notation as Sack. With this distinction and using the exact, mathematically derived formulas by Sack one gets the following expressions for the contributions of the external cells to the potential of the central cell.

In the nonoverlapping case (region S_3) the standard expression for the potential is obtained:

$$\begin{aligned} {}^3V_2^\mu(\mathbf{r}_1) = 2\sum_{L_1} 16\pi^2 Y_{L_1}(\hat{r}_1) \frac{r_1^{l_1}}{(2l_1+1)!!} \sum_{L_2} & (-)^{l_2+m_2} G_{L_2 L_1}^{L_3} \frac{(2l_1+2l_2-1)!!}{(2l_2+1)!!} \delta_{l_3,l_1+l_2} \\ & \times \sum_\nu Q_{L_2}^\nu R_{\mu\nu}^{-l_3-1} Y_{L_3}(\widehat{R_{\mu\nu}}) , \end{aligned} \tag{2.9}$$

where $G_{L_2 L_1}^{L_3}$ is the integral over the whole angle of a triple product of spherical harmonics (Gaunt numbers)

$$G_{L_1 L_2}^{L_3} = \int Y_{L_1}^*(\hat{r}) Y_{L_2}(\hat{r}) Y_{L_3}(\hat{r}) d\Omega . \tag{2.10}$$

The term $(l_1, m_1) = (0,0)$ corresponds to the Madelung potential. The cell multipole moment is given by $Q_L^\mu \equiv Q_L^\mu(r=\infty) \equiv Q_L^\mu(r = r_c)$ in Eq. (2.5).

To treat the overlap region (nearest-neighbor lattice vectors) one first subtracts from Eq. (2.9) the nonoverlapping contributions of the corresponding lattice vectors and uses instead

$$\begin{aligned} {}^0V_2^\mu(\mathbf{r}_1) = 2\sum_{L_1} & (-1)^{l_1} 4\pi^2 Y_{L_1}(\hat{r}_1) \sum_{L_2} (-1)^{l_2+m_2} \sum_{L_3} G_{\bar{L}_2 L_1}^{L_3} \\ \times \Bigg[\Bigg(& \tfrac{1}{2}(-1)^{l_1} \frac{4(2l_1-1)!!}{(2l_2+1)!!(2l_3+1)!!} \delta_{l_1,l_2+l_3} r_1^{-l_1-1} \sum_\nu {}^1\bar{Q}_{\bar{L}_2}^\nu(r_1) R_{\mu\nu}^{l_3} Y_{L_3}(\hat{R}_{\mu\nu}) \\ & + \tfrac{1}{2}(-1)^{l_2} \frac{4(2l_2-1)!!}{(2l_1+1)!!(2l_3+1)!!} \delta_{l_2,l_1+l_3} r_1^{l_1} \sum_\nu {}^2\bar{Q}_{\bar{L}_2}^\nu(r_1) R_{\mu\nu}^{l_3} Y_{L_3}(\hat{R}_{\mu\nu}) \\ & + \tfrac{1}{2}(-1)^{l_3} \frac{4(2l_3-1)!!}{(2l_1+1)!!(2l_2+1)!!} \delta_{l_3,l_1+l_2} r_1^{l_1} \sum_\nu [2Q_{\bar{L}_2}^\nu - {}^1\bar{Q}_{\bar{L}_2}^\nu(r_1)] R_{\mu\nu}^{-l_3-1} Y_{L_3}(\hat{R}_{\mu\nu}) \Bigg) \\ & - (-1)^{l_3} \frac{(2l_1-1)!!(2l_2-1)!!}{(l_1+l_2-l_3+1)!!!(l_1+l_2+l_3)!!![\frac{1}{2}(l_1+l_2+l_3)+1]} r_1^{-l_1-1} \sum_\nu R_{\mu\nu}^{l_1+l_2+1} Y_{L_3}(\hat{R}_{\mu\nu}) \\ & \times \sum_{u,v} \frac{\Gamma\{-[\frac{1}{2}(l_1+l_2+l_3)+1]+u+v\}\Gamma\{-[\frac{1}{2}(l_1+l_2-l_3)+1]+u+v\}\Gamma(\frac{1}{2}-l_1)\Gamma(\frac{1}{2}-l_2)}{\Gamma\{-[\frac{1}{2}(l_1+l_2+l_3)+1]\}\Gamma[-\frac{1}{2}(l_1+l_2-l_3)+1]\Gamma(\frac{1}{2}-l_1+u)\Gamma(\frac{1}{2}-l_2+v)} \\ & \times \left(\frac{r_1}{R_{\mu\nu}}\right)^{2u} \left(\frac{1}{R_{\mu\nu}}\right)^{2v} {}^2\bar{Q}_{-l_2-1+2v,-m_2}^\nu(r_1) \Bigg] , \end{aligned} \tag{2.11}$$

where $\Gamma(\alpha)$ is the Gamma function, $(n)!!$ denotes the double factorial $(-1)!! = (0)!! = 1$, $(n)!! = n(n-2)(n-4)\ldots$, u, v are integers, and $\bar{L} = (l, -m)$. The overlap multipole-moment-like functions ${}^1\bar{Q}^{\nu}_{\bar{L}}(r_1)$ and ${}^2\bar{Q}^{\nu}_{-l_2-1+2v,m_2}(r_1)$ are given by the following integrals:

$$ {}^1\bar{Q}^{\nu}_{L_2}(r_1) = \int_{|\mathbf{R}_{\mu\nu}|-|\mathbf{r}_1|}^{r_c} [\rho^{\nu}(\mathbf{r}_2)\sigma(\mathbf{r}_2) r_2^{l_2} Y_{L_2}(\hat{r}_2)] d\mathbf{r}_2 \tag{2.12} $$

$$ {}^2\bar{Q}^{\nu}_{-l_2-1+2v,m_2}(r_1) = \int_{|\mathbf{R}_{\mu\nu}|-|\mathbf{r}_1|}^{r_c} [\rho^{\nu}(\mathbf{r}_2)\sigma(\mathbf{r}_2) r_2^{-l_2-1+2v} Y_{L_2}(\hat{r}_2)] d\mathbf{r}_2 \, , \tag{2.13} $$

where ν runs over the index of the nearest neighbors. These integrals are quite easy to solve numerically. Using a finite number of spherical harmonics to represent the cell potential (L_1) and assuming a maximum l value for the L_2 sum all internal sums (L_3, u, v) are finite.

So far we assumed that the radii of the circumscribing spheres are only overlapping; which is legitimate if one divides the crystal into nonoverlapping WS cells. For less symmetric cells it is possible that a neighboring cell is contained completely within the circumscribing sphere of the central cell. In this case the bipolar expansion formulas valid in the domains S_1 or S_2 have to be used. Even in the case of overlapping cell charge densities the solution of Poisson's equation in terms of spherical harmonics is a straightforward extension of the above.

III. A NUMERICAL TEST CASE

To demonstrate the validity of Eqs. (2.4), (2.9), and (2.11) we chose as test charge density[4]

$$ \rho(\mathbf{r}) = B \sum_i \exp(\imath \mathbf{T}_i \cdot \mathbf{r}) \, , \tag{3.1} $$

where $\mathbf{T}_i$ is the set of eight vectors $< 1,1,1 > 2\pi/a$ of a fcc crystal with a lattice constant $a = 10.263$ Bohr radii and $B = 0.005$ Ry. With this set of parameters the cell potential is given by[4]

$$ V(\mathbf{r}) = 8\pi\rho(\mathbf{r})/T_i^2 + 0.241\,76 \text{ Ry} \, . \tag{3.2} $$

Expanding Eq. (3.1) into spherical harmonics,

$$ \rho(\mathbf{r}) = 4\pi B \sum_{l=0}^{l_\rho} \sum_{m=-l}^{l} \sum_{i=1}^{8} \imath^l j_l(T_i r) Y_{lm}(\hat{T}_i) Y_{lm}(\hat{r}) \, , \tag{3.3} $$

where $j_l(x)$ is a spherical Bessel function, we found that for $l_\rho \geq 8$ the series is converged.

Previously Eqs. (2.4) and (2.9) have been derived by Morgan.[4] In that paper it was argued that the discrepancy between the exact potential and the one obtained by using Eqs. (2.4) and (2.9) was not too large and could be neglected. It was also noted that for l_ρ larger than 4 the results become worse. The explanation for that mistaken observation is quite simple now. The correction [Eq. (2.11)] due to the overlap of the radii centered at different expansion centers *are* important and have to be taken into account. Morgan had compared the potential of Eq. (3.2), where the charge density of Eq. (3.1) was used, with the potential obtained by Eqs. (2.4) and (2.9), where the not-converged charge density of Eq. (3.3) with $l_\rho = 4$ was used. The error due to the nonconverged sum for the charge density incidentally cancels almost the neglect of the correction term Eq. (2.11). The same charge density should have been used when comparing the two different expressions for the potential. Then the result shows that the overlap corrections are important.

In the present calculation I used $l_\rho = l_1 = 8$ as maximum l values for the charge density as well as for the potential expansion into spherical harmonics. One must note that the integrals in Eqs. (2.5), (2.12), and (2.13) are extended over the WS cell and not over a sphere. Therefore higher multipole moments than $l_2 = 8$ exist and have to be included in the summations. These moments are only due to the shape of the WS cell, and can easily be calculated by using the expansion of the shape function into spherical harmonics (see the Appendix). Without these higher terms the result converges much slower and the expansion of the potential has to go up to higher l_1 values.

Figure 1 shows such a calculation for the (001) direction pointing to the farthest corner of the WS cell. The

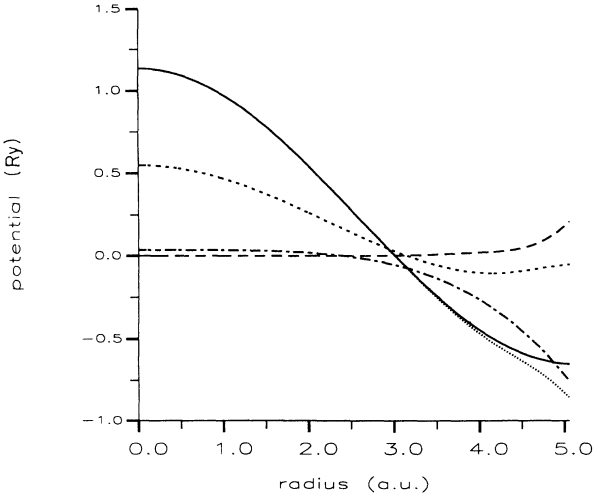

FIG. 1. Different contributions to the potential: exact result obtained by Eq. (3.2) or the sum of Eqs. (2.4), (2.9), and (2.11) (full line), the potential without the overlap corrections [sum of Eqs. (2.4) and (2.9)] (dotted line), the single cell term Eq. (2.4) (short dashed line), the correction term Eq. (2.11) (long dashed line), and contributions of the external cells Eq. (2.11) (dashed dotted line) for vectors pointing along the (001) direction.

exact result Eq. (3.2) (full line) was reproduced by the sum of Eqs. (2.4), (2.9), and (2.11), where multipole moments up to $l_2 = 16$ have been included. For illustration the different contributions to the potential have been included in Fig. 1: the single cell potential [Eq. (2.4)] starting at about 0.5 Ry, the term due to the external cells [Eq. (2.11)] starting slightly above 0.0 Ry, and the contribution coming from the nearest neighbors in the overlap region [Eq. (2.11)] beginning at 0.0 Ry. The dotted line is the total potential without the overlap corrections, which shows that the overlap corrections are important at the cell edges.

In a recent paper, Gonis, Sowa, and Sterne[8] treated the same problem using a different approach. In their paper they avoid the problem of having a mathematically correct angular-momentum expansion of $1/\mathbf{r}$, which is valid in the different regions, by the following procedure. First they shift a point lying in the region S_0 by a vector $\mathbf{b}$ into the region S_3, then they use the appropriate bipolar expansion, then they shift back by $-\mathbf{b}$ to the original point and perform another bipolar expansion. The usefulness of their final result in band-structure calculations is questionable, since for every nearest-neighbor lattice vector one has to calculate the structure constants up to $l = 30$ in order to obtain a converged result. Although in principle one has to do this for each WS cell only once, the computer memory it takes to store all these constants is enormous.

The approach presented here is based on a mathematically exact derivation of the bipolar expansion of $1/\mathbf{r}$. It has the advantage that the expansion does not depend on any direction. All angular and radial dependencies are factorized explicitly. The crystal potential is given as an expansion into spherical harmonics, and the expansion coefficients are presented explicitly. The expansion is convergent, in contrast to the one found by Gonis, Sowa, and Sterne.[8] Therefore the method is computationally quite fast (20 seconds for 700 radial points on a CRAY YMP). The most time consuming part is the summation of the overlap correction [Eq. (2.11)], which takes about $\frac{2}{3}$ of the computer time. Currently I am using this program in a full-potential Korringa-Kohn-Rostoker (KKR) (Ref. 6) method.

IV. SUMMARY

Without imposing any restrictions on the shape or extension of the separate charge domains, the solution of Poisson's equation in terms of spherical harmonics has been presented. In the case of nonoverlapping, space filling cell charge densities corrections must be included due to the overlap of the circumscribed spheres of two adjacent cells. The presented formulas are best suited for applications in self-consistent full-potential band-structure calculations that use the angular-momentum representation such as the KKR method, or the linear-muffin-tin-orbital method, and other related methods.

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APPENDIX: SHAPE FUNCTION

A convenient way to solve the three-dimenional integrals [Eqs. (2.5) and (2.6)] numerically is to expand the shape function into spherical harmonics,[4]

$$\sigma(\mathbf{r}) = \sum_L \sigma_L(r) Y_L(\hat{r}), \qquad \sigma_L(r) = \int \sigma(\mathbf{r}_1) Y_L^*(\hat{r}_1) d\Omega_1 . \tag{A1}$$

In order to obtain the coefficient $\sigma_L(r)$, I used 2016 (Ref. 9) special directions in 1/48 of the WS cell for the angular integral. In this way the evaluation of the three-dimensional integrals is reduced to a one-dimensional numerical integration over the radius. For a noncubic WS cell a numerical procedure to calculate the shape function was given by Stefanou, Akai, and Zeller.[10]

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[1] J.D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975).

[2] E. Madelung, Phys. Z. **19**, 524 (1918).

[3] P.P. Ewald, Ann. Phys. **64**, 253 (1921).

[4] J. van W. Morgan, J. Phys. C **10**, 1181 (1977).

[5] M. Weinert, J. Math. Phys. **22**, 2433 (1981).

[6] J. Korringa, Physica **13**, 392 (1947); W. Kohn and N. Rostoker, Phys. Rev. **94**, 111 (1954).

[7] R.A. Sack, J. Math. Phys. **5**, 260 (1964).

[8] A. Gonis, E.C. Sowa, and P.A. Sterne, Phys. Rev. Lett. **66**, 2207 (1991).

[9] The directions were generated by a program that is based on the prism method [G.M. Stocks, W. Temmermann, and B. L. Gyorffy, in *Electrons in Disordered Materials and at Metallic Surfaces,* edited by P. Phariseau, B. L. Gyorffy, and C. Scheire, NATO Advanced Study Institute Series B: Physics (Plenum, New York, 1979), Vol. 42, written by G. Hörmandinger.

[10] N. Stefanou, H. Akai, and R. Zeller, Comp. Phys. Commun. **60**, 231 (1990).