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Non-muffin-tin energy bands and Fermi surface for lead*

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The relativistic Korringa-Kohn-Rostoker method is used to calculate the energy bands and Fermi surface of lead. The bands are first calculated self-consistently, using a k-dependent muffin-tin potential. A non-muffin-tin potential is then generated from the resulting crystal charge density and the difference between this potential and final self-consistent muffin-tin potential is used in a perturbation calculation to correct the muffin-tin energy bands. Both the self-consistent muffin-tin potential and the non-muffin-tin potential are used to construct Fermi surfaces which are compared with measurements obtained from the de Haas–van Alphen effect. The muffin-tin Fermi surface shows reasonable agreement with experiment. The non-muffin-tin potential makes a significant change in the Fermi surface and improves the agreement.

INTRODUCTION

The first accurate quantitative description of the Fermi surface of lead was given by Anderson and Gold.[1] Using a four-parameter pseudopotential model, they constructed a Fermi surface which fits the existing data from the de Haas–van Alphen effect. A systematic error was discovered in the data they had used, and a second calculation was made by Anderson, O'Sullivan, and Schirber (AOS),[2] using the same least-squares method to fit a Fermi surface to the corrected data. More recent de Haas–van Alphen measurements[3] have agreed with the AOS values. A more ambitious pseudopotential calculation was done by van Dyke[4] using 30 orthogonalized plane waves to fit the data, instead of the four used by AOS. Van Dyke found that at high pressures the AOS calculation was inadequate but that their normal-pressure Fermi surface was correct. A more recent experiment[5] measures the effective mass of the electrons on the Fermi surface, and agrees with the effective mass calculated from the AOS energy bands.

The earliest first-principles calculation of the energy-band structure of lead was made by Loucks,[6] who used the relativistic augmented-plane-wave (APW) method. A second calculation was made by Sommers, Juras, and Segall,[7] using the relativistic form of the Korringa-Kohn-Rostoker (KKR) method. These authors carried out the calculations using two different exchange potentials, one with a Kohn-Sham-like exchange potential with a coefficient of $\frac{2}{3}$, and the other with a coefficient of 1. Only the first of these was found to be satisfactory. A more recent band-structure calculation for lead was carried out by Neto and Ferreira,[8] who also used the relativistic form of the KKR method. The potentials used in these calculations were all of the usual muffin-tin form.

The calculation reported here used the relativistic KKR method[9,10] to calculate the energy bands and the Fermi surface of lead, and includes an investigation of the effects of a non-muffin-tin potential. The first part of the calculation uses a k-dependent potential of the usual muffin-tin form. The potential and the electron wave functions are calculated self-consistently, and the results are compared with other calculations and with the measured Fermi surface. In the second part of the calculation the final self-consistent muffin-tin wave functions are used to calculate a nonspherical electron charge density and the resulting nonspherical crystal potential throughout the entire crystal cell. The non-muffin-tin part of this crystal potential is used with first-order perturbation theory to correct the muffin-tin energy bands and Fermi surface.

SELF-CONSISTENT MUFFIN-TIN ENERGY BANDS

A very useful approximation for the KKR method is the muffin-tin (MT) potential. The crystal cell is divided into two parts. Inside a sphere of radius r_i the potential is spherically symmetric and outside it is constant. The largest possible value is used for r_i. The regions inside and outside the MT spheres are labeled S and R, respectively.

The muffin-tin calculation used the Liberman[11] potential, in which the charge density is taken to be spherically symmetric in region S and constant in region R. This leads to the electrostatic potential

$$\phi_S(r) = -\frac{e^2 Z}{r} + \frac{e^2}{r}\int_0^r 4\pi r'^2 \rho(r')\,dr' + e^2\int_r^{r_i} \frac{1}{r'}\,4\pi r'^2 \rho(r')\,dr' + e^2 Z_R \langle 1/r\rangle_R\,, \qquad (1)$$

$$\phi_R = e^2(Z_S - Z)\langle 1/r\rangle_R + e^2 Z_R \langle 1/|\vec{r}_1 - \vec{r}_2|\rangle_{RR}\,, \qquad (2)$$

where Z_S and Z_R are the total number of electrons in the regions S and R. For a face-centered-cubic lattice of lattice constant a the required average values are

$$\langle 1/r\rangle_R = 1/0.378\,32a\,,\quad \langle 1/|\vec{r}_1-\vec{r}_2|\rangle_{RR} = 1/0.381\,57a\,.$$

The total effective crystal potential is obtained by adding to the electrostatic potential an appropriate exchange potential. For this exchange potential we have used the k-dependent potential given by Harford.[12] Correlation is included in this potential by using a screened Coulomb interaction. In atomic units this exchange potential is

$$V_k^{\text{ex}} = -\frac{e^2k_F(r)}{\pi}\,Q\left(\frac{k}{k_F(r)},\frac{K_S(r)}{k_F(r)}\right). \tag{3}$$

Here k is the modulus of the crystal momentum, with a reciprocal-lattice vector added to put it into the appropriate Brillouin zone. The potential is derived from a free-electron model, so that the other parameters are values for a free-electron gas of density ρ. Here k_F is the Fermi momentum

$$k_F = (3\pi^2\rho)^{1/3}\,, \tag{4}$$

and K_S is the Fermi-Thomas screening parameter

$$K_S^2 = (4/\pi)k_F\,. \tag{5}$$

The function $Q(\eta,\theta)$ is given by

$$Q(\eta,\theta) = 1+\frac{1}{4\eta}1-\eta^2+\theta^2)\ln\left(\frac{(1+\eta)^2+\theta^2}{(1-\eta)^2+\theta^2}\right) - \theta\left[\tan^{-1}\left(\frac{1+\eta}{\theta}\right)+\tan^{-1}\left(\frac{1-\eta}{\theta}\right)\right], \tag{6}$$

and for $\eta=0$ has the limiting value

$$Q(0,\theta) = 2-2\theta\tan^{-1}\theta^{-1}\,. \tag{7}$$

The same approximation is made here as was made for the electrostatic potential; the density is spherically symmetric inside the MT sphere and constant outside. Since the exchange potential depends upon r only through the density, this approximation puts the exchange potential into the MT form. The complete MT potential is

$$V_k(r) = \phi(r) + V_k^{\text{ex}}(r)\,. \tag{8}$$

The potential is shifted by a constant amount so that it vanishes throughout the outer region.

The initial MT potential was generated from the free-atom charge density.[13] The relativistic KKR method was then used to find the wave function and energy for any point in k space. The states with energy below the Fermi energy will be occupied and a new charge density is found from

$$\rho(\vec{r}) = \sum \psi_k^\dagger(\vec{r})\psi_k(\vec{r})\,, \tag{9}$$

summed over all the occupied states. This in turn is used to generate a new potential and the process is repeated until some criterion of convergence is satisfied. In practice, after the first iteration the average of the old charge density and the new was used to generate the next potential. Before the sum is taken each wave function is normalized and the electron density is made spherically symmetric.

In the relativistic KKR method the wave function inside the MT sphere is expanded in spherical wave solutions to the Dirac equation

$$\psi_k(\vec{r}) = \sum_{\kappa,\mu} C_{\kappa\mu}\psi_\kappa^\mu(\vec{r})\,, \tag{10}$$

with

$$\psi_\kappa^\mu = \begin{pmatrix} g_\kappa(r)\chi_\kappa^\mu(\hat{r}) \\ S_\kappa S_\mu f_\kappa(r)\chi_{-\kappa}^\mu(\hat{r}) \end{pmatrix}, \tag{11}$$

where S_κ and S_μ are the sign of κ and μ, respectively. The angular dependence is given by the two component spinors $\chi_\kappa^\mu(\hat{r})$.

The electron number density is not spherically symmetric, but the spherical average is easily found:

$$\rho_k(r) = \frac{1}{4\pi}\sum_{\kappa\mu}|C_{\kappa\mu}|^2[g_\kappa^2(r)+f_\kappa^2(r)]\,. \tag{12}$$

Each wave function is normalized separately, using the method suggested by Ham and Segall.[14]

The self-consistent calculations were carried out for 89 points in 1/48 of the zone, corresponding to 2048 points in the full zone, and for a number of bands. The wave function was expanded in the form of Eq. (10) to include all terms through $l=3$. Self-consistency of the energy eigenvalues was obtained to 2×10^{-5} Ry. The resulting energy bands are shown in Figs. 1 and 2. The bands are typical of free-electron behavior and are similar to those given by Anderson and Gold,[1] van Dyke,[4] and Loucks.[6] The bands calculated by Neto and Ferreira[8] show considerably more structure.

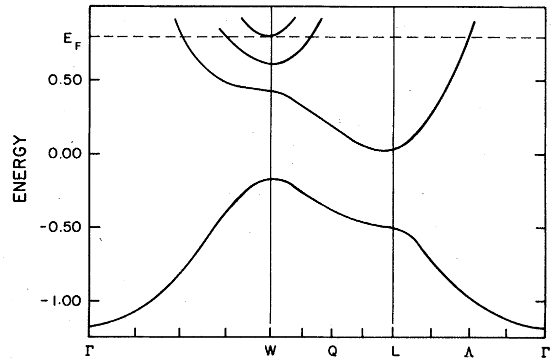

FIG. 1. Self-consistent muffin-tin energy bands for lead. The energy is given in units of $(2\pi/a)^2$.

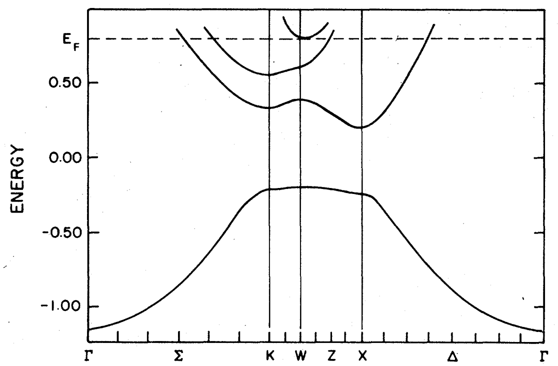

FIG. 2. Self-consistent muffin-tin energy bands for lead. The energy is given in units of $(2\pi/a)^2$.

Some results of the different calculations are compared in Table I. The calculated Fermi surface is compared with the experimental surface in the next section.

TABLE I. Comparison of band calculations for lead. The energies are in rydbergs and have been shifted to agree at point W in the first zone.

Point	Calculation	Zone 1	Zone 2	Zone 3	Zone 4
Γ	SCMT[a]	−0.4519			
	AOS[b]	−0.4241			
	NF[c]	−0.4164			
	Loucks[d]	−0.34			
	SJS[e]	−0.40			
W	SCMT	0.0000	0.2861	0.3685	0.4413
	AOS	0.0000			
	NF	0.0000	0.2171	0.5394	0.5621
	Loucks	0.00	0.28	0.42	0.50
	SJS	0.00	0.31	0.39	
X	SCMT	−0.0198	0.1779	0.5717	
	AOS	−0.0181			
	NF	−0.0139	0.2804	0.4818	
	Loucks	−0.01	0.22	0.59	
	SJS	−0.02	0.21	0.59	
K	SCMT	−0.0203	0.2444	0.3337	
	AOS	−0.0217			
	NF	−0.0139	0.1761	0.2661	
	Loucks	−0.01	0.37	0.28	
	SJS	−0.01	0.27	0.38	
L	SCMT	−0.1388	0.0916		
	AOS	−0.1391			
	NF	−0.1239	0.0261		
	Loucks	−0.13	0.15		
	SJS	−0.13	0.14		

[a] Present calculation (self-consistent muffin tin).

[b] Four-parameter pseudopotential model (Ref. 2).

[c] Relativistic KKR method (Ref. 8).

[d] Relativistic APW method (Ref. 6).

[e] Relativistic KKR method (Ref. 7).

NON-MUFFIN-TIN CALCULATIONS

Non-muffin-tin calculations with the KKR method have been done in the past using the discrete-variational method.[15,16] In this method, the crystal potential is evaluated numerically at any point by a direct superposition of overlapping atomic potentials and the necessary integrations are performed numerically by sampling a large number of points. The method used here derives the potential from the actual crystal charge density as determined by the electron wave functions found in the self-consistent MT calculation described in the preceding section. This charge density and the resulting crystal potential are written in terms of lattice harmonics and the non-MT part of the potential is used in a perturbation calculation to correct the energy bands and the Fermi surface found in the MT calculation.

In order to carry out the non-MT calculation an expression is needed for the wave function outside the MT spheres. To obtain this expression we start with the standard relation in terms of the Green's function $G(\vec{r}, \vec{r}\,')$:

$$\psi(\vec{r}) = \int_T G(\vec{r}, \vec{r}\,')V(\vec{r}\,')\psi(\vec{r}\,')\,d\vec{r}\,' . \tag{13}$$

This is transformed to a surface integral over the inscribed sphere

$$\psi(\vec{r}) = \frac{\hbar}{i} \int_{r'=r_i} G(\vec{r}, \vec{r}\,')c\vec{\alpha}\cdot\vec{n}\,'\psi(\vec{r}\,')\,ds' . \tag{14}$$

Equations (10) and (11) with $r = r_i$ can be used for $\psi(r)$ on the surface. The Green's function $G(\vec{r}, \vec{r}\,')$ can be expanded in the standard manner,[10] taking care that the expansion is appropriate to the region $r > r_i$. This leads to the following expression for the wave function in the outer region:

$$\begin{aligned}\psi(r) = -\hbar r_i^2 \sum_{\kappa\mu,\kappa'\mu'} C_{\kappa'\mu'}\,&[c f_{\kappa'}(r_i) j_{l'}(Kr_i) \\ &- S_{\kappa'}(\hbar K/2m) g_{\kappa'}(r_i) j_{\bar{l}'}(Kr_i)] \\ \times \Bigg[F_{\kappa\mu,\kappa'\mu'} &\begin{pmatrix} j_l(Kr)\chi^{\mu}_{\kappa}(\vec{r}) \\ S_{\mu}(\hbar K/2mc) j_{\bar{l}}(Kr)\chi^{\mu}_{-\kappa}(\vec{r}) \end{pmatrix} \\ + \delta_{\kappa\kappa'}\delta_{\mu\mu'} 2mK &\begin{pmatrix} n_l(Kr)\chi^{\mu}_{\kappa}(\vec{r}) \\ S_{\mu}(\hbar K/2mc) n_{\bar{l}}(Kr)\chi^{\mu}_{-\kappa}(\vec{r}) \end{pmatrix} \Bigg] .\end{aligned} \tag{15}$$

Here the $F_{\kappa\mu,\kappa'\mu'}$ are the usual structure constants [see, for example, Eq. (A13) of Ref. 9].

Nothing has been said about how the coefficients $C_{\kappa\mu}$ in Eq. (15) are to be found, only that an expansion of the form of Eqs. (10) and (11) is made for the wave function on the MT sphere. One way of determining these coefficients is by the variational method. An alternative method was used by Neto and Ferreira,[8] which does not use the variational approach. All that needs to be done is to require the wave function to be continuous at $r=r_i$. Equation (15) is used for the wave function for $r>r_i$ and Eqs. (10) and (11) for $r<r_i$. We evaluate both expressions at $r=r_i$ and set the upper components equal to each other to obtain

$$C_{\kappa\mu}g_\kappa = -\hbar r_i^2 \sum_{\kappa'\mu'} C_{\kappa'\mu'}\left(cf_{\kappa'}j_{l'} - S_{\kappa'}\frac{\hbar K}{2m}g_{\kappa'}j_{\bar{l}'}\right)(F_{\kappa\mu,\kappa'\mu'}j_l + \delta_{\kappa\kappa'}\delta_{\mu\mu'}2mKn_l)\,. \tag{16}$$

We equate the lower components to obtain

$$C_{\kappa\mu}S_\kappa S_\mu f_\kappa = -\hbar r_i^2 \sum_{\kappa'\mu'} C_{\kappa'\mu'}\left(cf_{\kappa'}j_{l'} - S_{\kappa'}\frac{\hbar K}{2m}g_{\kappa'}j_{\bar{l}'}\right)\left(F_{\kappa\mu,\kappa'\mu'}S_\mu\frac{hK}{2mc}j_{\bar{l}} + \delta_{\kappa\kappa'}\delta_{\mu\mu'}2mKS_\mu\frac{hK}{2mc}n_{\bar{l}}\right)\,. \tag{17}$$

Multiplying the first of these by f_κ and the second by $S_\kappa S_\mu g_\kappa$ and subtracting gives, after multiplying through by c,

$$\sum_{\kappa'\mu'} C_{\kappa'\mu'}\left(cf_{\kappa'}j_{l'} - S_{\kappa'}\frac{\hbar K}{2m}g_{\kappa'}j_{\bar{l}'}\right)\left[F_{\kappa\mu,\kappa'\mu'}\left(cf_\kappa j_l - S_\kappa\frac{\hbar K}{2m}j_{\bar{l}}\right) + \delta_{\kappa\kappa'}\delta_{\mu\mu'}2mK\left(cf_\kappa n_l - S_\kappa\frac{\hbar K}{2m}g_\kappa n_{\bar{l}}\right)\right] = 0\,. \tag{18}$$

This leads to exactly the same secular equation [see Eq. (2.32) of Ref. 9] that is obtained by requiring the wave function in the inner region to satisfy the KKR variational equation. Thus, the same energy E and coefficients $C_{\kappa\mu}$ should be used to construct the wave function inside and outside the MT spheres so that the wave function will be continuous and will be the best solution, in a variational sense, to the integral equation (13).

The construction of the nonspherical crystal charge density and the resulting non-MT potential is described in the Appendix. The electrostatic part of the potential is formed using the final self-consistent MT wave functions and is written in the form of an expansion in Kubic harmonics[17]

$$\phi(\vec{r}) = \sum_l \phi_l(r)K_l(\hat{r})\,. \tag{19}$$

This potential is defined throughout the entire cell. Since the MT wave functions were expanded to include all terms through $l=3$, this potential will include terms through $l=6$. This results in three terms in the expansion (19). No attempt was made to expand the exchange potential in this form, but the actual value at each radius in the outer region was calculated, instead of just the average value which is used in the MT potential.

The difference between this potential and the final self-consistent MT potential was used to perform a perturbation calculation for each state. The energy shift is given by

$$\Delta E = \int_\tau d\vec{r}\,\psi_k^\dagger(\vec{r})[V(\vec{r}) - V^{\mathrm{MT}}(r)]\psi_k(\vec{r})\,. \tag{20}$$

Expanding the functions in Kubic harmonics, we obtain for this energy shift

$$\Delta E = \sum_{l,l'} \int_0^{r_m} P_l(r)[V_{l'}(r) - \delta_{l',0}V^{\mathrm{MT}}(r)]4\pi r^2\,dr \times \int d\omega\,K_l(\hat{r})K_{l'}(\hat{r})\,, \tag{21}$$

where $V_0(r)$ includes the k-dependent exchange part of the potential. The angular integration is discussed in the Appendix. The $P_l(r)$ arises from an expansion of the charge density for a single state $\psi_k(\vec{r})$, normalized to a single cell. This single particle density need not have the full crystal symmetry, so that it may include Kubic harmonics of type other than α. However, only those of type α make a contribution to Eq. (21).

Some representative non-MT energy shifts as calculated with Eq. (21) are given in Table II, which shows also the individual contributions to the total energy shift arising from the different l values in the sum. Table III gives for a number of states the non-MT energy shifts together with the fraction of the total charge for the state that lies outside the MT sphere.

It can be seen from Table III that there is a good correlation between the energy shift and the fraction of the total charge for the state that lies outside the MT sphere. This is not surprising, since the more charge the state has in the outer region the greater is the perturbation. However, it points out a defect that is inherent in the MT potential. The perturbing potential is the difference between the actual potential and the MT potential, which

TABLE II. Some representative non-muffin-tin energy shifts. The individual contributions from the different l values in the charge density of the state are shown. Energy values are in units of $(2\pi/a)^2$. The points a, e, and m refer to points on the Fermi surface. The wave vector k is given in units of $\pi/4a$.

State		$(\Delta E)_l$			
k	Zone	$l=0$	$l=4$	$l=6$	Total
000	1	0.063 20	0.000 00	0.000 00	0.063 20
440	1	0.042 54	−0.000 44	−0.000 09	0.042 01
480	1	0.013 62	−0.000 01	−0.000 45	0.013 16
480	2	0.042 84	−0.001 33	−0.000 07	0.041 43
480	3	0.049 33	−0.001 86	−0.000 07	0.047 40
480	4	0.056 36	−0.003 30	0.000 10	0.059 77
a	2	0.022 70	0.000 40	−0.000 01	0.022 31
e	3	0.048 97	0.000 89	−0.000 34	0.049 53
m	3	0.045 50	−0.001 48	0.000 16	0.044 18

has been averaged in the outer region and is the same for all states. A more satisfactory method to obtain the MT average would be to weight the outer region according to the fraction of the charge for that state that lies in the outer region. This could be done most easily by choosing the zero-point MT energy shift to be different for different states and to depend upon the fraction of the state that lies outside the MT sphere. Simply put, a reasonable approximation to the effect of the non-MT potential can be obtained by neglecting all the terms in Eq. (21) except the term for $l=0$ and by taking the perturbing potential for this term to be independent of r. This procedure could be easily incorporated into a standard MT calculation.

Some calculated Fermi surface diameters for both the MT and non-MT calculations are given in Table IV. This table compares the Fermi-surface diameters found here with those calculated using the model of Van Dyke[4] which is based on a parametrized fit to the measured de Haas–van Alphen data and which reproduces the data well. The table shows an improved agreement with the experimental results for the non-MT Fermi surface as compared with the MT results.

TABLE III. Some representative non-muffin-tin energy shifts and the fraction of the state outside the muffin-tin sphere. The value of the energy shift is given in units of $(2\pi/a)^2$, with the fraction of the state outside the muffin-tin sphere following in parentheses. The wave vector k is given in units of $\pi/4a$.

State		ΔE	
k	Zone 1	Zone 2	Zone 3
000	0.0632 (0.1633)		
220	0.0595 (0.1573)		
440	0.0420 (0.1247)	0.0378 (0.1996)	
660	0.0148 (0.0516)	0.0449 (0.2043)	0.0539 (0.2723)
480	0.0132 (0.0418)	0.0414 (0.1899)	0.0474 (0.2192)
280	0.0134 (0.0544)	0.0465 (0.2054)	
080	0.0134 (0.0649)	0.0483 (0.2094)	
060	0.0383 (0.1250)	0.0297 (0.1429)	
040	0.0535 (0.1502)		
020	0.0610 (0.1606)		
000	0.0632 (0.1633)		

TABLE IV. Some calculated Fermi surface diameters for lead. Values are given in units of $2\pi/a$ and the notation is that of Ref. 1.

Diam	Van Dyke[a]	SCMT[b]	non-MT[c]
aa	1.301	1.349	1.334
cc	1.145	1.161	1.154
ee	0.4591	0.4262	0.4370
hh	0.6032	0.6119	0.6234
mm	0.8330	0.8443	0.8341
nn	0.4724	0.4514	0.4514

[a] Pseudopotential model (Ref. 4).

[b] Present self-consistent muffin-tin calculation.

[c] Present non-muffin-tin calculation.

Another approach to including a non-MT potential in the KKR method is to include the non-MT effects directly in the KKR matrix elements, instead of including them only as a perturbation. We are currently developing such an approach. If the potential is written as a sum of MT and non-MT parts, the KKR matrix elements can be separated in the same way:

$$\Lambda_{k,k'} = \Lambda^{\mathrm{MT}}_{k,k'} + \Lambda^{\text{non-MT}}_{k,k'} \, .$$

The MT part of the matrix element is already known and the non-MT part can be found by using the method for volume integrals developed in the Appendix. This calculation is made easier by the results shown in Table II. These results show that the effect of the nonspherical ($l=4, 6$) part of the potential is much smaller than the effect of the nonflat but spherically symmetric ($l=0$) potential in the interstitial region. This is important since if only the $l=0$ term of the potential is significant there will be no coupling between radial functions of different basis states, which is not the case if higher l values are significant.

APPENDIX

In this appendix we discuss the construction of the potential used in the non-MT calculations.

The electron number density $\rho(\vec{r})$ is given by

$$\rho(\vec{r}) = \sum \psi_k^\dagger(\vec{r})\psi_k(\vec{r}) \qquad \text{(A1)}$$

summed over all the occupied states $\vec{k}$. This will have the symmetry of the lattice point group and can be expanded in Kubic harmonics $K_n(\hat{r})$:

$$\rho(\vec{r}) = \sum_n p_n(r) K_n(\hat{r}). \tag{A2}$$

For a cubic crystal, the only harmonics that survive the summation are those of type α. The fixed atomic core density is included in the first term of this expansion.

The electrostatic potential energy is

$$\phi(r) = -Ze^2 \sum_i \frac{1}{|\vec{r} - \vec{R}_i|} + e^2 \sum_i \int_\tau \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}' - \vec{R}_i|} d\vec{r}' . \tag{A3}$$

The integration over τ means intergration over the cell centered at R_i. We can write this as an expansion in Kubic harmonics of the form

$$\phi(\vec{r}) = \sum_n \phi_n(r) K_n(\hat{r}) . \tag{A4}$$

Again, the only harmonics that occur in this sum are those of types α. This expansion can be made with the help of the identity

$$\frac{1}{|\vec{r} - \vec{r}'|} = \sum_l \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} K_l(\hat{r}) K_l(\hat{r}') . \tag{A5}$$

We consider in detail the first term ($R_i = 0$) in the electronic contribution to the potential energy. Using the expansion (A5) this term is written

$$e^2 \int dr' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} = e^2 \int_0^r r'^2 dr' \sum_{l,l'} \frac{4\pi}{2l+1} P_{l'}(r') \frac{r'^l}{r^l + 1} \times \int d\omega' K_{l'}(\hat{r}') K_l(\hat{r}) K_l(\hat{r}') + e^2 \int_r^{r_m} r'^2 dr' \sum_{l,l'} \frac{4\pi}{2l+1} P_{l'}(r') \frac{r^l}{r'^{(l+1)}} \int d\omega' K_{l'}(\hat{r}') K_l(\hat{r}) K_l(\hat{r}') . \tag{A6}$$

Here r_m is the maximum value of r in the cell ($r_m = \frac{1}{2}a$ for a face-centered-cubic lattice). In principle, the expansion (A5) includes Kubic harmonics of all types; however, only those of type α give any contribution to Eq. (A6). The angular integration on the right of this expression must be done carefully. For r less than the radius of the inscribed sphere the integration will be over all angles and the orthogonality of the Kubic harmonics can be used. However, in the outer regions of the cell not all angles are included. Nevertheless, the integrals can be evaluated at any radius, numerically if necessary. For now, we define, for r inside the cell,

$$\Delta_{ll'}(r) = \int d\omega K_l(\hat{r}) K_{l'}(\hat{r}) . \tag{A7}$$

These functions are evaluated later for a face-centered-cubic lattice. Clearly, however,

$$\Delta_{ll'}(r) = \delta_{ll'} \quad \text{for } r \leqslant r_i .$$

We define the functions

$$M_l(r) = \int_0^r r'^l 4\pi r'^2 \sum_{l'} \Delta_{ll'}(r') P_{l'}(r') \, dr' \tag{A8}$$

and

$$N_l(r) = \int_r^{r_m} \frac{4\pi r'^2}{r'^{(l+1)}} \sum_{l'} \Delta_{ll'}(r') P_{l'}(r') \, dr' . \tag{A9}$$

We may then write Eq. (A6) in the form

$$e^2 \int dr' \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} = e^2 \sum_l \frac{1}{2l+1} \left(\frac{1}{r^{l+1}} M_l(r) + r^l N_l(r) \right) K_l(\hat{r}) , \tag{A10}$$

which is just a multipole expansion in terms of Kubic harmonics. The other terms in the electronic contribution to the potential are evaluated in a similar manner, giving

$$\phi^{(e)}(\vec{r}) = e^2 \sum_l \frac{1}{2l+1} \left(\frac{1}{r^{l+1}} M_l(r) + r^l N_l(r) \right) K_l(\hat{r}) + e^2 \sum_{R_i \neq 0 \quad l} \frac{1}{2l+1} \times \left(\frac{1}{|\vec{r} - \vec{R}_i|^{l+1}} M_l(|\vec{r} - \vec{R}_i|) + |\vec{r} - \vec{R}_i|^l N_l(|\vec{r} - \vec{R}_i|) \right) K_l(\vec{r} - \vec{R}_i) . \tag{A11}$$

Since there are Z electrons in a cell

$$M_0^{(e)}(r) = Z \quad \text{for } r \geqslant r_m .$$

This means that outisde the circumscribed sphere the contribution of the nucleus is exactly canceled and only the higher multipole moments are left. We can incorporate the nuclear contribution to the potential energy in the integral M_0:

$$M_0(r) = M_0^{(e)}(r) - Z\ .$$

Then, for $r \geqslant r_m$,

$$M_0(r) = 0\ , \quad N_l(r) = 0 \quad (r \geqslant r_m)\ . \tag{A12}$$

The electrostatic potential energy can now be put into the desired form of Eq. (A4), with

$$\phi_l(r) = \frac{e^2}{2l+1}\left(\frac{1}{r^{l+1}} M_l(r) + r^l N_l(r)\right)$$

$$+ e^2 \sum_{l'} \sum_{R_i \neq 0} \frac{1}{2l'+1} \int d\omega \left(\frac{1}{|\vec{r} - \vec{R}_i|^{l'+1}} M_{l'}(|\vec{r} - \vec{R}_i|) + |\vec{r} - \vec{R}_i|^{l'} N_{l'}(|\vec{r} - \vec{R}_i|)\right) K_{l'}(\vec{r} - \vec{R}_i) K_l(\hat{r})\ . \tag{A13}$$

The second part of this is difficult to evaluate exactly. However, it can be approximated as follows: In view of the relations (A12), if $l' = 0$ the sum over R_i will contain only a single term that represents the contribution from the nearest neighbor. For $l' \neq 0$, other than for this nearest neighbor, only the terms with $M_l(|r - R_i|)$ contribute, and these contain factors of $|\vec{r} - \vec{R}_i|^{-(l'+1)}$. Since the lowest nonzero values of l' are $l' = 4$ and $l' = 6$, these terms will decrease rapidly. Thus we replace the sum over $R_i \neq 0$ by the single term that gives the contribution from the nearest neighbor only. A simple method can be used to evaluate this contribution. On the cell boundary, the direct term and the overlap term are exactly equal. Also, on the boundary $K_l(\hat{r}) = K_l(\vec{r} - \vec{R}_i)$. Thus, on the cell boundary

$$\phi_l(r) = \frac{2e^2}{2l+1}\left(\frac{1}{r^{l+1}} M_l(r) + r^l N_l(r)\right)\ . \tag{A14}$$

This expression is exact (assuming nearest-neighbor contribution only) on the cell boundary and can be used for all points in the cell with $r > r_i$.

For $r < r_i$ a similar method can be used, except that the overlap is evaluated for points along the line parallel to R_i. Again, since this is a symmetry direction for Kubic harmonics of type α,

TABLE V. Angular integrals of Kubic harmonics in the outer region of the cell for a face-centered-cubic crystal. The value of r is given in units of the lattice constant a. The radius for $n = 1$ is the radius of the inscribed sphere and for $n = 21$ corresponds to the maximum value in the cell.

				$\Delta_{ll'}(r)$			
n	r_n	(1, 1)	(1, 2)	(1, 3)	(2, 2)	(2, 3)	(3, 3)
1	0.353 553	1.000 000	0.000 000	0.000 000	1.000 000	0.000 000	1.000 000
2	0.360 876	0.878 257	0.062 875	0.201 984	0.965 141	−0.103 133	0.656 528
3	0.368 198	0.761 358	0.111 099	0.313 682	0.931 759	−0.138 268	0.536 075
4	0.375 520	0.649 016	0.147 233	0.360 257	0.889 843	−0.129 552	0.494 981
5	0.382 843	0.540 972	0.173 397	0.360 739	0.834 590	−0.094 054	0.466 008
6	0.390 165	0.436 984	0.191 351	0.329 475	0.764 465	−0.043 715	0.422 429
7	0.397 487	0.336 827	0.202 558	0.277 240	0.679 895	0.013 238	0.357 758
8	0.404 810	0.240 293	0.208 236	0.212 070	0.582 419	0.071 257	0.274 619
9	0.412 132	0.158 480	0.203 162	0.147 667	0.478 722	0.121 297	0.185 450
10	0.419 454	0.110 250	0.179 741	0.104 731	0.386 788	0.143 625	0.119 599
11	0.426 776	0.078 374	0.149 989	0.075 974	0.308 515	0.141 819	0.079 279
12	0.434 099	0.057 268	0.117 991	0.058 531	0.244 451	0.121 964	0.061 222
13	0.441 421	0.041 926	0.088 978	0.045 540	0.189 353	0.097 198	0.050 051
14	0.448 743	0.029 912	0.064 930	0.034 050	0.141 130	0.074 115	0.038 982
15	0.456 066	0.020 571	0.045 429	0.024 273	0.100 385	0.053 672	0.028 716
16	0.463 388	0.013 423	0.030 030	0.016 275	0.067 200	0.036 429	0.019 754
17	0.470 710	0.008 098	0.018 290	0.010 017	0.041 316	0.022 629	0.012 396
18	0.478 033	0.004 306	0.009 791	0.005 402	0.022 265	0.012 285	0.006 778
19	0.485 355	0.001 813	0.004 142	0.002 296	0.009 460	0.005 244	0.002 908
20	0.492 677	0.000 431	0.000 986	0.000 548	0.002 257	0.001 255	0.000 697
21	0.500 000	0.000 000	0.000 000	0.000 000	0.000 000	0.000 000	0.000 000

$K_l(\hat{r}) = K_l(\vec{r} - \vec{R}_i)$ and the potential along this line can be written

$$\phi_l(r) = \frac{e^2}{2l+1}\left(\frac{1}{r^{l+1}} M_l(r) + r^l N_l(r) + \frac{1}{r'^{(l+1)}} M_l(r') + r'^l N_l(r')\right), \tag{A15}$$

where, for a face-centered-cubic lattice,

$$r' = a/\sqrt{2} - r \, .$$

This expression can be used for all points in the cell with $r < r_i$.

The electrostatic potential in the form of Eq. (A4) with the radial functions given by (A15) will satisfy exactly the boundary condition

$$\vec{n} \cdot \nabla \phi = 0 \tag{A16}$$

on the surface of the cell. It should be noted also that if terms arising from other than the nearest neighbor are included in the evaluation of Eq. (A13) a potential can still be formed which will satisfy this boundary condition exactly and the radial functions can still be evaluated by a method similar to that which led to Eqs. (A14) and (A15).

The functions $\Delta_{ll'}(r)$ defined by Eq. (A7) have been evaluated numerically for a face-centered-cubic lattice and the results are given in Table V. These functions can be used to perform any volume integration in the cell, as long as the function to be integrated is written in the form of a Kubic harmonic expansion. These functions are used in the calculation for the effects of the non-muffin-tin potential on the energy bands and Fermi surface.

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[1] J. R. Anderson and A. V. Gold, Phys. Rev. 139, A1459 (1965).

[2] J. R. Anderson, W. J. O'Sullivan, and J. E. Schirber, Phys. Rev. B 5, 4683 (1972).

[3] J. R. Anderson, J. Y. M. Lee, and D. R. Stone, Phys. Rev. B 11, 1308 (1975).

[4] J. P. van Dyke, Phys. Rev. B 7, 2358 (1973).

[5] T. W. Haywood, J. D. Byrd, and E. N. Mitchell, Phys. Rev. B 13, 2887 (1976).

[6] T. L. Loucks, Phys. Rev. Lett. 14, 1073 (1965).

[7] C. B. Sommers, G. Juras, and B. Segall, J. Phys (Paris) 33, C3 (1972).

[8] A. A. Neto and L. G. Ferreira, Phys. Rev. B 14, 4390 (1976).

[9] S. Takada, Prog. Theor. Phys. 36, 224 (1966).

[10] Y. Onodera and M. Okazaki, J. Phys. Soc. Jpn. 30, 1575 (1966).

[11] D. Liberman, Phys. Rev. 153, 704 (1967).

[12] R. C. Harford, J. Phys. F 2, 1055 (1972).

[13] D. Liberman, J. T. Waber, and D. T. Cromer, Phys. Rev. 137, A27 (1965).

[14] F. S. Ham and B. Segall, Phys. Rev. 124, 1786 (1961).

[15] G. S. Painter, J. S. Faulkner, and G. M. Stocks, Phys. Rev. B 9, 2448 (1974).

[16] G. S. Painter, Phys. Rev. B 7, 3520 (1973).

[17] F. C. von der Lage and H. Bethe, Phys. Rev. 71, 612 (1947).