PHYSICAL REVIEW VOLUME 119, NUMBER 1 JULY 1, 1960

Theory of Nuclear Quadrupole Interaction in Beryllium Metal*†

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(Received December 29, 1959)

The theory of the origin of the field gradient at nuclei in metals has been analyzed. The contributions of the ion cores and conduction electrons have been separately considered. In the case of beryllium metal, using orthogonalized plane wave functions, the conduction electrons are shown to enhance, by about eight percent, the field gradient due to the ion cores. Combining the results of our calculations with Knight's experimental value of 48 kc/sec for the Be^9 coupling constant e^2qQ/h, a value of $Q=0.032\times10^{-24}$ cm^2 is obtained. The dependence of the potential for the conduction electrons on the model chosen is analyzed in some detail. The various uncertainties in our field-gradient calculation and the theoretical value of the Knight shift in beryllium metal are discussed.

INTRODUCTION

THE nuclear magnetic resonance in powdered metallic beryllium has been studied by Knight.[1] He found that the resonance signal had two equally spaced satellites in addition to a central signal, characteristic[2] of a nucleus with spin $\frac{3}{2}$ and a finite nuclear quadrupole moment eQ in an axially symmetric field gradient. The frequency separation between the two satellites yields a value for e^2qQ/h of 48 kc/sec. The value of Q for the Be^9 nucleus is not known from other sources, and to determine it from Knight's quadrupole coupling data requires a calculation of q. This paper will attempt to analyze the various sources that could contribute to the field gradients at nuclei in metals with special emphasis on beryllium metal. It is hoped that these deliberations will be useful in analyzing quadrupole coupling data in other metals with more complicated band structures, e.g., the pure nuclear quadrupole resonances[3,4] of $\mathrm{Ga}^{69,71}$ and $\mathrm{In}^{113,115}$ and the low-temperature specific heat measurements[5,6] in $\mathrm{Re}^{185,187}$ and Zn^{67}. Previous attempts to estimate q in metallic beryllium were made by Kittel[1] and Cohen.[7] Kittel estimated the contribution of the Be^{++} ion cores to q and Cohen suggested a method for calculating the contribution of the conduction electrons. The relations of the works of these authors to ours will be discussed in Secs. I and III.

Section I will list the various sources of contribution to q and deal in detail with the contributions from the array of Be^{++} ion cores. Section II will deal with an orthogonalized plane-wave calculation for the wave functions of the conduction electrons. Section III will discuss the contribution of the conduction electrons to q. In Sec. IV we shall discuss the accuracy of our field-gradient calculation and also briefly consider the Knight shift in metallic beryllium.

I. FIELD-GRADIENT DUE TO ARRAY OF Be^{++} ION CORES

Beryllium metal has a hexagonal close-packed structure with the c/a ratio equal[8] to 1.5671, somewhat different from the value $c/a=1.633$ for the ideal hcp lattice. From general symmetry considerations, we therefore expect the field gradient at the Be^9 nucleus to be axially symmetric about the threefold c axis. We thus have the asymmetry parameter $\eta=0$ and have only to calculate the single parameter q defining the field gradient.

The field gradient eq at the nucleus j may be defined by the general relation

$$q_j=\sum_i{}' \frac{3z_{ij}^2-r_{ij}^2}{r_{ij}^5}\rho(\mathbf{r}_i), \tag{1}$$

where $e\rho(\mathbf{r}_i)$ represents the charge density at the point $\mathbf{r}_i$. The summation sign is considered to imply that for continuous charge distributions it is to be replaced by integration. Also, the prime over the summation denotes that the charge on the nucleus j has to be excluded from the summation. The direction z is taken along the c axis of the hexagonal lattice.

We can write the general expression for $\rho(\mathbf{r}_i)$ as

$$\rho(\mathbf{r}_i)=[Z\textstyle\sum_N \delta(\mathbf{r}_i-\mathbf{r}_N)-\rho_{\mathrm{core}}(\mathbf{r}_i)-\rho_{\mathrm{cond.}}(\mathbf{r}_i)], \tag{2}$$

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* This work was included in a thesis submitted by M. Pomerantz to the faculty of the University of California, Berkeley, in partial fulfillment of the requirements for the Ph.D. degree.

† This research was supported in part by the Office of Naval Research and in part by the U. S. Air Force Office of Scientific Research.

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[1] W. D. Knight, Phys. Rev. **92**, 539 (1953).

[2] M. H. Cohen and F. Reif, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. V, p. 338.

[3] W. D. Knight, R. R. Hewitt, and M. Pomerantz, Phys. Rev. **104**, 271 (1956) ($\mathrm{Ga}^{69,71}$ resonances in metallic gallium). See also M. Pomerantz, thesis, University of California, Berkeley, 1958 (unpublished).

[4] R. R. Hewitt and W. D. Knight, Phys. Rev. Letters **3**, 18 (1959) ($\mathrm{In}^{113,115}$ resonances in metallic indium). Also W. W. Simmons and C. P. Slichter (private communication).

[5] P. H. Keesom and C. A. Bryant, Phys. Rev. Letters **2**, 260 (1959).

[6] G. Seidel and P. H. Keesom, Phys. Rev. Letters **2**, 261 (1959).

[7] M. H. Cohen, thesis, University of California, Berkeley, 1952 (unpublished).

[8] D. R. Schwarzenberger, Phil. Mag. **4**, 1242 (1959).

where Ze is the nuclear charge, $-e\rho_{\text{core}}$ is the charge density associated with the core electrons and $-e\rho_{\text{cond.}}$ is the charge density associated with the conduction electrons. For beryllium metal, $Z=4$, the core electrons correspond to the $1s$ electrons and the conduction electrons to the $2s$ electrons which now form a conduction band. The vectors $\mathbf{r}_N$ refer to the lattice sites and the summation in N extends over all the lattice sites in the metal. If we assume the core electrons to be localized at the lattice sites in the metal and no overlap between cores on neighboring lattice sites (a very good approximation usually), then we can write

$$\rho_{\text{core}}(\mathbf{r}_i)=\sum\nolimits_N \rho_{\text{core}}(\mathbf{r}_i-\mathbf{r}_N). \tag{3}$$

For the conduction electrons we can write

$$\rho_{\text{cond.}}(\mathbf{r}_i)=(2/\Omega_k)\int|\psi(\mathbf{k},\mathbf{r}_i)|^2 d\Omega_k, \tag{4}$$

where $\psi(\mathbf{k},\mathbf{r}_i)$ is the wave function for a conduction electron with wave vector $\mathbf{k}$ and Ω_k is the volume of the occupied region of the k space below the Fermi level.

In the free-electron approximation for the conduction electrons, we have

$$\rho_{\text{cond.}}(\mathbf{r}_i)=\text{constant}.$$

From Eq. (1) we then find that the conduction electrons would not contribute to the field gradient in the free-electron approximation.[9] In reality, however, the conduction-electron wave functions depart significantly from plane waves, especially in the neighborhood of the nuclei and make a finite contribution to the field gradient. This contribution will be discussed in Secs. II and III. In the present section, we shall consider the contributions of the nuclear charges and core electrons to q. Remembering that there are two core $1s$ electrons per lattice site from Eqs. (1), (2), and (3) the value of q due to sources other than the conduction electrons, viz., due to the array of Be^{++} ions is given by

$$q_{\text{lattice}}=\sum_{i\neq 0} 2\left(\frac{3z_i^2-r_i^2}{r_i^5}\right). \tag{5}$$

A correction factor $(1+\gamma_\infty)$ has to be used in Eq. (5) to correct for the Sternheimer shielding effects arising from the deformation of the $1s$ core electrons. The value of γ_∞ for free Be^{++} ion has been calculated[10] to be -0.185 and we do not expect it to be rather different for the core electrons in the metal. A correction for the small alteration would require a knowledge of the core wave functions in the metal, and to the order of accuracy at which we aim in the present calculations it did not seem worthwhile computing this correction.

$$q_{\text{Be}^{++}}=\sum_{i\neq 0} 2\left(\frac{3z_i^2-r_i^2}{r_i^5}\right)(1+\gamma_\infty). \tag{6}$$

A number of analytic methods[11] are available for obtaining the values of various lattice sums. We have used the method of Nijboer and deWette. The adaptation of Nijboer and deWette's method to compute the series in Eq. (6) and its application to a number of other metals with *hcp* structure will be discussed in a subsequent publication. For beryllium metal the series in Eq. (5) is calculated to be $0.2953a^{-3}$ which gives[8]

$$\begin{aligned} eq_{\text{Be}^{++}}&=2.37\times10^{-13}(1+\gamma_\infty)\ \text{esu/cm}^3\\ &=1.93\times10^{13}\ \text{esu/cm}^3, \end{aligned} \tag{7}$$

using $\gamma_\infty=-0.185$. The convergence of the Nijboer and deWette procedure assures that the result is correct to within 0.1%. The method of direct summation adopted by Bersohn[12] for other crystalline lattices seems to be unsuitable for the *hcp* lattice. We computed, by the direct summation method, the contributions to the series in Eq. (5) from points within spheres of radii $R=3\sqrt{3}a$, $7\sqrt{3}a$, and $8\sqrt{3}a$ corresponding respectively to the largest spheres that can be inscribed in hexagonal lattices with bases of side $6a$, $14a$, and $16a$. These contributions[13] were found to be

$$\begin{aligned} q&=0.7200a^{-3}, & R&=3\sqrt{3}a,\\ &=0.6832a^{-3}, & R&=7\sqrt{3}a,\\ &=0.8480a^{-3}, & R&=8\sqrt{3}a. \end{aligned} \tag{8}$$

The disturbing lack of convergence originates from the fact that the value of q, as given by the series Eq. (5), is the difference of two nearly equal large terms of opposite sign which arise from the two types of lattice points in the unit cell. For $R=8\sqrt{3}$ for example, the two opposing contributions are given by

$$\begin{aligned} q_1&=-9.5840a^{-3},\\ q_2&=+10.4320a^{-3}. \end{aligned} \tag{9}$$

Comparing the series (5) with a corresponding one that was obtained by McKeehan[14] in the calculation of the

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[9] This result should not be considered to be in contradiction with N. Bloembergen and T. J. Rowland's idea [Acta Met. **1**, 731 (1953)] that in a metal with an impurity atom with a larger valency than the host metal the extra conduction electron shields the field gradient due to the extra charge on the impurity core. In this latter case, the extra conduction electron does remain partly localized around the impurity ion core and produces a field gradient at a neighboring nucleus with a sign opposite of that from the extra charge on the impurity core.

[10] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).

[11] For a list of references see p. 352 of reference 2. Also see B. R. A. Nijboer and F. W. deWette, Physica **24**, 422 (1958); L. L. Campbell, J. M. Keller, and E. Koenigsberg, Phys. Rev. **84**, 1256 (1951).

[12] R. Bersohn, J. Chem. Phys. **29**, 358 (1958).

[13] The values of the lattice sums for $R=7\sqrt{3}a$ and $8\sqrt{3}a$ were obtained using a program written for the University of Illinois high speed computer Illiac, which was kindly supplied to us by H. S. Gutowsky and R. A. Bernheim. The value quoted for $R=3\sqrt{3}a$ was obtained using a program written for the IBM 704, furnished to us kindly by R. Bersohn. R. Bersohn informs us that the value quoted for q in reference 12 was obtained with an earlier program and probably involved an error.

[14] C. Kittel (private communication); L. W. McKeehan, Phys. Rev. **43**, 924, 1022 (1933).

magnetic field in a lattice of dipoles, Kittel[1,14] found the value of $eq_{\mathrm{Be}^{++}}=3.2\times10^{13}$ esu/cm^3 for $c/a=1.58$ without the factor $(1+\gamma_\infty)$. The difference between Kittel's value and our value of 2.37×10^{13} esu could probably be explained by the sensitive dependence[15] of $q_{\mathrm{Be}^{++}}$ on c/a.

II. OPW WAVE FUNCTIONS FOR THE CONDUCTION ELECTRONS

Calculations of the conduction-electron wave functions in beryllium metal have been performed by several authors.[16] Raimes and Donovan used the Wigner-Seitz approximation, and calculated the state $k=0$. Higher values of k were considered by Herring and Hill using the orthogonalized plane-wave method,[17] and also by Jacques using several methods. In their papers, Herring, Hill, and Jacques do not give the wave functions as a function of k in an explicit way. We have, therefore, recalculated the conduction-electron wave functions taking account of the general conclusions by Heine[18] regarding the convergence of the OPW method. In this section we shall present some details of this calculation and a discussion of the potential in which the conduction electrons move, with the hope that they will be useful in future detailed band-structure calculations of beryllium metal. In addition, the text of this section will be useful in assessing the accuracy of the calculation of the contribution of the conduction electrons to q (Sec. III).

Following Herring,[17] the OPW functions for the conduction electrons are of the form

$$(\mathrm{OPW},\mathbf{k},\mathbf{r})=A_{\mathbf{k}}\{[e^{i\mathbf{k}\cdot\mathbf{r}}/(NV_0)^{\frac{1}{2}}]-\textstyle\sum_l b_{\mathbf{k},l}\psi_{\mathbf{k},l}(\mathbf{r})\},\quad(10)$$

where $A_{\mathbf{k}}$ is a normalization factor, $N=$number of atoms in the crystal, $V_0=$volume per atom$=\frac{4}{3}\pi r_0^3$ ($r_0=$radius of Wigner-Seitz sphere), $\psi_{\mathbf{k},l}(r)$ is a Bloch function composed of atomic-like states. For beryllium, the only core states are $(1s)^2$. Thus

$$\psi_{\mathbf{k},l}=\psi_{\mathbf{k},1s}=(1/\sqrt{N})\textstyle\sum_\nu e^{i\mathbf{k}\cdot\mathbf{R}_\nu}\varphi_{1s}(\mathbf{r}-\mathbf{R}_\nu),\quad(11)$$

where $\varphi_{1s}(r)$ is an $1s$ atomic-like function, R_ν represents the νth lattice position. b_k is the orthogonalization parameter which is defined by the requirement that $(\mathrm{OPW},\mathbf{k},\mathbf{r})$ be orthogonal to $\psi_{\mathbf{k},l}(r)$. This gives

$$b_{k,1s}=\frac{1}{\sqrt{V_0}}\int_0^\infty\frac{\sin kr}{kr}\varphi_{1s}(r)d\tau.\quad(12)$$

A major problem is the determination of the core functions $\varphi_{nl}(r)$. Herman,[19] in applying the OPW method to diamond and germanium lattices, used the free atom core state wave functions. He found that the true wave functions for the conduction electrons were made up of linear combinations of a large number of OPW functions of the type (10). Heine[18] has analyzed the causes of the poor convergence in Herman's calculations. There are two reasons for the admixture of a number of OPW functions in an eigenfunction for the conduction electrons. First, if we make an error in our OPW functions for small $\mathbf{r}-\mathbf{R}_\nu$, i.e., near the nuclei, to correct for this error, apparently a large admixture of a number of OPW functions of higher k shall be required. Heine pointed out that this latter source of admixture can be avoided if we use for the $\varphi_{nl}(r)$ the lower eigenstates $\varphi_{nl}'(r)$ in the same potential in which the conduction electrons move. Herring and Hill[16] adopted this procedure in their calculations also, although they did not emphasize the points discussed by Heine. Secondly, even if our OPW functions are chosen properly, an admixture may be demanded by the nonspherically symmetric nature of the potential. This can be estimated once the potential has been calculated. In the present case, as will be seen later in this section, the influence of neighboring cells which impose hexagonal symmetry on the potential proves to be small, so that a single OPW $(\mathbf{k},\mathbf{r})$ may represent a good approximation to the true wave function $\psi_{\mathbf{k}}(\mathbf{r})$.

We shall now consider the potential in which the conduction electrons move. In the Hartree-Fock approximation, the conduction-electron wave function φ_k can be considered to satisfy the following equation:

$$(-\nabla^2+V_{d\,\mathrm{core}}+V_{d\,\mathrm{cond.}}+V_{\mathrm{exch.\,core}}+V_{\mathrm{exch.\,cond.}})\varphi_k(r)=E_k\varphi_k(r).\quad(13)$$

Atomic units will be used henceforth, viz., the unit of length equal to a_0, the first Bohr radius in the hydrogen atom, the unit of energy equal to the ionization energy of the first Bohr orbit, and $e=m=1$ for the charge and mass of the electron. $V_{d\,\mathrm{core}}$ represents the direct Coulomb potential produced by the nuclei and the core electrons, $V_{d\,\mathrm{cond.}}$ the direct Coulomb potential by the other conduction electrons, $V_{\mathrm{exch.\,core}}$ the exchange potential due to the core electrons, and $V_{\mathrm{exch.\,cond.}}$ the exchange potential due to the other conduction electrons. In addition to these terms in the potential, we have to consider corrections due to the correlations among the conduction electrons. This correction, and $V_{\mathrm{exch.\,cond.}}$ do not vary[20] strongly with r and so would not affect $\varphi_k(r)$ very much, although they have substantial effects on the energy. In computing the rest of the terms in the potential we shall confine ourselves to a Wigner-Seitz sphere[21] of radius r_0 around one of the nuclei.

The potential $V_{d\,\mathrm{core}}$ due to the core at the center of

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[15] See Campbell et al., reference 11.

[16] C. Herring and A. G. Hill, Phys. Rev. **58**, 132 (1940); S. Raimes, Phil. Mag. **41**, 568 (1950); B. Donovan, Phil. Mag. **43**, 868 (1952); R. Jacques Cahiers de Physique **70**, 1 (1956); **71–72**, 31 (1956).

[17] C. Herring, Phys. Rev. **57**, 1169 (1940).

[18] V. Heine, Proc. Roy. Soc. (London) **A240**, 340 (1957); thesis, Cambridge University, 1956 (unpublished).

[19] F. Herman, Phys. Rev. **91**, 1214 (1954).

[20] D. Pines, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. I, pp. 392–393 and 400–401.

[21] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1940).

the Wigner-Seitz sphere is given by

$$V_{d\ \mathrm{core}}(r)=[2Z-4Y_0(1s,1s|r)]/r, \tag{14}$$

where in Hartree's[22] notation

$$Y_k(nl,n'l'|r)=\int_0^r P(nl|r')P(n'l'|r')\left(\frac{r'}{r}\right)^k dr' +\int_r^\infty P(nl|r')P(n'l'|r')\left(\frac{r}{r'}\right)^{k+1} dr', \tag{15}$$

and $P(nlr)=ru_{nl}(r)$ where $u_{nl}(r)$ is the radial part of $\varphi_{nl}(r)$. For φ_{1s} we took the $1s$ function of Morse, Young, and Haurwitz[23] for the neutral Be atom,

$$\varphi_{1s}(r)=u_{1s}(r)Y_0{}^0(\theta,\varphi)=(\mu^3a^3/\pi)^{\frac{1}{2}}e^{-\mu ar}, \tag{16}$$

with $\mu a=3.69$.

The potential $V_{d\ \mathrm{cond.}}$ was obtained in two ways, namely (a) by considering both the electrons in the Wigner-Seitz sphere in OPW states and finding the Coulomb potential produced by them and (b) from the Hartree-Fock potential for the $2s$ electrons in the neutral beryllium atom. In the first procedure, two OPW states corresponding to $k=0$ and $k=k_0$ [radius of Fermi sphere given by $k_0{}^3=8\sqrt{3}\pi^2(a^2c)^{-1}$ from the theory of Brillouin zones][21] were considered. The Fermi surface was approximated by a sphere wherever it was used. Thus, we took

$$V_{\mathrm{OPW},d}(r)=4\left[a_0\int\frac{|(\mathrm{OPW},0,r')|^2}{|\mathbf{r}-\mathbf{r}'|}d\tau' +a_{k0}\int\frac{|(\mathrm{OPW},k_0,r')|^2}{|\mathbf{r}-\mathbf{r}'|}d\tau'\right], \tag{17}$$

the OPW functions being defined by (10), (11), and (12) with the function $\varphi_{1s}(r)$ taken as in (16). A more explicit form for (17) is given in (A.1) in the Appendix. The choices made for the weighting factors were $a_0=\frac{3}{4}$ and $a_{k0}=\frac{1}{4}$, which are intended to represent wave functions with $\frac{7}{8}$ s character and $\frac{1}{8}$ p character. This choice is somewhat arbitrary, but it turned out that the contribution from the plane-wave part of the OPW to $V_{\mathrm{OPW},d}$ was dominant and this made the potential rather insensitive to the weighting factors. It is to be noted that in (17) we have a factor of 4; a factor of 2 comes from the use of atomic units and another from the fact that an electron inside the Wigner-Seitz sphere sees the Coulomb potential due to two conduction electrons,[24] instead of one, as in the case of the $2s$ electron of a neutral beryllium atom.

In procedure (b), $V_{d,\ \mathrm{cond.}}$ (denoted by $V_{\mathrm{HF},d}$ in this case) was taken as the weighted mean of twice the potentials seen by a $2s$ electron in the $1s^22s^2$ configuration and a $2p_z$ electron in the $1s^22p_z{}^2$ configuration of the neutral beryllium atom. The weighting factors were taken as $\frac{7}{8}$ for the $1s^22s^2$ and $\frac{1}{8}$ for the $1s^22p_z{}^2$ configurations to agree with the corresponding assumption made for $V_{\mathrm{OPW},d}$. Thus,

$$V_{\mathrm{HF},d}=4\left\{\frac{7}{8}\left[\frac{Y_0(2s,2s|r)}{r}\right] +\frac{1}{8}\left[\frac{Y_0(2p,2p|r)+(4/25)Y_2(2p,2p|r)}{r}\right]\right\}. \tag{18}$$

The factor of 4 in (18) is used for the same reason as in the OPW approximation.

In calculating $V_{\mathrm{exch.\ core}}$, three alternative procedures were compared.

(a) The OPW approximation: In this approximation, we took

$$V_{\mathrm{OPW},x}(r)=-2\left\{a_0\left[\int\frac{\varphi_{1s}{}^*(r')(\mathrm{OPW},0,r')d\tau'}{|\mathbf{r}-\mathbf{r}'|}\right] \times\frac{\varphi_{1s}(r)}{(\mathrm{OPW},0,r)}+a_{k0}\left\langle\left[\int\frac{\varphi_{1s}{}^*(r')(\mathrm{OPW},\mathbf{k}_0,r')}{|\mathbf{r}-\mathbf{r}'|}d\tau'\right] \times\frac{\varphi_{1s}(r)}{(\mathrm{OPW},\mathbf{k}_0,r)}\right\rangle_{\mathbf{k}_0}\right\}, \tag{19}$$

where $\langle\ \ \rangle_{\mathbf{k}_0}$ means an average over all directions of $\mathbf{k}_0$. In the second term on the right, the averaging over the directions of k_0 is rather complicated because (OPW,k_0,r) occurs both in the numerator and denominator. We made the simplifying approximation of averaging the numerator and denominator separately over the directions of $\mathbf{k}_0$. a_0 and a_{k0} were taken as $\frac{3}{4}$ and $\frac{1}{4}$, respectively. The detailed expression for $V_{\mathrm{OPW},x}$ is given in Appendix (A.2a).

(b) The Hartree-Fock approximation: In this approximation a weighted mean was taken of the exchange potential seen by a $2s$ electron in the $1s^22s^2$ configuration and a $2p_z$ electron in the $1s^22p_z{}^2$ configuration.

$$V_{\mathrm{HF},x}(r)=\frac{7}{8}\left[\frac{2Y_0(1s,2s|r)}{r}\frac{P(1s|r)}{P(2s|r)}\right] +\frac{1}{8}\left[\frac{2}{3}\frac{Y_1(2p,1s|r)}{r}\frac{P(1s|r)}{P(2p|r)}\right]. \tag{20}$$

The weighting factors are the same as in calculating $V_{\mathrm{HF},d}$.

(c) Slater free-electron approximation: According to Slater's free-electron approximation,[25] the exchange

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[22] D. R. Hartree, *Calculation of Atomic Structures* (John Wiley & Sons, New York, 1957).

[23] P. M. Morse, L. A. Young, and E. S. Haurwitz, Phys. Rev. 48, 948 (1935).

[24] Each conduction electron in the metal sees the Coulomb potential due to $(2N-1)$ conduction electrons, corresponding to $(2N-1)/N\cong 2$ electrons per Wigner-Seitz cell.

[25] J. R. Reitz, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1.

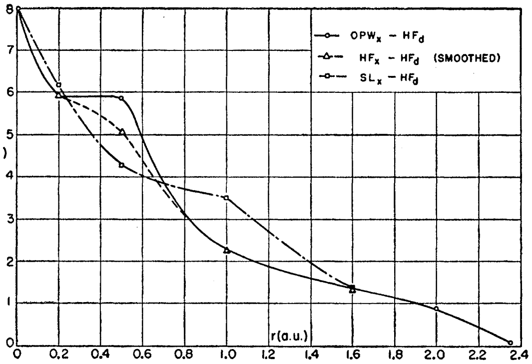

FIG. 1. $2Z(r)=rV(r)$ vs r for three methods of computing the conduction-electron potential in a Wigner-Seitz cell.

potential at any point is given by

$$-6[(3/8\pi)\sum_i|\psi_i(r)|^2]^{\frac{1}{3}}. \tag{21}$$

Since we are interested in $V_{\text{exch. core}}$ we have to subtract from (21) the contribution of the exchange among the conduction electrons themselves. The detailed expression for $V_{\text{Sl},x}$ after making this subtraction is given in the Appendix (A.2b).

We thus have a choice of six potentials obtained by combining the two choices of $V_{d\,\text{cond.}}$ with the three choices of $V_{\text{exch. core}}$. The sum of $V_{d\,\text{core}}+V_{d\,\text{cond.}}+V_{\text{exch. core}}$ is written as $2Z(r)/r$, and plots of $2Z(r)$ are given in Figs. 1 and 2 for the six possible choices of the potential. It is seen that the $Z(r)$ curves obtained from the four potentials which do not use Slater free exchange approximation show irregularities and divergences between $0.5a_0$ and $0.6a_0$. This divergence is spurious and arises from the fact that the node of the approximate (OPW,k,r) or $P_{2s}(r)$ in the denominator of the expressions for the exchange potential [Eqs. (19) and (20)] does not fall exactly at the node of the integrals in the numerator. Apart from this, it is seen that the two $Z(r)$ curves obtained from combinations of HF$_x$ with OPW$_d$ and of OPW$_x$ with OPW$_d$ agree quite well over most of the range of r. The former was chosen for the final calculation for the following reasons: $V_{\text{OPW},d}$ gives a better measure of the direct potential $V_{d\,\text{cond.}}$ than $V_{\text{HF},d}$ since the OPW functions more adequately describe the behavior of conduction electrons than atomic $2s$ or $2p_z$ functions. Secondly, of the three choices for $V_{\text{exch. core}}$, the Slater approximation is the least justified because the core electrons are strongly localized. The expression $V_{\text{OPW},x}(r)$ suffers from the averaging approximation described before. The expression $V_{\text{HF},x}(r)$ is expected to represent the exchange between the core and conduction electrons quite well, because near the nucleus, where the main overlap between the conduction electrons and core electrons occurs, the use of atomic $2s$ functions for the former is not a bad approximation. The smoothed $Z(r)$ employed in our calculations is shown in Fig. 3.

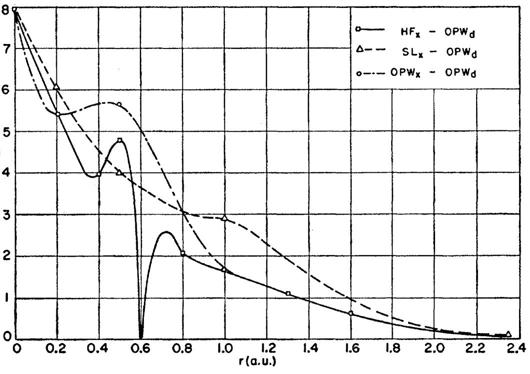

FIG. 2. $2Z(r)=rV(r)$ vs r for three methods of computing the conduction-electron potential in a Wigner-Seitz cell.

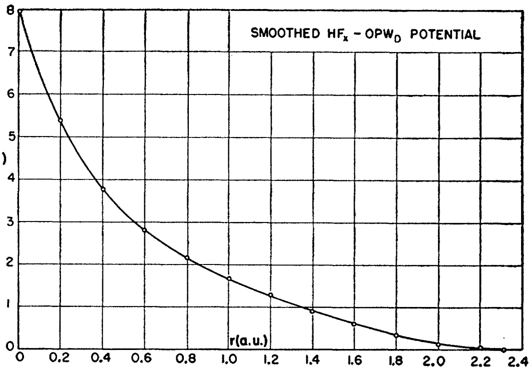

FIG. 3. $2Z(r)$ vs r used in the present calculation.

Using the potential depicted in Fig. 3, a normalized wave function $\varphi_{1s}'(r)$ was calculated by the usual numerical integration procedure.[22] The eigenvalue corresponding to this function was found to be -4.83 rydbergs which is to be compared with the value -4.55 rydbergs found by Herring and Hill.[16] Our lower eigenvalue probably arises out of the use of a better potential for the conduction electrons. In Fig. 4 $P_{1s}(r)=(4\pi)^{\frac{1}{2}}r\varphi_{1s}'$ is plotted against r together with the $P_{1s}(r)$ functions in Be^{++} as calculated by Hartree.[26] The $P_{1s}(r)$ function in neutral beryllium is practically identical to the function in Be^{++}. It can be seen from Fig. 3 that the potential in which the conduction electrons move is less binding than the potential for the core electrons in Be atoms, which results in a spreading of the $1s$ function and a (numerical) reduction of the energy eigenvalue. Because, as seen from Eq. (12), further integrations involving $P_{1s}(r)$ are necessary, it was attempted to fit the function $P_{1s}(r)/r$ by two exponentials. This did not prove accurate enough, so the remaining integrations were performed numerically. Using the curve for $P_{1s}(r)$ in Fig. 4 and Eq. (12) in the form

$$b_k=\frac{1}{|k|}\left(\frac{3}{r_0{}^3}\right)^{\frac{1}{2}}\int_0^\infty P(r)\sin|k|r\,dr, \tag{12'}$$

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[26] D. R. Hartree and W. Hartree, Proc. Roy. Soc. (London) **A149**, 210 (1935).

values of b_k within the Fermi sphere were calculated. These are plotted against k in Fig. 5. Using this plot of b_k and Eq. (10) in the form

$$(\text{OPW},k,r)=\frac{A_k}{N^{\frac{1}{2}}}\left[\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{V_0^{\frac{1}{2}}}-\frac{b_k}{(4\pi)^{\frac{1}{2}}}\frac{P_{1s}(r)}{r}\right], \quad (10')$$

we can obtain (OPW,k,r) for all conduction electrons within the Fermi sphere.

III. CONTRIBUTIONS OF CONDUCTION ELECTRONS TO q

If we assume the conduction electrons to be adequately represented by single OPW functions, then we can use (10′) and (4) to compute the charge density as a function of r. Using a spherical Fermi surface of radius k_0, we find that $\rho_{\text{cond.}}(\mathbf{r})$ comes out as a function of r alone. In Fig. 6 $\rho_{\text{cond.}}(r)$ is plotted against r. The horizontal lines ρ_0, ρ_i, and ρ_a indicate the following densities: ρ_0 $(=-0.04)$ stands for the almost constant density in the outer regions of the sphere ($r\geqq 1.6a_0$). The volume between $r=1.6a_0$ and $2.35a_0$ is about 70% of the volume of the Wigner-Seitz sphere. ρ_i represents the average density in the inner regions of the sphere ($r<1.6a_0$). $\rho_a=2/V$ represents the average density in the unit cell if the conduction electrons were distributed uniformly (free-electron approximation). The effect of the atomic-like oscillations in the conduction-electron wave functions near the nuclei is thus seen to result in a diminished average density ρ_i $(=-0.03)$ near the nuclei and an enhanced density in the outer regions of the unit cells. This step function in the average density of charge can be represented, as far as the contribution to q at a nucleus from conduction electrons in external cells is concerned, by a density of -0.04 throughout the entire unit cell and a fictitious hole of density $+0.01$ in the region $r=1.6a_0$ to $r=0$, so that the average charge density there is still $r=-0.04+0.01=-0.03$. The hole around each nucleus is spherically symmetric and in computing q is equivalent to a point charge of magnitude $+0.01\times(4\pi/3)(1.6)^3=+0.16$ at $r=0$. Thus, the charge density seen by a nucleus is effectively (a) a uniform electron density of -0.04 throughout the metal, (b) an average hole density of 0.01 around itself distributed within a sphere of radius $r=1.6a_0$, and (c) positive charges of $+0.16$ in addition to the ionic charges $+2$ at the other lattice sites. Using Eq. (1) it is seen that the distributions (a) and (b) make zero contribution to q while the additional charges (c) of $+0.16$ at the other lattice sites enhance the field gradient due to the ion cores, as given by (7), by 8%. We, thus, find our final calculated value of q to be given by

$$\begin{aligned} q&=1.93\times1.08\times10^{13}\text{ esu cm}^{-3}\\ &=2.08\times10^{13}\text{ esu cm}^{-3}. \end{aligned} \quad (22)$$

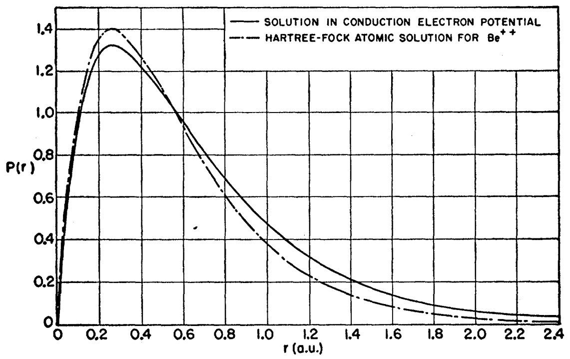

FIG. 4. The $1s$ solution in the conduction-electron potential compared to the $1s$ function in Be^{++}.

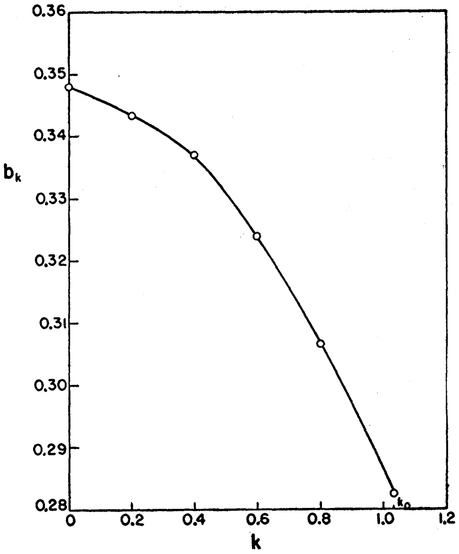

FIG. 5. The orthogonalization parameter b_k vs k.

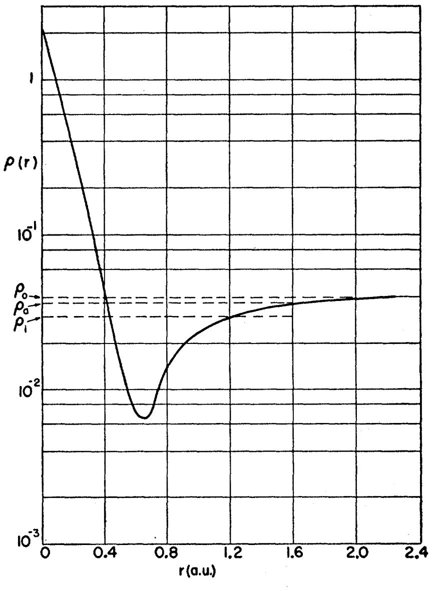

FIG. 6. Charge density in a Wigner-Seitz cell of Be metal.

Combining this with Knight's observed value for $e^2qQ/h=48$ kc/sec, we find the Be^9 quadrupole moment to be

$$Q(\mathrm{Be}^9)=0.032\times10^{-24}\ \mathrm{cm}^2. \qquad (23)$$

Since only frequency splittings are measured in Knight's experiment, it is not possible to assign a particular sign to Q by the present calculations. The magnitude of Q seems to fit on the semiempirical plot of Townes, Foley, and Low.[27] Bernheim and Gutowsky[28] have recently computed q at Be^{++} lattice sites in beryl. Combing their result with the NMR measurements of Be^9 and Al^{27} in beryl,[29] they find $Q(\mathrm{Be}^9)=0.039\times10^{-24}$ cm^2, in fair agreement with our value. Both these values agree well with the semi-empirical curve of Townes, Foley, and Low.[27] It will be possible to assess better the accuracy of these calculations when an independent measurement of the Be^9 quadrupole moment is made either by an atomic beam study of optically excited atoms[30] in the $(1s^22s2p)^3P_1$ state or by the study of high-energy electron scattering by Be^9 nuclei.[31]

The accuracy of our calculation is discussed in the next section. At this point, however, we would like to remark on a method of calculation suggested by Cohen.[7] He proposes to divide the metal into polyhedra around each of the lattice points as in the cellular approximation. Each of these polyhedra has a center of symmetry and contains two conduction electrons, and therefore it has zero over-all charge and zero dipole moment, but a finite quadrupole moment. The quadrupole moment of each polyhedron can be computed if one knows the conduction-electron wave functions. The field gradient q at a nucleus can then be obtained by integrating over the charge distribution within the polyhedron surrounding the nucleus and summing over a more convergent series than (6) for the contribution from the electronic quadrupole moment of the other polyhedra. Since both Cohen's approach and ours are artifices to take account of the departure in uniformity of the charge density of the conduction electrons, we believe that if the same conduction-electron wave functions are employed, both methods would give equivalent results.

IV. DISCUSSION

To assess the accuracy of our result it is helpful to list the various uncertainties involved in our calculation of the contribution of the conduction electrons to q.

1. The first uncertainty arises from the sensitivity of the conduction-electron potential to the model chosen, as is evident from Figs. 1 and 2. This uncertainty is still an obstacle to accurate quantum mechanical calculations of wave functions in solids, since it is extremely laborious at present to try to attain self-consistency in band-structure calculations.

2. We have neglected the effects of the correlation and exchange between the conduction electrons on their density distribution. This is again a difficult point, as discussed by Callaway[32] in a recent review. An improvement over our procedure would be to consider a shielded interaction of the type found by Bohm and Pines[20] between the conduction electrons to compute the contribution of the exchange interaction between the conduction electrons to the effective potential in which they move. It is to be noted that the main contribution of the conduction electrons to q comes from the oscillations in their density in the neighborhood of the nuclei. In the neighborhood of the nuclei, one might argue that the effect of the correlation between the conduction electrons is relatively small compared to the core potential, and so the effect on the charge density near the nuclei is small. However, the charge density at the further ends of the Wigner-Seitz cell would be affected by correlation, and, by normalization requirements, the charge density near the nuclei would also be altered.[33]

3. In computing $\varphi_{1s}'(r)$, we did not consider in the conduction-electron potential the contribution from adjacent Wigner-Seitz spheres. From Fig. 3, however, the value of $2Z(r)$ between $r=2.0a_0$ and $2.4a_0$ is found to be less than 0.1 and so the overlap of the potentials of adjacent cells has probably a not too important effect on $\varphi_{1s}'(r)$.

4. In computing the charge density due to the conduction electrons in Sec. III, we have assumed (a) that the conduction-electron wave functions are adequately represented by single OPW functions, and (b) that the Fermi surface is spherical. Assumption (a) includes assumption (b). Our belief that assumption (a) was not very erroneous was based on similar results obtained by Heine[18] in aluminum metal using his prescription for the functions φ_{nl} of Eq. (11). He found that for most of the conduction-electron states the admixture of higher OPW functions was small. We have examined the admixture of higher OPW states at a few points in k space in the first and second Brillouin zones and find such admixtures to be in general less than 5%. In particular, we find that at the point[16] Γ, for the lowest energy state with Γ_1^+ symmetry ($k=0$), the admixtures of the higher and next higher OPW states of the same

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[27] C. H. Townes, H. M. Foley, and W. Low, Phys. Rev. **76**, 1415 (1949).

[28] R. Bernheim and H. S. Gutowsky, J. Chem. Phys. (to be published).

[29] J. Hatton, B. V. Rollin, and E. F. W. Seymour, Phys. Rev. **83**, 672 (1951); also see L. C. Brown and D. Williams, J. Chem. Phys. **24**, 751 (1958); Phys. Rev. **95**, 1110 (1954).

[30] See, for example, M. L. Perl, I. I. Rabi, and B. Senitzky, Phys. Rev. **98**, 611 (1955). *Note added in proof.*—A. Lurio (private communication), from recent preliminary measurements of this type, has found a value of 0.03×10^{-24} cm^2 for the Be^9 quadrupole moment.

[31] M. K. Pal [Phys. Rev. **117**, 566 (1960)] has considered the theory for evaluating nuclear quadrupole moments from high-energy electron scattering.

[32] J. Callaway, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7.

[33] A. Mukherjee and T. P. Das, Phys. Rev. **111**, 1479 (1958).

symmetry are, respectively, 3.6% and 1.5%. In this calculation of the mixing the overlapping of adjacent cell potentials (point 3 above) was not considered. Inclusion of this overlap might increase the higher k mixing somewhat. It is evident from Eq. (1) that departures from the assumptions (a) and (b) would lead to departure from spherical symmetry of the fictititious hole around each nucleus and this would cause an additional contribution to q. Whether this contribution would enhance our calculated value of q or reduce it depends on details of the band structure.[34] It would be useful to recalculate the conduction-electron contribution to q when more detailed band-structure calculations involving evaluation of the wave functions at a larger number of points in k space than those considered by Herring and Hill are available, together with a better knowledge of the Fermi surface from experimental measurements of the anomalous skin effect[35] and the de Haas-Van Alphen effect.[36]

We should like now to make some comments on further checks on our calculation. Pressure measurement analogous to those of Kushida, Benedek, and Bloembergen[37] on powdered Cu_2O should be made to examine our observation that the ion cores are the principal contributors to q. If our analysis is correct, and c/a is constant, then the value of e^2qQ should vary inversely as the volume. If c/a changes with pressure, then the change in e^2qQ can be predicted for the ionic model following Sec. I and using the same 8% correction due to conduction electrons as in Sec. III.

An estimate of the Knight shift of the Be^9 nucleus due to the spin paramagnetism can also be made from our OPW functions using the formula of Townes, Herring, and Knight[38]

$$\Delta H/H=(8\pi/3)\chi_p M\langle|\psi_F(0)|^2\rangle_{\mathrm{av}}. \qquad (24)$$

Using the value of bk_0 from Fig. 5 for $k_0=1.0332$ at the surface of the Fermi sphere, we find $\langle|\psi_F(0)|^2\rangle_{\mathrm{av}}=1.028$. Using Feher and Kip's approximate experimental[39] value of the mass spin susceptibility χ_p of 1×10^{-7} cgs we then get

$$\Delta H/H\approx0.009\%, \qquad (25)$$

which is larger by about a factor of five than Knight's observed[40] value of $<0.002\%$. Townes, Herring, and Knight[38] find, using the functions of Herring and Hill,[16] a value of 0.4 for

$$\langle|\psi_F(0)|^2\rangle/|\psi_0(0)|^2$$

[$\psi_0(0)$ referring to the value of the wave function near the nucleus for $k=0$] while our wave functions give 0.6. The difference could be partly ascribed to our use of single OPW functions and spherical Fermi surface. However a more detailed calculation of the wave functions would not be expected to reduce the value of $\Delta H/H$ by as much as a factor of five below Eq. (25). A more precise experimental value of χ_p is desirable. A reason for the disagreement might also be found in the following two sources. One mechanism which could reduce the calculated Knight shift is the exchange polarization effect on the core $1s$ electrons by the unpaired conduction electrons analogous to that found in atoms.[41] In addition, a careful analysis should be made of the orbital contribution to the shielding effect of the $1s$ core electrons in the metal from that in the Be^{++} ion. It should be noted, however, that the calculated values of the Knight shift and spin susceptibility due to conduction electrons depend on the conduction-electron wave functions in the neighborhood of the Fermi surface alone. Hence an error in the wave function near the Fermi surface or the shape of the Fermi surface affects the Knight shift quite sensitively while the electric field gradient at the nuclei would not necessarily be much affected because it depends on all the region of k space within the Fermi sphere.

Finally, we may remark that our considerations in Sec. III indicate that the field gradient due to the conduction electrons depends on both the momentum and position dependences of the wave functions. The difference in the momentum dependence of the wave functions for normal and superconducting states as envisaged in the Bardeen, Cooper, and Schrieffer theory[42] would therefore entail a change in the field gradient at the nuclei. Evidence for such change has recently been found for gallium and indium metals by Hammond and Knight.[43]

ACKNOWLEDGMENTS

The authors are deeply indebted to Professor W. D. Knight for his continuing interest and advice during the course of this work. We are grateful also to Professor R. Bersohn for several helpful suggestions and communications. We have profited very much from a

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[34] In view of these comments, it should be remarked that our result that the conduction electrons in beryllium metal contribute little to the field gradient should not be generalized to other metals. Thus in the case of gallium metal, there is reason to believe (reference 3) from a consideration of various physical properties that there is appreciable covalent bonding among gallium atoms. This would imply an appreciable departure from spherical symmetry in the conduction-electron distribution around the gallium nuclei and consequently an important contribution to q.

[35] As an example of the investigation on shape of Fermi surface from anomalous skin effect measurements, see A. B. Pippard, Phil. Trans. Roy. Soc. (London) **A250**, 325 (1957).

[36] As an example of the use of de Haas-van Alphen effect measurements in investigating the shape of the Fermi surface, see A. V. Gold, Phil. Trans. Roy. Soc. (London) **A251**, 85 (1958).

[37] T. Kushida, G. B. Benedek, and N. Bloembergen, Phys. Rev. **104**, 1364 (1956).

[38] C. H. Townes, C. Herring, and W. D. Knight, Phys. Rev. **77**, 852 (1950).

[39] G. Feher and A. F. Kip, Phys. Rev. **98**, 337 (1955).

[40] W. D. Knight, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2.

[41] R. M. Sternheimer, Phys. Rev. **86**, 316 (1952); see also subsequent papers on this subject to J. H. Wood and G. W. Pratt, Phys. Rev. **107**, 995 (1957) and V. Heine, Phys. Rev. **107** 1002 (1957).

[42] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[43] R. H. Hammond and W. D. Knight (private communication).

number of helpful discussions with Dr. V. Heine and from the communication of unpublished results by Professor H. S. Gutowsky and Dr. R. Bernheim, and Dr. R. H. Hammond. Finally, one of the authors would like to thank Professor E. L. Hahn for the hospitality extended in his laboratory at the University of California, Berkeley.

APPENDIX

1. Direct potential due to conduction electrons using OPW *functions:*

Using Eq. (17) together with Eqs. (10) and (11) for the OPW wave functions, we get

$$\begin{aligned} V_{\mathrm{OPW},d}(r)=4a_0A_0^2\Big\{&\frac{3}{2r_0}\left(1-\frac{r^2}{3r_0^2}\right)-2b_0\left(\frac{3}{r_0^3}\right)^{\frac{1}{2}}\\ &\times\left[\frac{1}{r}\int_0^r P(r')r'dr'+\int_r^{r_0} P(r')dr'\right]\\ &+b_0^2\left[\frac{1}{r}\int_0^r P^2(r')dr'+\int_r^{r_0}\frac{P^2(r')}{r'}dr'\right]\Big\}\\ &+4a_{k_0}A_{k_0}^2\Big\{\frac{3}{2r_0}\left(1-\frac{r^2}{3r_0^2}\right)-\frac{2b_{k_0}}{k_0}\left(\frac{3}{r_0^3}\right)^{\frac{1}{2}}\\ &\times\left[\frac{1}{r}\int_0^r P(r')\sin k_0r'dr'+\int_r^{r_0}\frac{P(r')}{r'}\sin k_0r'dr'\right]\\ &+b_{k_0}^2\left[\frac{1}{r}\int_0^r P^2(r')dr'+\int_r^{r_0}\frac{P^2(r')}{r'}dr'\right]\Big\}. \end{aligned} \tag{A.1}$$

2. Contribution to the conduction-electron potential from the exchange with core electrons:

(*a*) *The* OPW *approximation:* Using Eq. (19) together with Eqs. (10) and (11) for the OPW wave functions and making the approximation mentioned in the text of averaging the numerators and denominators in Eq. (19) separately, we get

$$\begin{aligned} V_{\mathrm{OPW},x}(r)=0.75\Big\{&\left(\frac{3}{r_0^3}\right)\\ &\times\left[\frac{1}{r}\int_0^r P(r')r'dr'+\int_r^{\infty} P(r')dr'\right]\\ &-b_0\left[\frac{1}{r}\int_0^r P^2(r')dr'+\int_0^{\infty}\frac{P^2(r')}{r'}dr'\right]\Big\}\\ &\times\frac{P(r)/r}{(3/r_0^3)^{\frac{1}{2}}-b_0P(r)/r}+0.25\Big\{\frac{1}{k_0}\left(\frac{3}{r_0^3}\right)^{\frac{1}{2}}\\ &\times\left[\frac{1}{r}\int_0^r \sin k_0r'P(r')dr'+\int_r^{\infty}\frac{P(r')\sin k_0r'}{r'}dr'\right]\\ &-b_{k_0}\left[\frac{1}{r}\int_0^r P^2(r')dr'+\int_r^{\infty}\frac{P^2(r')dr'}{r'}\right]\Big\}\\ &\times\frac{P(r)/r}{(3/r_0^3)^{\frac{1}{2}}\sin k_0r/k_0r-b_{k_0}P(r)/r}. \end{aligned} \tag{A.2}$$

(*b*) *Slater free-electron approximation:* Using Eq. (21) twice, including the core electrons and excluding them, respectively, and subtracting the result of the latter from the former, we get the following expression for the exchange potential arising from exchange with the core electrons:

$$\begin{aligned} V_{\mathrm{SI},x}(r)=-6\Big\{&\frac{3}{4\pi^2}\Big[\frac{P^2(r)}{r^2}\\ &+0.75A_0^2\left(\frac{3}{4r_0^3}-b_0\left(\frac{3}{r_0^3}\right)^{\frac{1}{2}}\frac{P(r)}{2r}+b_0\frac{P^2(r)}{2r^2}\right)\\ &+0.25A_{k_0}^2\Big(\frac{3}{4r_0^3}-b_{k_0}\left(\frac{3}{r_0^3}\right)^{\frac{1}{2}}\frac{\sin k_0r}{k_0r}\frac{P(r)}{2r}\\ &+b_{k_0}^2\frac{P^2(r)}{4r^2}\Big)\Big]\Big\}^{\frac{1}{3}}+\left(\frac{9}{16\pi^2r_0^3}\right)^{\frac{1}{3}}. \end{aligned} \tag{A.3}$$