Superconductivity in Nontransition Metals. I*

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The theoretical calculation of superconducting-state parameters $\langle V_{ph}\rangle$, $\langle V_C\rangle$, and Z_0 [$\langle V_{ph}\rangle$ estimates the phonon-mediated attractive electron-electron interaction in the metal; $\langle V_C\rangle$, the Coulomb pseudopotential, measures the effectiveness of the Coulomb repulsion in inhibiting superconductivity; and Z_0, the quasiparticle mass (or energy) renormalization parameter, takes into account the many-body renormalization effects due to electron-phonon and Coulomb interactions] is undertaken for both nonsuperconductors and simple-metal (nontransition-metal) superconductors. The two questions faced are: why nonsuperconductors (alkali, alkaline-earth, and noble metals) are nonsuperconductors (this question arises from the startling prediction by Morel and Anderson that all metals should be superconductors); and whether better agreement can be achieved between theoretically estimated superconducting-state parameters and empirical parameters—better, e.g., than those of Pines and of Morel and Anderson. Our calculation is differentiated from that of Morel and Anderson first in using electron-phonon and Coulomb-interaction matrix elements between Bloch electron states, secondly in using for the electron-phonon matrix element the form suggested by Harrison for the orthogonalized-plane-wave form factor, and lastly in including the renormalization effects due to electron-phonon and Coulomb interactions. The renormalization due to Coulomb interaction is included by taking the values from the calculations by Rice. The Bloch electron states are calculated in a model in which the ionic core is replaced by a three-dimensional constant repulsive potential, and the wave function is determined in the spirit of the Wigner-Seitz approximation and first-order perturbation theory. The theoretically estimated parameters $\langle V_{ph}\rangle$, $\langle V_C\rangle$, and Z_0 are compared with the empirically estimated parameters. These are also compared with the parameters estimated by Garland. A good comparison—better than that of Morel and Anderson—is found between theoretical and empirical parameters. It is pointed out that if renormalization effects are included in the calculation by Morel and Anderson, then their apparently good comparison with empirical parameters does not remain so good. In the case of nonsuperconductors, we find that the phonon-mediated attractive interaction fails to dominate over the Coulomb repulsion, contrary to the conclusions of Morel and Anderson, and the effective interaction strength $(\langle V_{ph}\rangle-\langle V_C\rangle)/Z_0$, which is analogous to the BCS parameter N_0V, is repulsive or very slightly attractive. The nonsuperconducting status is thus restored to alkali and alkaline-earth metals.

I. INTRODUCTION

SUPERCONDUCTIVITY theory, with its present sophisticated Green's-function formalism[1,2] treating the retarded electron-phonon interaction and including the important energy renormalization effects due to many-body interactions, has entered its final stage of quantitative predictions. There are few doubts now that the basic theory treating first-order screened electron-phonon (hereafter EPI) and Coulomb interactions (hereafter CI) is essentially correct for nontransition-metal superconductors. The theoretical predictions have been verified experimentally, directly, and in close detail, thanks to the electron-tunneling technique.[3–9] The theoretical efforts were directed, since the inception of the Bardeen-Copper-Schrieffer (BCS) theory of superconductivity,[10] towards the calculation of superconducting-state parameters with a view to getting reliable estimates which might serve as a basis for establishing a criterion for the occurrence of superconductivity. The two major attempts to arrive at a semiquantitative understanding of the criterion of superconductivity based upon the microscopic theories have been those of D. Pines[11] (hereafter DP) and Morel and Anderson[12] (hereafter MA).

First, we briefly give their accounts.

Pines attempted to develop a criterion for the occurrence of superconductivity and to explain the famous Matthias regularities based on the original formulation of the BCS theory, in which the net electron-electron interaction, which is the sum of phonon-induced attractive interaction and Coulomb repulsion, is approximated by an instantaneous square-well two-body interaction (only electrons having energy in a narrow energy shell of thickness $\sim\hbar\omega_{ph}$, the maximum phonon energy, near

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the Fermi level participate in the interaction). The BCS criterion—that the phonon-induced interaction dominates over Coulomb repulsion—was used. The single parameter N_0V of BCS was calculated for individual elements using appropriate EPI and CI matrix elements, approximating the Bloch electron state $|\mathbf{k}\rangle$ by the plane-wave state $\exp(i\mathbf{k}\cdot\mathbf{r})$. Both normal and umklapp processes were included. DP stressed the role of umklapp processes in producing an attractive contribution. In fact, according to him, the normal processes alone were unable to produce an attractive interaction. It was shown by these calculations that this BCS criterion is indeed fairly satisfactory and Matthias regularities do show up, however weakly, in estimated values of N_0V, both for nontransition and transition elements. But particularly disconcerting was the fact that the estimated values of N_0V fall well below the empirical values. This was again ascribed to the underestimation of the umklapp contribution to EPI. It was argued that this is due to several reasons, one of which is the neglect of the influence of the periodic potential on the wave functions of electrons participating in the interaction.

Nevertheless, DP's work lent substantial support to the simple BCS model, and it strengthened the view that a single-parameter model for a phenomenon of such universality as superconductivity could not only work but could be justified from elementary considerations as well. Out of several predictions made, Mo, W and Sb, Se, and Te (in the high-pressure metallic phase) were indeed found to be superconducting.[13]

The two basic assumptions of DP (i.e., instantaneous phonon-induced interaction and magnification of the role of the umklapp processes) were criticized by MA. They stressed the necessity of using a realistic EPI which is not an instantaneous δ-function interaction but is retarded in space as well as time. The removal of the rather nonphysical phenomenological BCS effective interaction led to a different and more complicated energy-gap integral equation, different from BCS in many essential aspects. The essential result is that the energy-gap function satisfies a four-dimensional integral equation in space-time coordinates or, after Fourier transformation, the energy gap is found to be a function of wave vector $\mathbf{k}$ and frequency ω. The frequency or energy dependence of the energy gap is a direct consequence of the retarded nature of the interaction in time. For the time being, ignoring the less important variation of the energy-gap parameter over the Fermi surface (hereafter FS), it turned out to have a significant energy (or frequency) dependence. A realistic handling of EPI was made possible by a Green's-function formalism developed for the theory of superconductivity by Gor'kov[14] and by Éliashberg.[15] MA's work triggered considerable activity in this direction, and soon not only was the theoretical side of the Green's-function formalism nearly perfected, but also the results of the realistic model of EPI were verified experimentally in close detail.[3–9] The conclusions of MA were as interesting as the strength of their approach. The first conclusion concerned the ineffectiveness of Coulomb repulsion in inhibiting superconductivity. The CI is instantaneous—a "hard core" in time—which the electron pairs can manage to avoid. The reduced effectiveness of CI is made explicit by theoretically rigorous calculations. Now this in turn implied that part of the CI was overestimated by DP by putting it on the same basis as the EPI. The fact is that the EPI is more useful for superconductivity because of its time-retarded nature, whereas the effectiveness of the CI is reduced because of its instantaneous nature. The parameter $\lambda-\mu^*$ of MA, which is analogous to N_0V of BCS, is of the right order of magnitude for all metals, and this fact demonstrated the spurious nature of the criterion developed by DP (his parameters were too low compared to the empirical ones). But the distinction between superconductors and nonsuperconductors was completely missing from the work of MA. They came out with the startling prediction that all metals should be superconductors, though their transition temperatures may be arbitrarily low—much to the displeasure of experimentalists. But nonsuperconductors, e.g., alkali metals and alkaline-earth metals, have remained nonsuperconductors in the five or six years which have followed. The prophetic claim of Anderson that the superconductivity theory has entered the third stage of quantitative predictions of transition temperature T_c and other superconducting-state properties was no doubt true, as later theoretical work has amply proved. But the question why nonsuperconductors are nonsuperconductors is still not satisfactorily answered. It is remarked that no empirical correlation or criterion for the occurrence of superconductivity has ever predicted alkali and alkaline-earth metals to be superconductors. A new empirical correlation has recently been pointed out by the authors.[16] An interesting fact is discovered when the clear distance between two metal ions is plotted versus the nearest-neighbor distance: All the superconducting elements agglomerate in a certain region of the plot. The clear distance between two metal ions is obtained as a difference between the nearest-neighbor distance and the ionic diameter (by "ionic" we understand that the atom has been stripped of all electrons in incompletely filled valance

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shells). It is observed that all superconducting elements fall in a particular region, which we shall hereafter refer to as the "region of superconductivity," irrespective of the valency and crystal structure of the element, while the nonsuperconductors lie unmistakably scattered far from the region. Obviously this peculiar distribution raises a question which should be faced by superconductivity theory. We get a clue from the region of superconductivity. Granted the assumption that a simple empirical correlation should be explained by a simple reasoning, we look for possible effects of the size of the ion core in superconductivity theory.[17] For the conduction electrons at the top of the FS, which participate in interactions leading to superconductivity, the ionic core acts very much like a "hard core" in space. Its presence then modifies the conduction-electron wave function and hence the CI and EPI matrix elements. Will the departure from plane-wave matrix elements, which have always been used so far, make some difference? To check this, a model calculation is performed in which the ionic core is replaced by a three-dimensional constant repulsive potential, and the conduction-electron wave function is calculated in the spirit of the Wigner-Seitz approximation and first-order perturbation theory.

The second point which differentiates the present calculations from that of MA is that for the EPI matrix element we use the single-parameter model proposed by Harrison[18] for the orthogonalized-plane-wave (OPW) form factor. The last, and most important point, is the inclusion of the renormalization effects due to many-body EPI and CI. The renormalization effects were neglected by MA. We use the energy-gap integral equation developed by Schrieffer, which includes these important effects.

We now outline the plan of the paper. In Sec. II, we write the energy-gap integral equation, and we proceed to the calculation of superconducting-state parameters in Sec. III. We give the calculation of $\langle V_{\rm ph}\rangle$, $\langle V_{\rm C}\rangle$, and Z_0 [$\langle V_{\rm ph}\rangle$ estimates the phonon-mediated attractive electron-electron interaction; $\langle V_{\rm C}\rangle$, the Coulomb pseudopotential, measures the effectiveness of Coulomb repulsion in inhibiting superconductivity; and Z_0, the quasiparticle mass (or energy) renormalization parameter, takes into account the many-body renormalization effects due to EPI and CI]. The theoretical calculation of these parameters is undertaken for both nonsuperconductors and simple-metal superconductors. A model calculation along the lines mentioned above has been performed. Section IV deals with the results of the present calculations and their comparison with earlier results due to MA, DP, etc., and with appropriate parameters extracted from the empirical data in the way outlined in the same section. The two questions which we hope to answer are: why nonsuperconductors are nonsuperconductors, and whether better agreement can be obtained between theoretically estimated and empirical superconducting-state parameters.

II. ENERGY-GAP INTEGRAL EQUATION

The renormalized energy gap $\Delta(\omega)$ and renormalization parameter $Z(\omega)$ satisfy the following equation[1]:

$$\begin{pmatrix}\Delta(\omega)Z(\omega)\\ \omega[Z(\omega)-1]\end{pmatrix}=\int_0^{\omega_c} d\omega'\,\mathrm{Re}[\omega'^2-\Delta^2(\omega')]^{-1/2} \times\begin{pmatrix}\Delta(\omega') & 0\\ 0 & \omega'\end{pmatrix}\begin{pmatrix}R_+(\omega,\omega')-\langle V_{\rm C}\rangle\\ R_-(\omega,\omega')\end{pmatrix}, \quad (1)$$

where the kernels $R_\pm$ are

$$R_\pm(\omega,\omega')=\frac{m^*}{m}(8\pi^2k_F)^{-1}\sum_\lambda\int_0^{2k_F} q\,dq\,|\tilde g_{\mathbf{q}+\mathbf{K},\lambda}|^2 \times[D_\lambda{}^l(\mathbf{q},\omega-\omega')\pm D_\lambda{}^u(\mathbf{q},\omega+\omega')]. \quad (2)$$

In (1), $\langle V_{\rm C}\rangle$ is the Coulomb pseudopotential, introduced as a measure of the reduction in effectiveness of the Coulomb interactions, and ω_c is a cutoff frequency, typically taken to be several times the Debye frequency ω_D. In (2), $\tilde g$ is the screened EPI coupling constant; m^*/m is the reduced effective mass as determined from electronic specific-heat data; k_F is the Fermi wave number (we work in atomic units, putting $\hbar=k=c=1$, $e=\sqrt{2}$, and $m=\frac{1}{2}$; length is measured in Bohr radii and energy in rydbergs); $D_\lambda{}^l$ and $D_\lambda{}^u$ are, respectively,

$$D_\lambda{}^l(\mathbf{q},\omega-\omega')=\int_0^\infty d\nu\,B_\lambda(\mathbf{q},\nu)(\omega'-\omega+\nu-i\delta)^{-1},$$
$$D_\lambda{}^u(\mathbf{q},\omega+\omega')=\int_0^\infty d\nu\,B_\lambda(\mathbf{q},\nu)(\omega'+\omega+\nu-i\delta)^{-1}; \quad (3)$$

$B_\lambda(\mathbf{q},\nu)$ is the phonon spectral-weight function; and λ is the phonon-polarization mode. The nonlinear energy-gap equation can be quasilinearized by following a method suggested by Garland.[19] The normalized energy gap is defined as

$$\Xi(\omega)=\Delta(\omega)/\Delta_0,\quad \Delta_0=\Delta(\Delta_0). \quad (4)$$

[17] In an interesting paper, G. Gusman and R. Brout [J. Phys. Chem. Solids **26**, 223 (1965)] discuss a repulsive interaction arising from "ion-ion" interactions and estimate that if the primary contribution to the bulk modulus of the metal is due to interactions between the ion cores rather than the bulk modulus of the conduction electrons, then the effective electron-electron interaction is repulsive at low frequencies. This mechanism possibly suppresses superconductivity in noble metals, where large ion size determines the main contribution to the bulk modulus. There are no other nontransition metals in which this mechanism may be of importance. This is especially true for alkali and alkaline-earth metals. Their nonsuperconductivity can only be explained by an EPI of considerably smaller magnitude than has been estimated so far.

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[19] J. W. Garland, Phys. Rev. **153**, 460 (1967).

The normalized kernel is defined as

$$I_+(\omega,\omega')=K_+(\omega,\omega')/K_+(\Delta_0,\Delta_0)\,, \tag{5}$$

where $K_+(\omega,\omega')=R_+(\omega,\omega')-\langle V_C\rangle$. We get, after some manipulation,

$$\Xi(\omega)=Z^{-1}(\omega)\Big[I_+(\omega,\Delta_0)Z(\Delta_0)+\int_0^{\omega_c}d\omega' \times\mathrm{Re}\left(\frac{\Xi(\omega')}{[\omega'^2-\Delta_0^2\Xi^2(\omega')]^{1/2}}\right) \times[K_+(\omega,\omega')-K_+(\omega,\Delta_0)I_+(\Delta_0,\omega')]\Big]. \tag{6}$$

The above equation for the normalized energy gap is nonhomogeneous and nonlinear, but the nonlinearity factor $\Xi(\omega')/[\omega'^2-\Delta_0^2\Xi^2(\omega')]^{1/2}$ is now multiplied by a new kernel: $K_+(\omega,\omega')-K_+(\omega,\Delta_0)I_+(\Delta_0,\omega')$. It may be seen that this kernel vanishes at the point of maximum nonlinearity $\omega'=\Delta_0$. It is also vanishing at $\omega=\Delta_0$. This quasilinearization method reduces the magnitude of the nonlinear effect considerably. The inhomogeneous term of (6) is $Z^{-1}(\omega)Z(\Delta_0)I_+(\omega,\Delta_0)$, which can be used as a first approximation for $\Xi(\omega)$.

III. SUPERCONDUCTING-STATE PARAMETERS

A. Coulomb Pseudopotential

The Coulomb pseudopotential is calculated from[20]

$$\langle V_C\rangle=\bar{V}_C/[1+\bar{V}_C\ln(\omega_m/\omega_c)], \tag{7}$$

where $\bar{V}_C$ is the spherical average of V_C over the FS of the matrix element for the screened CI between Bloch electrons, and ω_m is the cutoff frequency for Coulomb interactions, and is of the order of Fermi energy E_F. The matrix element for direct Coulomb interaction between the Bloch electrons is given by

$$V_C(\mathbf{k}'-\mathbf{k})=\langle\mathbf{k}'\uparrow,-\mathbf{k}'\downarrow|\,2/(\mathbf{r}_i-\mathbf{r}_j)\,|\mathbf{k}\uparrow,-\mathbf{k}\downarrow\rangle, \tag{8}$$

where $\mathbf{r}_i$, and $\mathbf{r}_j$ are electron-position coordinates The Bloch state is

$$\psi_{\mathbf{k}}(\mathbf{r})=U_{\mathbf{k}}(\mathbf{r})\,\exp i(\mathbf{k}\cdot\mathbf{r}). \tag{9}$$

The matrix element is equal to

$$V_C(\mathbf{k}'-\mathbf{k})=\frac{8\pi}{|\mathbf{k}'-\mathbf{k}|^2}\left|\frac{1}{v_c}\int_{\text{cell}}U_{\mathbf{k}'}{}^*(\mathbf{r})U_{\mathbf{k}}(\mathbf{r})d\mathbf{r}\right|^2, \tag{10}$$

[20] Garland (unpublished) has emphasized the importance of determining the Coulomb pseudopotential exactly while discussing the deviations from the simple isotope effect for simple and transition-metal superconductors. He suggests a method for doing this, but it is, of course, undesirable to do so here, if only because of the amount of computation involved. Equation (7), however, gives a fairly reasonable approximation for $\langle V_C\rangle$.

where use has been made of $U_{\mathbf{k}}{}^*(\mathbf{r})=U_{-\mathbf{k}}(\mathbf{r})$. The Bloch function $U_{\mathbf{k}}(\mathbf{r})$ is calculated using first-order perturbation theory, and zeroth- and first-order functions are determined within the Wigner-Seitz (WS) approximation. The evaluation of the matrix element is outlined in the Appendix. The result is

$$V_C(\mathbf{k}'-\mathbf{k})=\frac{8\pi}{|\mathbf{k}'-\mathbf{k}|^2}\left(\frac{3}{r_{WS}{}^3}\int_0^{r_{WS}}U_0{}^2(r)r^2dr +\frac{\mathbf{k}\cdot\mathbf{k}'}{r_{WS}{}^3}\int_0^{r_{WS}}r^4[v_1(r)-U_0(r)]^2dr\right)^2. \tag{11}$$

We are interested only in the CI matrix element which connects Bloch states near the FS, i.e., $|\mathbf{k}|=|\mathbf{k}'|=k_F$. Putting $|\mathbf{k}'-\mathbf{k}|=q$ and $\cos\angle(\mathbf{k},\mathbf{k}')=\mu=1-q^2/2k_F{}^2$, we get

$$V_C(\mathbf{q},\mu)=\frac{8\pi}{q^2}\left(\frac{3}{r_{WS}{}^3}\int_0^{r_{WS}}U_0{}^2(r)r^2dr +\frac{\mu k_F{}^2}{r_{WS}{}^3}\int_0^{r_{WS}}r^4[v_1(r)-U_0(r)]^2dr\right)^2 =\frac{8\pi}{q^2}(A_1+\mu A_2)^2. \tag{12}$$

This CI matrix element is reduced by the static electronic dielectric function, since the dispersion effects of the CI come into the picture only at the plasmon frequencies, not at the small quasiparticle energies. The screened matrix element is taken to be

$$\bar{V}_C(\mathbf{q},\mu)=V_C(\mathbf{q},\mu)/\epsilon(q). \tag{13}$$

The wave-number-dependent Hartree dielectric function is used for $\epsilon(q)$:

$$\epsilon(q)=1+\frac{k_s{}^2}{q^2}\left(\frac{1}{2}+\frac{4k_F{}^2-q^2}{8k_Fq}\ln\left|\frac{2k_F+q}{2k_F-q}\right|\right). \tag{14}$$

The spherical average of the screened matrix element is taken over the FS by fixing the initial state $\mathbf{k}$ and letting the final state $\mathbf{k}'$ span the entire FS. Let us make the change of variables from $\mathbf{k}'$, θ', and ϕ' to $\mathbf{q}$, $\tilde{\epsilon}_{k'}$, and ϕ', where θ' and ϕ' are the spherical angles of $\mathbf{k}'$, and $\tilde{\epsilon}_{k'}$ is the normal-state quasiparticle energy measured from the Fermi level:

$$\tilde{\epsilon}_{k'}\simeq(m/m^*)(k'-k_F)2k_F. \tag{15}$$

We make the replacement

$$(2\pi)^{-3}\int d\mathbf{k}'\rightarrow\frac{m^*}{m}(8\pi^2k_F)^{-1}\int\int q\,dq d\tilde{\epsilon}_{k'}. \tag{16}$$

The angular integral is evaluated in getting $\bar{V}_C$, i.e.,

$$\bar{V}_C=\frac{m^*}{m}(8\pi^2k_F)^{-1}\int_0^{2k_F}dq\,q\bar{V}_C(q,\mu) \quad (17)$$

$$=\frac{m^*}{m}(\pi k_F)^{-1}\int_0^1 dn\frac{[A_1+(1-2n^2)A_2]^2}{n\epsilon(n)}, \quad (18)$$

where $n=q/2k_F$.

Combining Eqs. (7) and (18), we evaluate the Coulomb pseudopotential $\langle V_C\rangle$, taking $\omega_m=E_F$ in (7).

B. Electron-Phonon Coupling Strength $\langle V_{ph}\rangle$

The EPI matrix element is given by

$$g_{q+K,\lambda}=(N/M)^{1/2}V_{q+K}i(\mathbf{q}+\mathbf{K})\cdot\mathbf{e}_{q\lambda}(2\omega_{q\lambda})^{-1/2}, \quad (19)$$

where $\omega_{q\lambda}$ is the energy of the phonon $\mathbf{q}$, λ, $\mathbf{K}$ is a reciprocal-lattice vector, N is the ionic-number density, M is the ionic mass, $\mathbf{e}_{q\lambda}$ is the unit polarization vector, and V_{q+K} is the OPW form factor, i.e., the matrix element of the ionic psuedopotential between initial and final states lying on the FS. Harrison[18] has proposed a single-parameter model for approximating OPW form factors:

$$V_q=(-8\pi Z^*/q^2+\beta)/\epsilon(q), \quad (20)$$

where Z^* is the ionic valency and β is a parameter which takes the repulsive δ-function contribution from the orthogonalization of the conduction states to the core states. The screening is handled by the dielectric function $\epsilon(q)$. The factor $-8\pi Z^*/q^2$ is the matrix element of the Coulomb attraction of the bare ion and the conduction electron between plane-wave states. Harrison has approximated the conduction-electron state $|\mathbf{k}\rangle$ by the plane-wave $\exp i(\mathbf{k}\cdot\mathbf{r})$. Since we are using the Bloch states, we need an evaluation of the matrix element $\langle\mathbf{k}'|-Z^*/2(\mathbf{R}-\mathbf{r})|\mathbf{k}\rangle$ between the Bloch states. The computation of this matrix element is similar to the previous one. The result is[21]

$$-(8\pi Z^*/q^2)[A_1+(1-q^2/2k_F^2)A_2] \quad \text{(in a.u.)}.$$

The factors A_1 and A_2 are the same as defined in Eq. (12). We use this matrix element in place of the $-8\pi Z^*/q^2$ term in Eq. (20). Combining these results, we use the following expression for the screened EPI matrix element:

$$\tilde{g}_{q+K,\lambda}=\left(\frac{N}{M}\right)^{1/2}\frac{i(\mathbf{q}+\mathbf{K})\cdot\mathbf{e}_{q\lambda}}{(2\omega_{q\lambda})^{1/2}\epsilon(q)}\{-(8\pi Z^*/q^2)$$
$$\times[A_1+(1-q^2/2k_F^2)A_2]+\beta\}. \quad (21)$$

It is known that the phonon-induced interaction is mediated primarily through short-wavelength phonons. A good amount of experimental and theoretical data indicates that the short-wavelength part of the phonon spectrum is rather sharply peaked about a few definite frequencies which are described as longitudinal in character.[7,8,22–24] Thus the approximation, susceptible to simple mathematical treatment, of an Einstein spectrum consisting of one or two single frequencies towards the end of the phonon spectrum is justifiably reasonable. Accordingly, we approximate the longitudinal-phonon density of states by a single δ function centered at ω_D. As we shall see later, this crude approximation is more workable than is thought at first sight. We ignore the umklapp processes. See, in this connection, the discussion given by MA[12] and Schrieffer *et al.*[9] The previous calculations and results[5,7,22] indicate that the electron–transverse-phonon coupling strength is smaller by a factor of nearly 2 than the electron–longitudinal-phonon coupling strength in the case of Pb.

For single-frequency undamped Einstein phonons (to be unambiguous, we take them to be at ω_D), the phonon spectral-weight function B_λ reduces to a δ function:

$$B_\lambda(\mathbf{q},\nu)=\delta(\nu-\omega_D). \quad (22)$$

Setting $\lambda=l$ (longitudinal), $\mathbf{K}=0$ (no umklapp process), and giving the definition

$$\langle V_{ph}\rangle=\frac{m^*}{m}(8\pi^2k_F)^{-1}\int_0^{2k_F}\frac{2qdq}{\omega_D}|\tilde{g}_{ql}|^2, \quad (23)$$

we find that the kernels $R_\pm(\omega,\omega')$ are written as

$$R_\pm(\omega,\omega')=\langle V_{ph}\rangle\{[(\omega'-\omega+\omega_D-i\delta)^{-1}$$
$$\pm(\omega'+\omega+\omega_D-i\delta)^{-1}]\tfrac{1}{2}\omega_D\}. \quad (24)$$

Defined in this way, $\langle V_{ph}\rangle$ is analogous to the parameter λ of MA. This parameter, which we estimate theoretically and regard as a measure of phonon-induced interaction, is

$$\langle V_{ph}\rangle=\frac{m^*}{m}(8\pi^2k_F)^{-1}\frac{N}{M}\omega_D^{-2}\int_0^{2k_F}dq\,q^3\{-(8\pi Z^*/q^2)$$
$$\times[A_1+(1-q^2/2k_F^2)A_2]+\beta\}^2/\epsilon^2(q). \quad (25)$$

It is put in a form convenient for numerical computation by putting $q/2k_F=n$:

$$\langle V_{ph}\rangle=\frac{m^*}{m}\frac{N}{M}\frac{2k_F^3}{\pi^2\omega_D^2}\int_0^1 n^3dn\{-(2\pi Z^*/k_F^2n^2)$$
$$\times[A_1+(1-2n^2)A_2]+\beta\}^2/\epsilon^2(n). \quad (26)$$

[21] This correction factor, which we include in the simple point-ion model of Harrison, improves the agreement of model OPW form factor with the exact values.

[22] A. J. Bennett, Phys. Rev. **140**, A1902 (1965).

[23] B. N. Brockhouse, T. Arase, G. Caglioti, K. R. Rao, and A. D. B. Woods, Phys. Rev. **128**, 1099 (1962).

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IV. RESULTS AND DISCUSSION

The two characteristic parameters of the superconducting state—the effective parameter for phonon-induced interaction $\langle V_{\rm ph}\rangle$ and the Coulomb pseudopotential $\langle V_C\rangle$—are computed for individual elements, both superconductors and nonsuperconductors, from Eqs. (26), and (18), and (7) of Sec. III.

A. Empirical Parameters

The next job is to compare the theoretically estimated parameters with appropriate parameters extracted from experimental data. It is felt that this point requires more discretion because of certain considerations. Both DP and MA have compared their theoretically estimated parameters with the BCS parameter N_0V, which is obtained from

$$\frac{1}{N_0V}=\ln\left(\frac{2\gamma}{\pi}\frac{\omega_D}{T_c}\right), \tag{27}$$

where $\ln\gamma=0.5772$. The above expression is obtained when the net attractive interaction between electrons is approximated by a square well, so that it is zero beyond $\tilde{\epsilon}_k=\omega_D$. DP's work is based on the BCS model of square-well average interaction, since the integral equation satisfied by the energy gap is the simple BCS equation with the above-mentioned result. On the other hand, the energy-gap integral equation which MA solve is different from BCS, but they still manage to compare their parameter λ (or $\lambda-\mu^*$) with the BCS parameter N_0V by introducing certain approximations. They have managed to do by using a suitable first approximation [$\Sigma_1(\omega)=\Delta U(\omega)$; see MA Eq. (22)] to solve their energy-gap integral equation in order to obtain, finally, the BCS equation [see MA Eqs. (23) and (24)]. It is also useful to recall at this point a suggestive result of Sec. II, where the inhomogeneous quasilinear energy-gap equation (6) was found to have the following nonhomogeneous part:

$$\Delta(\omega)=\Delta_0Z(\Delta_0)Z^{-1}(\omega)I(\omega,\Delta_0),$$

and it is quite natural to use this as the first approximation for the next iteration of the energy-gap equation (6). MA do not consider the renormalization effects due to EPI and CI, so in their version of the situation $Z(\Delta_0)Z^{-1}(\omega)=1$, and they use $\Delta(\omega)=\Delta_0I(\omega,0)$ as the first approximation. The approximate reduction of Eq. (20) of MA to their Eq. (24) is in effect nothing but replacing the phonon kernel by a constant λ up to the frequency ω_1 (the single frequency of the Einstein spectrum) and then by zero beyond it. Leaving out important energy renormalization effects due to many-body interactions and the further approximation of the square-well interaction allows the direct comparison of $\lambda-\mu^*$ of MA with N_0V of BCS. As is pointed out later, the inclusion of renormalization effects deteriorates their good comparison with N_0V.

We do not consider it proper to compare the obtained theoretical parameters with the BCS parameter. Instead, we extract from the experimental data (i.e., Δ_0, Θ_D, T_c, etc.) suitable empirical parameters by following a procedure as outlined and justified below.

The procedure which we wish to follow for extracting appropriate empirical parameters is bound to be dependent on the nature of (or approximation to) the phonon spectrum of the particular element. To be consistent with the previous approximation of the phonon spectrum by an Einstein peak of longitudinal phonons at ω_D, we use it again here. To be sure, such a drastic assumption about the nature of phonon spectrum is very crude, and is at best barely workable. The nature of the phonon spectrum, which enters in a significant way into the energy-gap integral equation, will matter a lot if one approximation is replaced by another. But still, if a crude approximation is taken for the estimation of the theoretical parameter as well as the empirical parameter, it will certainly result in cancellation of the error due to a crude approximation, and will provide at least a check on whether the theoretically estimated parameters have any good comparison with the empirical ones.

We outline the procedure to get $\langle V_{\rm ph}\rangle_{\rm emp}$ and $Z(\Delta_0)_{\rm emp}$ as follows. The equations which $\Delta(\omega)$ and $Z(\omega)$ satisfy are

$$\Delta(\omega)=Z^{-1}(\omega)\int_{\Delta_0}^{\omega_c}d\omega'\,{\rm Re}\frac{\Delta(\omega')}{[\omega'^2-\Delta^2(\omega')]^{1/2}}\{\langle V_{\rm ph}\rangle \times[(\omega'+\omega+\omega_D-i\delta)^{-1}+(\omega'-\omega+\omega_D-i\delta)^{-1}] \times\tfrac{1}{2}\omega_D-\langle V_C\rangle\} \tag{28}$$

and

$$\omega[1-Z(\omega)]=\int_{\Delta_0}^{\omega_c}\omega'd\omega'\,{\rm Re}[\omega'^2-\Delta^2(\omega')]^{-1/2}\langle V_{\rm ph}\rangle\tfrac{1}{2}\omega_D \times[(\omega'+\omega+\omega_D-i\delta)^{-1}-(\omega'-\omega+\omega_D-i\delta)^{-1}]. \tag{29}$$

Taking the first of these equations, setting $\omega=\Delta_0$, and setting $\Delta(\omega')=\Delta_0$ inside the integral by making use of the smallness of Δ, we have

$$\Delta_0=Z^{-1}(\Delta_0)\int_{\Delta_0}^{\omega_c}d\omega'\Delta_0(\omega'^2-\Delta_0^2)^{-1/2} \times\{\langle V_{\rm ph}\rangle\omega_D(\omega_D+\omega')[(\omega_D+\omega')^2-\Delta_0^2]^{-1}-\langle V_C\rangle\}, \tag{30}$$

so that

$$1=Z^{-1}(\Delta_0)\int_{\Delta_0}^{\omega_c}d\omega'(\omega'^2-\Delta_0^2)^{-1/2} \times\left[\langle V_{\rm ph}\rangle\left(\frac{\omega_D+\omega'}{\omega_D}-\frac{\Delta_0^2}{\omega_D(\omega_D+\omega')}\right)^{-1}-\langle V_C\rangle\right]. \tag{31}$$

Now taking Eq. (29), rearranging the terms, setting $\omega=\Delta_0$, and putting $\Delta(\omega')=\Delta_0$ inside the integral, we get

$$Z(\Delta_0)=1+\int_{\Delta_0}^{\omega_c} d\omega'\omega'(\omega'^2-\Delta_0^2)^{-1/2} \times\langle V_{\rm ph}\rangle\omega_D[(\omega'+\omega_D)^2-\Delta_0^2]^{-1}. \quad (32)$$

From Eqs. (31) and (32), after feeding the values of ω_D and Δ_0 for the individual superconducting element, we determine the empirical parameters. We choose $\omega_c=10\omega_D$ consistently throughout. First, by ignoring $\langle V_C\rangle$ in Eq. (31), we calculate $Z(\Delta_0)/\langle V_{\rm ph}\rangle$ from the equation

$$\frac{Z(\Delta_0)}{\langle V_{\rm ph}\rangle}=\int_{\Delta_0}^{10\omega_D} d\omega(\omega^2-\Delta_0^2)^{-1/2} \times[(\omega_D+\omega)/\omega_D-\Delta_0^2\omega_D^{-1}(\omega_D+\omega)^{-1}]^{-1} =I_1 \text{ (say)}. \quad (33)$$

The integral is evaluated by dividing it into two parts, the first from Δ_0 to $10\Delta_0$ and the second from $10\Delta_0$ to $10\omega_D$. The second integral is analytically evaluated, while the first one is done by a 16-point Gauss quadrature formula. The integral in the second equation,

$$\frac{Z(\Delta_0)}{\langle V_{\rm ph}\rangle}=\langle V_{\rm ph}\rangle^{-1}+\int_{\Delta_0}^{10\omega_D} d\omega\,\omega(\omega^2-\Delta_0^2)^{-1/2} \times\omega_D[(\omega+\omega_D)^2-\Delta_0^2]^{-1} =I_2 \text{ (say)}, \quad (34)$$

is also evaluated numerically by the same method. We obtain

$$Z(\Delta_0)/\langle V_{\rm ph}\rangle=I_1$$

and

$$Z(\Delta_0)/\langle V_{\rm ph}\rangle=\langle V_{\rm ph}\rangle^{-1}+I_2.$$

The initial values of $Z(\Delta_0)$ and $\langle V_{\rm ph}\rangle$ are determined and the value of $\langle V_{\rm ph}\rangle$ and $\langle V_C\rangle$ substituted in Eq. (31) to evaluate a better approximation for $Z(\Delta_0)/\langle V_{\rm ph}\rangle$. This iteration is continued until consistent values of $Z(\Delta_0)$ and $\langle V_{\rm ph}\rangle$ are obtained. These are our empirical parameters $Z(\Delta_0)_{\rm emp}$ and $\langle V_{\rm ph}\rangle_{\rm emp}$ with which we compare the theoretically estimated parameters. It is seen that for the superconductors with weak electron-phonon coupling ($\Delta_0/\omega_D\ll1$), we have

$$Z(\Delta_0)=Z_0\simeq1+(10/11)\langle V_{\rm ph}\rangle. \quad (35)$$

The same result is true for the normal state.

Table I lists the relevant parameters and data for the simple metals for which the calculations have been done.

TABLE I. Relevant quantities which enter into the calculation and theoretical estimates of superconducting-state parameters.

Element	a T_c (°K)	b r_s	c k_F	d Θ_D (°K)	e β	f γ	g m^*/m
Na		3.93	0.488	158	27.0		1.13[h]
K		4.88	0.393	90	31.5		1.16[h]
Be		5.77	0.333	1160	31.0		0.46[i]
Mg		2.65	0.723	400	42.0		1.30[i]
Ca		4.12	0.466	230	50.6		0.75[i]
Cu		2.67	0.906	343	2.2	0.69[j]	1.09
Zn	0.852	2.31	0.833	310	26.5	0.66	0.88
Al	1.183	2.07	0.926	428	36.6	1.36	1.50
In	3.396	3.04	0.632	108	31.0	1.81	0.93
Hg	4.153	2.63	0.730	87	50.0	1.91	1.96
Tl	2.36	2.49	0.772	87	25.0	1.47	1.12
Sn	3.722	2.80	0.687	199	55.0	1.75	1.06
Pb	7.23	2.30	0.835	110	60.0	3.0	2.01

[a] Reference 13.
[b] Characteristic interelectron distance (in a.u.) calculated from the crystallographic data.
[c] Fermi wave number (in a.u.) calculated from $k_F=1.92/r_s$.
[d] *American Institute of Physics Handbook* (McGraw-Hill Book Co., New York, 1963). Value for Hg is from Ref. 13.
[e] Reference 17.
[f] Reference 13 (in mJ/mole °K²).
[g] Calculated from the expression $m^*/m=3.85\gamma k_F^2/Z^*$, with γ in mJ/mole °K² and k_F in a.u.
[h] J. M. Ziman, *Electron and Phonons* (Oxford University Press, New York, 1960), Table 2.1, p. 109.
[i] Reference 12.
[j] N. E. Philips, in *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisc., 1958).

B. Nonsuperconductors

The calculated parameters $\langle V_{\rm ph}\rangle$ and $\langle V_C\rangle$ for some nonsuperconductors (two alkali metals, three alkaline-earth metals, one noble metal) are tabulated in Table II. Also included in the table are parameters λ and μ^* of MA, DP's parameter N_0V, and the renormalization parameter. The renormalization due to CI can be in-

TABLE II. Superconducting-state parameters for nonsuperconductors.

Element	a $\langle V_C\rangle$	b $\langle V_{\rm ph}\rangle$	c MA parameters μ^*	c MA parameters λ	d DP's N_0V	e $Z_{0\,\rm ph}$	f $Z_{0\,C}$	g Z_0	h $(\langle V_{\rm ph}\rangle-\langle V_C\rangle)/Z_0$	i $\lambda-\mu^*$
Na	0.16	0.15	0.12	0.25	−0.39	1.14	1.58	1.72	−0.006	0.13
K	0.16	0.22	0.12	0.25	−0.24	1.20	1.73	1.93	+0.03	0.13
Be	0.26	0.003			+0.17	1.00	1.87	1.87	−0.14	
Mg	0.15	0.17	0.12	0.32	−0.01	1.15	1.38	1.53	+0.01	0.20
Ca	0.17	0.05	0.11	0.27	+0.06	1.05	1.78	1.83	−0.07	0.16
Cu	0.14	0.23	0.10	0.20	−0.20	1.12	1.39	1.51	+0.06	0.10

[a] Calculated from Eqs. (18) and (7).
[b] Calculated from Eq. (26).
[c] Reference 12.
[d] Calculated from Eq. (21) of Ref. 11.
[e] Calculated by following the procedure given in Sec. III.
[f] Reference 24.
[g] $Z_0=(Z_0=1)_{\rm ph}+Z_{0\,C}$.

cluded at this point according to the simple prescription

$$Z_0=(Z_0-1)_{\rm ph}+Z_{0\,\rm C}.$$

The Coulomb contribution to Z_0 is given by

$$Z_{0\,\rm C}=z_{p_F}^{-1},$$

where z_{p_F} is the wave-function renormalization constant of Landau's theory of Fermi liquids. It is taken directly from the calculations by Rice.[25] In column h of Table II, we calculate the theoretical estimate of the effective interaction strength for these nonsuperconductors, which is taken to be equal to $(\langle V_{\rm ph}\rangle-\langle V_{\rm C}\rangle)/Z_0$. If we include the renormalization effects in the simple BCS theory, then it is easily seen that the effective interaction strength should be $(\langle V_{\rm ph}\rangle-\langle V_{\rm C}\rangle)/Z_0$ and not $\langle V_{\rm ph}\rangle-\langle V_{\rm C}\rangle$. Leaving the renormalization effects, MA take their $\lambda-\mu^*$ as the effective interaction strength.

We find that our theoretically estimated effective interaction strengths are negative (the Coulomb repulsion dominates over the phonon-induced interaction). In some cases, those of K, Mg, and Cu, it comes out to be positive, but is much smaller than the value estimated by MA. Clearly, all the results indicate either repulsive or slightly attractive interaction for these metals. There are three reasons why our results differ from those of MA: (i) We find the effect of the Coulomb repulsion to be enhanced, (ii) the phonon-induced attractive contribution is smaller than that estimated by MA, and (iii) the renormalization effects reduce the effective net interaction strength still further.

We believe that the present estimates are nearer to the true picture. The present six calculations for nonsuperconductors are representative of their group.

C. Superconductors

The theoretically estimated $\langle V_{\rm ph}\rangle$ and $\langle V_{\rm C}\rangle$ for some nontransition-metal superconductors are tabulated in Table III. Also in the same table are MA's parameters λ and μ^*, DP's parameter N_0V, the empirical parameters $\langle V_{\rm ph}\rangle_{\rm emp}$ and $Z_{0\,\rm ph\,emp}$, theoretically estimated $Z_{0\,\rm ph}$, $Z_{0\,\rm C}$, and Z_0, the net effective interaction strength $(\langle V_{\rm ph}\rangle-\langle V_{\rm C}\rangle)/Z_0$, the net effective interaction strength $(\lambda-\mu^*)/Z_0$, which is obtained when renormalization is included in MA's theory, and the empirical BCS parameter.

We also wish to compare our results with those given by Garland.[26] This is done in Table IV, where $\langle V_{\rm C}\rangle$ is compared with $2K_e^*$, the corresponding parameter estimated by Garland; $\langle V_{\rm ph}\rangle$, both theoretical and empirical, are compared with the corresponding parameter $|2\langle K_{\rm ph}\rangle|$ of Garland; and $Z_{0\,\rm ph}$, both theoretically estimated and empirical, is compared with the $Z_{0\,\rm ph}$ of Garland.

The results shown in Table III clearly indicate that the theoretically estimated $\langle V_{\rm ph}\rangle$ and $Z_{0\,\rm ph}$ compare very well with the empirical parameters $\langle V_{\rm ph}\rangle_{\rm emp}$ and $Z_{0\,\rm ph\,emp}$, as do the effective interaction strength and the BCS parameter. In some cases the agreement is very good, while in others it is not so. The results shown in Table IV also compare very well with the estimates of Garland. The empirical estimate, which we obtain by following the method described earlier and which is certainly a simple and crude method, is very close to that obtained by Garland in the weak-coupling cases. Our $\langle V_{\rm ph}\rangle_{\rm emp}$ is within 6% of $|\langle 2K_{\rm ph}\rangle|$ for Al, Sn, and Zn, and it is within 30% for the strong-coupling cases Hg, Pb, and Tl. Very similar is the comparison of $Z_{0\,\rm ph\,emp}$ with $Z_{0\,\rm ph}$ estimated by Garland. It confirms our earlier statement that even the crude approximation of the entire phonon spectrum by a single-frequency Einstein peak of longitudinal phonons at ω_D can provide close enough estimates of the parameters $\langle V_{\rm ph}\rangle$ and $Z_{0\,\rm ph}$. It is, of course, convenient to get a good estimate by following a simple method first.

The important conclusions of the present calculations are as follows.

In the calculation of the Coulomb pseudopotential $\langle V_{\rm C}\rangle$, we find that the correction factor

$$[A_1+(1-2n^2)A_2]^2,$$

TABLE III. Superconducting-state parameters of simple-metal superconductors.

	a	b	c	d		e	f	g	h	i			j
				MA parameters		DP's							BCS
Element	$\langle V_{\rm C}\rangle$	$\langle V_{\rm ph}\rangle$	$\langle V_{\rm ph}\rangle_{\rm emp}$	λ	μ^*	N_0V	$Z_{0\,\rm ph}$	$Z_{0\,\rm ph\,emp}$	$Z_{0\,\rm C}$	Z_0	$(\langle V_{\rm ph}\rangle-\langle V_{\rm C}\rangle)/Z_0$	$(\lambda-\mu^*)/Z_0$	N_0V
Zn	0.14	0.17	0.25	0.25	0.09	−0.075	1.15	1.41	1.34	1.49	0.02	0.11	0.20
Al	0.13	0.43	0.43	0.33	0.10	−0.013	1.39	1.39	1.31	1.70	0.18	0.14	0.19
In	0.12	0.41	0.56	0.34	0.10	+0.018	1.37	1.50	1.44	1.81	0.16	0.13	0.34
Hg	0.12	0.84	0.84	0.37	0.10	−0.049	1.76	1.74	1.38	2.14	0.34	0.13	0.45
Tl	0.12	0.53	0.60	0.32	0.09	+0.033	1.48	1.54	1.36	1.84	0.22	0.12	0.32
Sn	0.13	0.20	0.59	0.34	0.10	+0.078	1.18	1.53	1.40	1.58	0.04	0.15	0.30
Pb	0.14	1.70	0.82	0.40	0.10	+0.089	2.54	1.70	1.34	2.88	0.54	0.10	0.50

[a] Calculated from Eqs. (18) and (7).
[b] Calculated from Eq. (26).
[c] Calculated by following the procedure outlined in Sec. III.
[d] Reference 12.
[e] Calculated from Eq. (21) of Ref. 11.
[f] Calculated from Eq. (35).
[g] Calculated by following the procedure outlined in Sec. III.
[h] Reference 24.
[i] $Z_0=(Z_{0\,\rm ph}-1)+Z_{0\,\rm C}$.
[j] Calculated from Eq. (27).

[25] T. M. Rice, Ann. Phys. (N. Y.) **31**, 100 (1965).
[26] J. W. Garland (unpublished).

TABLE IV. Comparison of estimated superconducting-state parameters for some simple-metal superconductors with those estimated by Garland.

Element	a $\langle V_C \rangle$	b $2K_2^*$	c $\langle V_{ph} \rangle$	d $2\langle K_{ph} \rangle$	e $\langle V_{ph} \rangle_{emp}$	f $Z_{0\,ph\,emp}$	g $Z_{0\,ph}$	h Garland $Z_{0\,ph}$
Al	0.13	0.113	0.43	0.42	0.43	1.39	1.39	1.50
Hg	0.12	0.110	0.84	1.01	0.84	1.74	1.76	2.15
Pb	0.14	0.105	1.70	1.08	0.82	1.70	2.54	2.23
Sn	0.13	0.105	0.20	0.62	0.59	1.53	1.18	1.71
Tl	0.12	0.096	0.53	0.83	0.60	1.54	1.48	1.95
Zn	0.14	0.096	0.17	0.42	0.45	1.41	1.15	1.50

[a] Calculated from Eqs. (18) and (7).
[b] Reference 25.
[c] Calculated by following the procedure outlined in Sec. III.
[d] Reference 25.
[e] Calculated from Eq. (21) of Ref. 11.
[f] Calculated from Eq. (35).
[g] Calculated by following the procedure outlined in Sec. III.
[h] Reference 25.

which occurs in Coulomb pseudopotential expression (18) and which arises because the Coulomb matrix element is taken between Bloch states and not the plane-wave states, enhances the pseudopotential by 20–40%. Our estimated Coulomb pseudopotentials are larger than all previous estimates. We find that, especially in the case of nonsuperconductors, this effect is of more importance.

The calculation of the phonon-mediated interaction strength $\langle V_{ph} \rangle$ has been done by taking for the electron-phonon matrix element the form suggested by Harrison. This EPI matrix element is modified by multiplication by a correction factor $A_1+(1-2n^2)A_2$ [see Eq. (21)]. The approximation of the phonon spectrum by a longitudinal Einstein peak at ω_D is thought to be good enough to begin with, to get a first estimate of the theoretical and the empirical phonon-mediated attraction parameter. This statement is supported by a good comparison of the empirical parameters with the parameters estimated by Garland. It is expected that substituting the real phonon spectrum into the energy-gap equation will give more reliability to the estimates of $\langle V_{ph} \rangle$ and $Z_{0\,ph}$.

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APPENDIX

The function $U_k(\mathbf{r})$ is given by the following expression[27]:

$$U_k(\mathbf{r})=U_0(\mathbf{r})+i\mathbf{k}\cdot\mathbf{r}[P(r)/r^2-U_0(r)], \quad \text{(A1)}$$

where $U_0(r)$ and $P(r)$ satisfy the following radial equations and boundary conditions in the WS approximation:

$$[d^2/dr^2+\epsilon_0-V(r)]U_0(r)/r=0, \quad \text{(A2)}$$

$$[d^2/dr^2+\epsilon_0-V(r)]P(r)=0 \quad \text{(A3)}$$

and

$$|dU_0(r)/dr|_{r=r_{WS}}=0,$$
$$P(0)=0, \quad P(r_{WS})=r_{WS}^2U_0(r_{WS}).$$

These equations are in atomic units. $V(r)$ is a spherically symmetric crystal potential which is the sum of the ion-core potential, the exchange between core and conduction electrons, and the self-consistent field of the conduction electrons. ϵ_0 is the energy at the bottom of the conduction band, and r_{WS} is the radius of the WS cell in atomic units. To make simple model calculations, we approximate $V(r)$ as

$$V(r)=V_0(\text{const}), \quad r>r_0$$
$$=-2Z^*/r, \quad r>r_0. \quad \text{(A4)}$$

r_0 is the ion-core radius. ϵ_0 is given by

$$\epsilon_0=\epsilon_{coh}+\epsilon_I-E_0-E_2, \quad \text{(A5)}$$

where ϵ_{coh} is the (negative) cohesive energy per electron, ϵ_I is the (negative) ionization energy of the free atom, E_0 is the ground-state energy per electron, E_2 is $1.2Z^*/r_{WS}$, the Coulomb term,[28] and

$$E_0=E_{kinetic}+E_{exchange}+E_{correlation}$$
$$=\alpha 2.21/r_s^2-0.916/r_s-0.115+0.031\ln r_s. \quad \text{(A6)}$$

The correlation energy is taken to be of the form suggested by Nozières and Pines.[29] It is quite satisfactory for metallic densities (r_s=2–6). Here α is m/m^*, and r_s is the characteristic interelectron spacing related to r_{WS} by

$$r_s=r_{WS}Z^{*-1/3}. \quad \text{(A7)}$$

Taking $V(r)$ as given by (A4) and ϵ_0 as given by (A5) and (A6) combined, the radial equations (A2) and (A3) are integrated numerically and the appropriate boundary conditions are satisfied.

[27] S. Raimes, *The Wave Mechanics of Electrons in Metals* (North-Holland Publishing Co., Amsterdam, 1961), Sec. 9.3.

[28] David Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1962).

[29] P. Nozières and D. Pines, Phys. Rev. **111**, 442 (1958).

Now let us consider the integral

$$I=\frac{1}{v_c}\int_{\text{cell}} U_k^*(\mathbf{r})U_k(\mathbf{r})d\mathbf{r}, \tag{A8}$$

where $U_k(\mathbf{r})$, from (A1), is

$$U_k(\mathbf{r})=U_0(r)+i\mathbf{k}\cdot\mathbf{r}v(r). \tag{A9}$$

This gives

$$I=\frac{1}{v_c}\int_{\text{cell}}[U_0^2+i\mathbf{k}\cdot\mathbf{r}U_0v-i\mathbf{k}'\cdot\mathbf{r}U_0v +(\mathbf{k}'\cdot\mathbf{r})(\mathbf{k}\cdot\mathbf{r})v^2]d\mathbf{r}. \tag{A10}$$

Choosing the direction of vector $\mathbf{k}$ as polar axis, we have

$$\angle(\mathbf{k},\mathbf{r})=\Theta;$$

then

$$I=\frac{1}{v_c}\int_{\text{cell}}[U_0^2+iU_0v(\mathbf{k}\cdot\mathbf{r}-\mathbf{k}'\cdot\mathbf{r})+(\mathbf{k}'\cdot\mathbf{r})(\mathbf{k}\cdot\mathbf{r})v^2] \times r^2dr\sin\Theta\, d\Theta d\Phi. \tag{A11}$$

It can be easily seen that the integrals of the type

$$\int_{\text{cell}}\mathbf{k}\cdot\mathbf{r}f(r)r^2dr\sin\Theta\, d\Theta d\Phi$$

vanish, and for integral I we get

$$I=\frac{1}{v_c}\int\int\int[U_0^2+(\mathbf{k}'\cdot\mathbf{r})(\mathbf{k}\cdot\mathbf{r})v^2]r^2dr\sin\Theta\, d\Theta d\Phi. \tag{A12}$$

Next, we define

$$I_1=\frac{1}{v_c}\int\int\int U_0^2r^2dr\sin\Theta\, d\Theta d\Phi =\frac{4\pi}{v_c}\int_0^{r_{\text{WS}}}U_0^2r^2dr \tag{A13}$$

and

$$I_2=\frac{1}{v_c}\int\int\int kk'r^2\cos\angle(\mathbf{k},\mathbf{r})\cos\angle(\mathbf{k}',\mathbf{r}) \times v^2r^2dr\sin\Theta\, d\Theta d\Phi =\frac{kk'}{v_c}\int_0^{r_{\text{WS}}}r^2v^2drI_{\text{angular part}}. \tag{A14}$$

$I_{\text{angular part}}$ is determined as

$$I_{\text{angular part}}=\tfrac{4}{3}\pi\cos\angle(\mathbf{k},\mathbf{k}'). \tag{A15}$$

Combining results for I_1 and I_2, we obtain

$$I=\frac{3}{r_{\text{WS}}^3}\int_0^{r_{\text{WS}}}U_0^2(r)r^2dr+\frac{\mathbf{k}\cdot\mathbf{k}'}{r_{\text{WS}}}\int_0^{r_{\text{WS}}}r^4 \times\left(\frac{P(r)}{r^2}-U_0(r)\right)^2dr. \tag{A16}$$

Finally, the Coulomb contribution is given as

$$V_C=(\pi k_F)^{-1}\int_0^1\frac{dn\,[A_1+A_2(1-2n^2)]^2}{\epsilon(n)}. \tag{A17}$$

To obtain A_1 and A_2, we first evaluate

$$I_1=\frac{3}{r_{\text{WS}}^3}\int_0^{r_{\text{WS}}}U_0^2dr, \tag{A18}$$

$$I_2=\frac{4\pi k_F^2}{3v_c}\int_0^{r_{\text{WS}}}\left(\frac{P}{r^2}-U_0\right)r^4dr =\frac{k_F^2}{r_{\text{WS}}^3}\int_0^{r_{\text{WS}}}\left(\frac{P}{r^2}-U_0\right)r^4dr. \tag{A19}$$

In the text, $P(r)/r^2$ is put equal to $v_1(r)$. From these we get

$$A_1=I_1/(I_1+I_2),\quad A_2=I_2/(I_1+I_2). \tag{A20}$$

$\epsilon(n)$ is given as

$$\epsilon(n)=1+(2\pi k_Fn^2)^{-1}\left(1+\frac{1-n^2}{2n}\ln\left|\frac{1+n}{1-n}\right|\right). \tag{A21}$$