Scattered impurity states in transition metals. II. Approximate solutions using phase shifts

A. Holas, S. Olszewski, and A. Wierzbicki

Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

(Received 23 April 1985)

To solve the problem of a transition metal with an impurity, the one-electron linear-combination-of-atomic-orbitals wave functions are constructed in terms of spherical harmonics multiplied by spherical Bessel or spherical Neumann functions. These solutions are approximated afterwards by the standing-wave-like projected-coefficient (SWLPC) functions, calculated in the preceding paper, and their modifications. At large distances from the impurity area the impurity wave function has the form of a scattered wave. Any solution for an imperfect crystal differs from that obtained for a perfect crystal by the presence of a phase shift. In each case the electron states can be quantized according to the requirement that their wave functions vanish at the crystal boundary, which is assumed to be spherical. This makes the analysis of the impurity problem in a crystal very similar to that done by Friedel in the free-electron case. However, any present phase shift depends on the symmetry index of the SWLPC function, the branch of the solution of the secular problem, and the wave vector belonging to the irreducible part of the Brillouin zone. The phase shifts, which can be expressed in terms of the perturbation matrix, are proportional to corresponding components of the density of states of the unperturbed metal. An expression for the change in the number of metal electrons due to scattering is obtained. In its derivation the phase shifts found in the present paper enter into a modified Friedel's formula given originally for the free-electron case.

I. INTRODUCTION

In many dilute alloys of transition metals, e.g., NiFe and NiCo, the area of the perturbation potential due to the impurity atom is limited to the neighborhood of one lattice site.[1,2] In other cases, e.g., NiCr,[2,3] the perturbation potential is extended over more than one lattice site, although the potential perturbation does not occupy many lattice sites. Outside a certain area the perturbation can be considered negligibly small. Nevertheless, the electronic structure of the matrix metal is modified by the impurity atoms also outside the area occupied by them.

Friedel[4-6] considered metal as jellium and the perturbation due to an impurity as a spherical potential on which the jellium electrons were scattered. Providing the bound states were neglected, the effects of the impurity were phase shifts of the wave functions of the jellium. These phase shifts took account of the change of the electron structure at distances far from the impurity; they were very useful in the calculation of such quantities of the perturbed metal as electron density, density of states, and residual resistivity.

Koster and Slater[7-9] first gave a method for description of the impurity states in a metal in which the periodic structure of the crystal potential of the matrix was taken into account; cf. also Ref. 10 here. The electron wave functions were given in the linear-combination-of-atomic-orbitals (LCAO) representation. The difficulties of this approach, based on the Bloch LCAO wave functions, were discussed in the preceding paper,[11] hereafter referred to as I. A different approach, based on the standing-wave-like LCAO wave functions, was proposed there. This approach seems to be more suitable for the treatment of the impurity problem. In the present paper

this approach is applied to find the solution of the problem of a transition metal perturbed by the presence of an impurity which can be a single substitutional atom or a cluster of them. As the beginning the boundaries of the metal block are chosen to be spherical, so the electron wave functions can be quantized in this spherical potential box. This kind of quantization allows for an easy calculation of the change of the unperturbed wave functions of the perfect metal due to the presence of an impurity at large distances from the impurity position. The changes are given in the form of phase shifts of the original wave functions; therefore a complicated Green's-function calculation is avoided. The phase shifts can be readily obtained on condition that the impurity potential is a known quantity. (In this paper we do not consider the bound states which may be caused by the impurity potential.) This makes the method very suitable for the calculation of such quantities as the total change of the density of states in a crystal, or the scattering effects at large distances from the area occupied by impurities. From this point of view the present method seems to be easier to handle than much more refined approaches to the impurity problem based on the Korringa-Kohn-Rostoker approximation.[12-19] These methods are particularly well suited to a local description of the impurity effect: they surround the impurity atom, or a cluster of the impurity atoms, by a sphere, and then take into account the effect of scattering of an electron on one or many atoms by means of the Green's-function technique.

In subsequent sections we present—as the first step—how the standing-wave approach to the LCAO method works in the case of a one-dimensional metal. As the next step the boundary of the whole three-dimensional crystal is changed to a sphere and the wave function for this crys-

tal is expressed in the spherical coordinate system. This allows us to approximate the coefficient functions of the LCAO wave functions in terms of the combinations of spherical harmonics multiplied by spherical Bessel functions used for a perfect crystal. On the other hand, the LCAO coefficient functions for a crystal with impurities can be expressed in terms of combinations of spherical harmonics multiplied by spherical Bessel functions and spherical Neumann functions. In effect, at large distances from the impurity area, the coefficient function of the perturbed crystal differs from the coefficient function of the perfect crystal by the presence of a phase shift. The phase shifts can be easily estimated from the energy difference between the perturbed and the unperturbed electron states.

An approach of this kind to the impurity problem was done earlier, but was limited solely to the s-electron states.[20] Moreover, it was based on the standing-wave LCAO wave functions obtained from a tedious diagonalization process which was accompanied by convergence difficulties for certain areas of the spectrum of the energy states. In the present paper we avoid these difficulties using the LCAO wave functions which have the standing-wave-like projected-coefficient (SWLPC) functions obtained in I. The method can be applied equally to any set of s, p, d, and other atomic states, and the necessary coefficient functions are obtained by a simple projection-operator technique. It is shown also how the phase shifts are related to the density of states of the perfect metal and—in the last step—the phase shifts are applied to the

calculation of the change of the electron charge in the matrix produced by the presence of impurities.

II. THE CASE OF ONE-DIMENSIONAL METAL

To give a better idea of our method, we present it at first for a very simple example of a one-dimensional crystal which has only two types of the atomic orbitals. These are an orbital symmetric with respect to the nucleus,

$$\Phi_s(-x)=\Phi_s(x) ,\qquad(2.1)$$

labeled by s, and an antisymmetric one,

$$\Phi_p(-x)=-\Phi_p(x) ,\qquad(2.2)$$

labeled by p. The LCAO function in the present case is

$$\Psi(x)=\sum_{L,\mu} A_{\mu L}\Phi_\mu(x-X_L)\qquad(2.3)$$

$$\mu=\{s,p\}=\{1,2\}, \quad L=0,\pm1,\pm2,\ldots, \quad X_L=La\qquad(2.3a)$$

where a is a lattice constant. The atomic orbitals Φ_μ and the matrix elements of $\hat{H}$, Eq. (2.7) of I, may be chosen real. Therefore

$$H_{\mu L,\mu'L'}=H_{\mu'L',\mu L} ,\qquad(2.4)$$

because $\hat{H}(x)$ is Hermitian. If the tight-binding approximation (the interaction between atoms limited to nearest neighbors) is assumed, then the translational symmetry of $\hat{H}$, Eq. (2.8) of I, the symmetry properties of the atomic orbitals (2.1) and (2.2), and the invariance of the Hamiltonian upon inversion, viz., $\hat{H}(-x)=\hat{H}(x)$, give the following matrix elements:

$$H_{s0,s0}, \quad H_{p0,p0}, \quad H_{s0,s(-1)}=H_{s0,s1}, \quad H_{p0,p(-1)}=H_{p0,p1}, \quad H_{s0,p(-1)}=-H_{s0,p1}=H_{p0,s1}=-H_{p0,s(-1)} .\qquad(2.5)$$

Other nonvanishing elements can be obtained from (2.5) by means of Eq. (2.4); the remaining matrix elements are zero. The difference equation (2.9) of I is now

$$\begin{bmatrix} H_{s0,s0} & 0 \\ 0 & H_{p0,p0} \end{bmatrix}\begin{bmatrix} A_{sL} \\ A_{pL} \end{bmatrix}+\begin{bmatrix} H_{s0,s1} & H_{s0,p1} \\ -H_{s0,p1} & H_{p0,p1} \end{bmatrix}\begin{bmatrix} A_{s(L+1)} \\ A_{p(L+1)} \end{bmatrix}+\begin{bmatrix} H_{s0,s1} & -H_{s0,p1} \\ H_{s0,p1} & H_{p0,p1} \end{bmatrix}\begin{bmatrix} A_{s(L-1)} \\ A_{p(L-1)} \end{bmatrix}=E\begin{bmatrix} A_{sL} \\ A_{pL} \end{bmatrix},\qquad(2.6)$$

while its differential form, see (2.11) and (2.12) of I, is

$$\begin{bmatrix} H_{s0,s0}+H_{s0,s1}(e^{a(d/dX)}+e^{-a(d/dX)}) & H_{s0,p1}(e^{a(d/dX)}-e^{-a(d/dX)}) \\ -H_{s0,p1}(e^{a(d/dX)}-e^{-a(d/dX)}) & H_{p0,p0}+H_{p0,p1}(e^{a(d/dX)}+e^{-a(d/dX)}) \end{bmatrix}\begin{bmatrix} A_s(X) \\ A_p(X) \end{bmatrix}=E\begin{bmatrix} A_s(X) \\ A_p(X) \end{bmatrix}.\qquad(2.7)$$

Expression (2.7) is taken for $X=X_L$. One of the solutions can be written in the Bloch form,

$$A_\mu^k(X)=Ce^{ikX}a_\mu^k, \quad -\pi/a<k<\pi/a .\qquad(2.8)$$

Then (2.7) is transformed into

$$\begin{bmatrix} H_{ss}^k & H_{sp}^k \\ H_{sp}^{*k} & H_{pp}^k \end{bmatrix}\begin{bmatrix} a_s^{k\lambda} \\ a_p^{k\lambda} \end{bmatrix}=E^{k\lambda}\begin{bmatrix} a_s^{k\lambda} \\ a_p^{k\lambda} \end{bmatrix},\qquad(2.9)$$

where

$$H_{ss}^k=H_{s0,s0}+H_{s0,s1}2\cos(ka) ,$$

$$H_{pp}^k=H_{p0,p0}+H_{p0,p1}2\cos(ka) ,\qquad(2.10)$$

$$H_{sp}^k=H_{s0,p1}2i\sin(ka) .$$

The eigenequation (2.9) has two solutions (called branches) labeled by the index $\lambda=1,2$. They have, respectively, the energies

$$E^{k1}=\tfrac{1}{2}(H_{ss}^k+H_{pp}^k-h^k), \quad E^{k2}=\tfrac{1}{2}(H_{ss}^k+H_{pp}^k+h^k) ,\qquad(2.11)$$

where

$$h^k=[(H_{ss}^k-H_{pp}^k)^2+4|H_{sp}^k|^2]^{1/2} .$$

The corresponding eigenvectors are

$$\begin{bmatrix} a_s^{k\lambda} \\ a_p^{k\lambda} \end{bmatrix}=[(H_{pp}^k-E^{k\lambda})^2+|H_{sp}^k|^2]^{-1/2}\begin{bmatrix} H_{pp}^k-E^{k\lambda} \\ H_{sp}^k \end{bmatrix};\qquad(2.12)$$

note that $a_s^{k\lambda}$ is real, while $a_p^{k\lambda}$ is imaginary because of (2.10).

Each eigenvalue (2.11) is doubly degenerate since

$$E^{(-k)\lambda} = E^{k\lambda} . \tag{2.13}$$

Therefore we are free to choose alternative eigenvectors, instead of (2.8). These can be any two combinations of $\Psi^{k\lambda}(x)$ and $\Psi^{(-k)\lambda}(x)$. A particularly convenient choice is

$$\Psi^{\pm 1 k\lambda}(x) = \frac{1}{\sqrt{2}}[\Psi^{k\lambda}(x) \pm \Psi^{(-k)\lambda}(x)] . \tag{2.14}$$

To avoid repetition in the counting of the electron states, the wave number k must be taken as $k \geq 0$, for the two states (2.14) denoted by $\Psi^{\omega k\lambda}(x)$, where $\omega = +1, -1$.

With the help of Eqs. (2.3) and (2.8) and taking into account that $a_\mu^{(-k)\lambda} = a_\mu^{*k\lambda}$ on the basis of the equation which is conjugate to Eq. (2.9), we find

$$\begin{bmatrix} A_s^{+1k\lambda}(X) \\ A_p^{+1k\lambda}(X) \end{bmatrix} = \sqrt{2}C \begin{bmatrix} a_s^{k\lambda}\cos(kX) \\ ia_p^{k\lambda}\sin(kX) \end{bmatrix} , \tag{2.15a}$$

$$\begin{bmatrix} A_s^{-1k\lambda}(X) \\ A_p^{-1k\lambda}(X) \end{bmatrix} = \sqrt{2}C \begin{bmatrix} ia_s^{k\lambda}\sin(kX) \\ a_p^{k\lambda}\cos(kX) \end{bmatrix} . \tag{2.15b}$$

It is evident from Eqs. (2.15), (2.3), (2.1), and (2.2) that any combination $\Psi^{\omega k\lambda}(x)$ given in (2.14) exhibits a definite symmetry in respect to the reflection of the coordinate axis at the point $x = 0$, viz., $\Psi^{\omega k\lambda}(x)$ is symmetric for $\omega = +1$ and antisymmetric for $\omega = -1$.

The X dependence of the coefficient function $A_\mu^k(X)$ taken in the Bloch form (2.8) represents a running wave, whereas the coefficient functions given in (2.15) have the

form of standing waves. It follows from the construction of $A_\mu^{\omega k\lambda}(X_L)$ given above that these coefficient functions form the eigenvector of Eq. (2.6) or (2.7) with the eigenvalue $E = E^{k\lambda}$ independent of ω.

An impurity can be introduced to the metal, replacing the matrix atom at $X = 0$. Then Eq. (2.7) is still valid outside the perturbed region, and the same is true for the solutions (2.15), but to construct the general solutions, which must be matched with the solutions valid in the perturbed region, we need in the unperturbed region another set of the solutions of (2.7), which are linearly independent of the solutions $A_\mu^{\omega k\lambda}(X)$ given in Eqs. (2.15). We find these solutions in the form

$$\begin{bmatrix} B_s^{+1k\lambda}(X) \\ B_p^{+1k\lambda}(X) \end{bmatrix} = \sqrt{2}C \begin{bmatrix} a_s^{k\lambda}\sin(k\,|X\,|\,) \\ -ia_p^{k\lambda}\mathrm{sgn}(X)\cos(kX) \end{bmatrix} , \tag{2.16a}$$

$$\begin{bmatrix} B_s^{-1k\lambda}(X) \\ B_p^{-1k\lambda}(X) \end{bmatrix} = \sqrt{2}C \begin{bmatrix} -ia_s^{k\lambda}\mathrm{sgn}(X)\cos(kX) \\ a_p^{k\lambda}\sin(k\,|X\,|\,) \end{bmatrix} . \tag{2.16b}$$

The functions $B_\mu^{\omega k\lambda}(X)$ have the same symmetry properties as the functions $A_\mu^{\omega k\lambda}(X)$. Functions (2.16) are related to the solutions (2.15) in the sense that $\cos\phi$ in A is replaced by $\sin\phi$ in B, while $\sin\phi$ is replaced by $-\cos\phi$, for positive phase ϕ. The symmetry requirements are applied to obtain the functions (2.16) for negative ϕ. By a direct substitution of $B_\mu^{\omega k\lambda}(X)$ instead of $A_\mu^{\omega k\lambda}(X)$ into Eq. (2.7), it may be easily checked that the $B_\mu^{\omega k\lambda}(X)$ are eigenvectors of Eq. (2.7) with eigenvalues $E = E^{k\lambda}$ given in (2.13). As an example, let us check that $B_\mu^{-1k\lambda}(X)$ fulfills the second equation of the set (2.7) in the region of $\phi = kX > 0$:

$$-H_{s0,p1}(e^{a(d/dX)} - e^{-a(d/dX)})B_s^{-1k\lambda}(X) + [H_{p0,p0} + H_{p0,p1}(e^{a(d/dX)} + e^{-a(d/dX)})]B_p^{-1k\lambda}(X)$$

$$= \sqrt{2}C(-H_{s0,p1}(-ia_s^{k\lambda})\{\cos[k(X+a)] - \cos[k(X-a)]\} + H_{p0,p0}a_p^{k\lambda}\sin(kX)$$

$$+ H_{p0,p1}a_p^{k\lambda}\{\sin[k(X+a)] + \sin[k(X-a)]\})$$

$$= \sqrt{2}C\sin(kX)\{-2iH_{s0,p1}a_s^{k\lambda}\sin(ka) + [H_{p0,p0} + H_{p0,p1}2\cos(ka)]a_p^{k\lambda}\}$$

$$= \sqrt{2}C\sin(kX)(H_{sp}^{k*}a_s^{k\lambda} + H_{pp}^k a_p^{k\lambda}) = \sqrt{2}C\sin(kX)E^{k\lambda}a_p^{k\lambda} = E^{k\lambda}B_p^{-1k\lambda}(X) .$$

In this proof we used definitions (2.10) and the fact that the $a_\mu^{k\lambda}$ fulfill Eq. (2.9).

Therefore a general solution for the perturbed crystal may be written as

$$A_{\mu L}^{\mathrm{per},\omega k\lambda} = A_{\mu L}^{\omega k'\lambda}\cos(\delta^{\omega k\lambda}) - B_{\mu L}^{\omega k'\lambda}\sin(\delta^{\omega k\lambda}) . \tag{2.17}$$

The parameter k' is the wave number characterizing the solution in the imperfect crystal. This solution is obtained from that labeled by k for the perfect crystal as a result of perturbation. In particular, the substitution of Eqs. (2.15) and (2.16) into Eq. (2.17) gives

$$\begin{bmatrix} A_{sL}^{\mathrm{per},+1k\lambda} \\ A_{pL}^{\mathrm{per},+1k\lambda} \end{bmatrix} = \sqrt{2}C \begin{bmatrix} a_s^{k\lambda}\cos(k'\,|X_L\,|\,+\delta^{+1k\lambda}) \\ ia_p^{k\lambda}\sin(k'\,|X_L\,|\,+\delta^{+1k\lambda})\mathrm{sgn}(X_L) \end{bmatrix} , \tag{2.18a}$$

$$\begin{bmatrix} A_{sL}^{\mathrm{per},-1k\lambda} \\ A_{pL}^{\mathrm{per},-1k\lambda} \end{bmatrix} = \sqrt{2}C \begin{bmatrix} ia_s^{k\lambda}\sin(k'\,|X_L\,|\,+\delta^{-1k\lambda})\mathrm{sgn}(X_L) \\ a_p^{k\lambda}\cos(k'\,|X_L\,|\,+\delta^{-1k\lambda}) \end{bmatrix} . \tag{2.18b}$$

By comparison of (2.18) with (2.15), we see that the phase $k\,|X\,|$ of the ideal-crystal solution labeled by $\omega k\lambda$ is replaced by the phase $k'\,|X\,|\,+\delta^{\omega k\lambda}$ in the case of the perturbed-crystal solution.

The allowed values of the wave number k, or k', are to be determined from the boundary conditions. We adopt here the cyclic (Born—von Kármán) conditions, according to which a crystal of $N = 2M + 1$ atoms is bent into a circle, so the atom at the crystal end is now in the immediate neighborhood of the atom at the crystal beginning. Then the coefficient function which is symmetric with respect to the central atom (the cosinelike function) must have an extremum at the crystal boundary at $X = R_b = \frac{1}{2}Na$, while the antisymmetric (sinelike) function must go there through zero. Both requirements can be met with a single condition that the phase at the crystal boundary before and after the perturbation is the same:

$$kR_b = n\pi = k'R_b + \delta^{\omega k\lambda} , \tag{2.19}$$

so

$$k' - k = -\delta^{\omega k \lambda}/R_b \ . \tag{2.20}$$

Therefore, if the phase shift $\delta^{\omega k \lambda}$ is known [e.g, from the solution in the perturbed region matched with the solution (2.17) outside this region], then the corresponding perturbed energy can be determined from the unperturbed band energy according to the formula

$$E^{\text{per},\omega k \lambda} = E^{k' \lambda} \Big|_{k' = k - \delta^{\omega k \lambda}/R_b}$$

$$= E^{k \lambda} - \frac{\delta^{\omega k \lambda}}{R_b} \frac{dE^{k \lambda}}{dk} + \cdots \ . \tag{2.21}$$

On the other hand, the truncated expansion (2.21) may be used for an approximate calculation of $\delta^{\omega k \lambda}$ provided the energy shift due to the perturbation, viz., $\Delta E^{\text{per},k \lambda} = E^{\text{per},\omega k \lambda} - E^{k \lambda}$, is a known quantity. This energy shift can be approximated, for example, by the terms which are linear in the perturbation matrix elements calculated according to the first-order perturbation theory:

$$\Delta E^{\text{per},\omega k \lambda} = \sum_{L,\mu,L',\mu'} A_{\mu L}^{*\omega k \lambda} V_{\mu L, \mu' L'} A_{\mu' L'}^{\omega k \lambda} \ . \tag{2.22}$$

So, finally, the phase shift is approximated by

$$\delta^{\omega k \lambda} = -\left[R_b \Big/ \frac{dE^{k \lambda}}{dk} \right]$$

$$\times \left[\sum_{L,\mu,L',\mu'} A_{\mu L}^{*\omega k \lambda} V_{\mu L, \mu' L'} A_{\mu' L'}^{\omega k \lambda} \right] \ . \tag{2.23}$$

Because the perturbation is well localized, the summation over L and L' in (2.23) is limited to the position $X = 0$ and, eventually, some of its neighbors. As an example, let us suppose that the nonzero matrix elements of the localized perturbation are $V_{s0,s0}$ and $V_{p0,p0}$ only. Then,

$$\delta^{+1 k \lambda} = -\left[a \Big/ \frac{dE^{k \lambda}}{dk} \right] V_{s0,s0} |a_s^{k \lambda}|^2 \ ,$$

$$\delta^{-1 k \lambda} = -\left[a \Big/ \frac{dE^{k \lambda}}{dk} \right] V_{p0,p0} |a_p^{k \lambda}|^2 \ , \tag{2.24}$$

where the square of the normalization constant $C^2 = N^{-1} = a/(2R_b)$, together with the condition

$$|a_s^{k \lambda}|^2 + |a_p^{k \lambda}|^2 = 1 \ , \tag{2.25}$$

are taken into account. In the calculation of C we assumed that $\Phi_\mu(x - X_L)$ form an orthonormal set

$$\int dx \, \Phi_\mu^*(x - X_L) \Phi_{\mu'}(x - X_{L'}) = \delta_{LL'} \delta_{\mu\mu'} \ , \tag{2.26}$$

and thus from (2.3) and (2.8) we have

$$1 = \int_{-R_b}^{+R_b} dx \, |\Psi^{k \lambda}(x)|^2$$

$$= \sum_{L,\mu} |A_{\mu L}^{k \lambda}|^2 = C^2 N \sum_{\mu} |a_\mu^{k \lambda}|^2 = C^2 N \ . \tag{2.27}$$

A similar idea of the solution can be applied to an impurity problem in a real, three-dimensional crystal. Then all the above-mentioned steps must be correspondingly modified and extended. The construction of the standing-wave-like solutions, similar to those given in Eq. (2.14), was done in a systematic way in Sec. III of paper I. Then, symmetry properties of the crystal are of considerable use; see Secs. IV and V of paper I. In order to guess the second kind of solutions, which are necessary for the impurity problem and are similar to those given in Eq. (2.16), we are going to expand the coefficient functions obtained for a perfect crystal in terms of spherical harmonics and spherical Bessel functions (Sec. III). Finally, the phase shifts like those given in (2.17) are used to describe the solution for the perturbed crystal; see Eq. (3.25) and Sec. IV.

III. APPROXIMATE SOLUTIONS EXPRESSED IN TERMS OF SPHERICAL EXPANSIONS

A well-known and simple approach to the impurity problem is when the matrix metal is represented by the free electrons enclosed in a spherical potential box.[4-6] The electrons are scattered by an impurity placed at the center of the box, whereas the impurity potential is assumed to have spherical symmetry. The scattered wave functions are expressed in terms of phase shifts. We are now going to generalize this approach for a metal described in terms of the LCAO wave functions. To this purpose we construct in this section an approximate solution that is as close as possible to the scattering picture for free electrons mentioned above.

Let us modify the original Wigner-Seitz shape of the crystal block to be a sphere of radius R_b; the sphere contains N atoms. If v_{at} is the volume per atom, the relation $N v_{\text{at}} = \frac{4}{3} \pi R_b^3$ holds. Obviously, the change of the crystal shape does not influence the bulk properties of the crystal. Consequently, the Wannier-Slater equation (2.11) of I, which determines the energy spectrum and the corresponding coefficient functions $A_\mu(\mathbf{R})$, has to be solved with new boundary conditions. [These solutions $A_\mu(\mathbf{R})$ will be denoted by $\mathscr{A}_\mu(\mathbf{R})$.] Within a spherical box this task can be done approximately in a variational way by expanding the coefficient functions in the series of spherical harmonics (dependent on the angles) multiplied by the spherical Bessel functions (dependent on the radial coordinate). This means the expansion is done in terms of the eigenfunctions of the kinetic-energy operator expressed in a spherical coordinate system:

$$\mathscr{A}_\mu(\mathbf{R}) = \sum_{l=0}^{l_0} \sum_{m=-l}^{l} \sum_{\kappa} a_{\mu l m}^\kappa Y_{lm}\left[\frac{\mathbf{R}}{R}\right] j_l(\kappa R) \ . \tag{3.1}$$

Practically, only a finite number, l_0, of the Bessel functions is used. The allowed values of the radial quantum number κ for each l are determined from zeros z_{ln}, of the Bessel function of this l through the relation $\kappa R_b = z_{ln}$; these κ are limited by $\kappa \leq \kappa_{\text{max}}$. Originally we were interested in the solutions of Eq. (2.11) of I at the discrete points $\mathbf{R} = \mathbf{R}_L$. Now—for the sake of simplicity—we consider these solutions as continuous functions valid at

any point $\mathbf{R}$ within the sphere. Moreover, in the calculation of the matrix elements of $\hat{W}_{\mu\mu'}(\mathbf{R})$ and the scalar products of the functions dependent on $\mathbf{R}$, we integrate over d^3R within the volume of the sphere. These in-

tegrals replace the original summations over $\mathbf{R}_L$ in N atomic positions. Then we arrive at the following eigen-equation:

$$\sum_{\mu',l',m',\kappa'} W_{\mu,\mu'}^{lm\kappa,l'm'\kappa'}[j]a_{\mu'l'm'}^{\kappa'} = E \sum_{\mu',l',m',\kappa'} S_{\mu,\mu'}^{lm\kappa,l'm'\kappa'}[j]a_{\mu'l'm'}^{\kappa'} \ , \tag{3.2}$$

where

$$W_{\mu,\mu'}^{lm\kappa,l'm'\kappa'}[j] = \int_{4\pi} d^2\Omega_{(\mathbf{R}/R)} \int_0^{R_b} dR\,R^2 Y_{lm}^*\left[\frac{\mathbf{R}}{R}\right] j_l(\kappa R)\hat{W}_{\mu\mu'}(\mathbf{R})Y_{l'm'}\left[\frac{\mathbf{R}}{R}\right]j_{l'}(\kappa' R) \tag{3.3a}$$

and

$$S_{\mu,\mu'}^{lm\kappa,l'm'\kappa'}[j] = \int_{4\pi} d^2\Omega_{(\mathbf{R}/R)} \int_0^{R_b} dR\,R^2 Y_{lm}^*\left[\frac{\mathbf{R}}{R}\right] j_l(\kappa R)\delta_{\mu\mu'}Y_{l'm'}\left[\frac{\mathbf{R}}{R}\right]j_{l'}(\kappa' R) \ . \tag{3.3b}$$

The symbol $[j]$ on the left-hand sides of (3.3) points to the fact that the matrix elements are calculated on the basis of the spherical Bessel functions j_l and $j_{l'}$.

A general treatment of Eq. (3.2) is a very complicated task, but the problem may be much simplified if, instead of solutions valid within the whole spherical crystal, we consider the solutions in a restricted crystal, which has a sphere of radius R_s hollowed out from the crystal center. This R_s has to be large enough that the Bessel functions entering Eq. (3.3) and integrated within the interval $R_s < R < R_b$ can be approximated by the first term of their asymptotic expansions. Let us note that within the interval $R_s < R < R_b$ the Wannier-Slater operator is not affected by the perturbation due to impurities, since the impurities are located close to the crystal center. Therefore in the same interval we may look for $\mathscr{B}_\mu(\mathbf{R})$—the second kind of solutions of the Wannier-Slater equation (2.11) of I besides the solutions (3.1). These are the combinations of the products of the spherical Neumann functions $n_l(\kappa R)$ and the spherical harmonics $Y_{lm}(\mathbf{R}/R)$, because these products are the second kind of the eigenfunctions of the kinetic-energy operator. Consequently, we try the following form of the coefficient function:

$$\mathscr{B}_\mu(\mathbf{R}) = \sum_{l=0}^{l_0} \sum_{m=-l}^{l} \sum_\kappa \mathscr{A}_{\mu lm}^\kappa Y_{lm}\left[\frac{\mathbf{R}}{R}\right]n_l(\kappa R) \ . \tag{3.4}$$

This function, when substituted into the Wannier-Slater equation (2.11) of paper I in place of $A_\mu(\mathbf{R})$, leads to the following matrix equation:

$$\sum_{\mu',l',m',\kappa'} W_{\mu,\mu'}^{lm\kappa,l'm'\kappa'}[n]\mathscr{A}_{\mu'l'm'}^{\kappa'}$$
$$= E \sum_{\mu',l',m',\kappa'} S_{\mu,\mu'}^{lm\kappa,l'm'\kappa'}[n]\mathscr{A}_{\mu'l'm'}^{\kappa'} \ . \tag{3.5}$$

The form of the matrix elements W and S is the same as given in (3.3), except that the functions j_l are replaced by the functions n_l. Because the inner sphere within the crystal is removed, the lower limit of the integrals over R entering (3.3) must now be R_s instead of the limit 0. The radius R_s must satisfy the following two conditions:

$$\kappa R_s \gg l_0$$

and

$$\kappa(R_b - R_s) \gg \pi$$

for any κ within the range of interest. The first condition allows for the use of the following asymptotic expressions:

$$j_l(z) = \begin{cases} \pm\dfrac{\sin(z)}{z} + O\left[\dfrac{1}{z^2}\right] & \text{for } l = 4k+1\mp1 \ , \\[3mm] \mp\dfrac{\cos(z)}{z} + O\left[\dfrac{1}{z^2}\right] & \text{for } l = 4k+2\mp1 \ , \end{cases}$$
$$k = 0, \pm1, \ldots \ . \tag{3.6}$$

Analogous asymptotic expressions hold for $n_l(z)$; they can be easily obtained from (3.6) because for large z we have

$$n_l(z) = j_{l+1}(z) + O\left[\frac{1}{z^2}\right] \ . \tag{3.7}$$

If f_l denotes either j_l or n_l, and the formulas (3.6) or (3.7) are applied, we find, for the overlap integral (3.3b),

$$S_{\mu,\mu'}^{lm\kappa,l'm'\kappa'}[f] = \delta_{\mu'\mu}\delta_{l'l}\delta_{m'm}\delta_{\kappa'\kappa}\mathscr{C}(\kappa) \ , \tag{3.8}$$

where

$$\mathscr{C}(\kappa) = \int_{R_s}^{R_b} dR\,R^2 \left[\frac{\sin(\kappa R)}{\kappa R}\right]^2$$
$$= \int_{R_s}^{R_b} dR\,R^2 \left[\frac{\cos(\kappa R)}{\kappa R}\right]^2 = \tfrac{1}{2}(R_b - R_s)/\kappa^2 \ . \tag{3.9}$$

The result (3.8) has a diagonal form in the indices l and m because the spherical harmonics Y_{lm} are orthonormal functions. For $\kappa' \neq \kappa$ the integrand in the radial part of the integration is a sum of two oscillating functions (sine or cosine) with the arguments equal to $(\kappa' - \kappa)R$ and $(\kappa' + \kappa)R$. These functions, when integrated over many of their periods (see the second condition for R_s), give a result which is negligibly small in comparison to (3.9). In the case of $\kappa' = \kappa$, the corresponding radial part of the integral is calculated in (3.9). To analyze in some detail the matrix elements of $\hat{W}_{\mu\mu'}$, Eqs. (3.3a), we need to examine

the structure of their components. A well-known fact is that spherical harmonics may be expressed as the following multiple sums:

$$Y_{lm}\left[\frac{\mathbf{R}}{R}\right]=\sum_{i_1,i_2,i_3} y_{lm}^{i_1 i_2 i_3}\left[\frac{X}{R}\right]^{i_1}\left[\frac{Y}{R}\right]^{i_2}\left[\frac{Z}{R}\right]^{i_3}, \qquad (3.10)$$

where

$$\mathbf{R}=(X,Y,Z), \quad 0\le i_1+i_2+i_3\le l, \quad i_n=0,1,2,\dots .$$

The exponent occurring in the operator (2.12) of paper I

$$w_{lkl'\kappa'}^{isi'}[f]=\int_{4\pi}d^2\Omega(\mathbf{R}/R)\int_{R_s}^{R_b}dR\,R^2\left[\frac{X}{R}\right]^{i_1}\left[\frac{Y}{R}\right]^{i_2}\left[\frac{Z}{R}\right]^{i_3}f_l(\kappa R)\left[\frac{\partial}{\partial X}\right]^{s_1}\left[\frac{\partial}{\partial Y}\right]^{s_2}\left[\frac{\partial}{\partial Z}\right]^{s_3}\left[\frac{X}{R}\right]^{i_1'}\left[\frac{Y}{R}\right]^{i_2'}\left[\frac{Z}{R}\right]^{i_3'}$$

$$\times f_{l'}(\kappa'R) . \qquad (3.13)$$

The differentiation of the versor $\mathbf{R}/R$ component, e.g.,

$$\frac{\partial}{\partial X}\left[\frac{X}{R}\right]=\frac{1}{R}\left[1-\left[\frac{X}{R}\right]^2\right], \qquad (3.14)$$

gives the result which is approximately R^{-1} times smaller then the original expression; since R is large results of this kind can be neglected. The repetition of the differentiations of this kind leave (3.13) with the differential operators acting only on the function $f_{l'}(\kappa'R)$. Let us recall the exact relation which is valid for the spherical functions, either j_l or n_l, viz.,

$$\frac{d}{dz}f_l(z)=f_{l-1}(z)-\frac{l+1}{z}f_l(z) . \qquad (3.15)$$

This relation allows us to calculate the following derivative:

$$\frac{\partial}{\partial X}f_l(\kappa R)=\kappa\left[\frac{X}{R}\right]\left[f_{l-1}(\kappa R)-\frac{l+1}{\kappa R}f_l(\kappa R)\right]. \qquad (3.16)$$

The second term, as it is proportional to R^{-1}, is negligible. The repetition of these steps finally gives

$$w_{lkl'\kappa'}^{isi'}[f]=(\kappa')^{(s_1+s_2+s_3)}w_{i+s+i'}^{\text{ang}}$$

$$\times w_{lk(l'-s_1-s_2-s_3)\kappa'}^{\text{rad}}[f] , \qquad (3.17)$$

where

$$w_{\mathbf{t}}^{\text{ang}}=\int_{4\pi}d^2\Omega_{(\mathbf{R}/R)}\left[\frac{X}{R}\right]^{t_1}\left[\frac{Y}{R}\right]^{t_2}\left[\frac{Z}{R}\right]^{t_3}, \qquad (3.18)$$

$$w_{lkl''\kappa'}^{\text{rad}}[f]=\int_{R_s}^{R_b}dR\,R^2 f_l(\kappa R)f_{l''}(\kappa'R) . \qquad (3.19)$$

The radial integral (3.19) may be easily calculated applying (3.6), (3.7), and taking into account the arguments which were used in the calculation of the overlap integral (3.8). This gives

can be expanded in the power series

$$\hat{W}_{\mu\mu'}(\mathbf{R})=\sum_{s_1,s_2,s_3}h_{\mu\mu'}^{s_1 s_2 s_3}\left[\frac{\partial}{\partial X}\right]^{s_1}\left[\frac{\partial}{\partial Y}\right]^{s_2}\left[\frac{\partial}{\partial Z}\right]^{s_3}$$

$$s_n=0,1,2,\dots \quad (3.11)$$

so the matrix element (3.3a) is

$$W_{\mu,\mu'}^{lm\kappa,l'm'\kappa'}[f]=\sum_{i,s,i'}y_{lm}^{*i}h_{\mu\mu'}^s\,y_{l'm}^{i'}\cdot w_{lkl'\kappa'}^{isi'}[f] , \qquad (3.12)$$

where

$$w_{lkl''\kappa'}^{\text{rad}}[f]=\delta_{\kappa'\kappa}\begin{cases}\pm\mathscr{C}(\kappa) & \text{for } l-l''=4k-1\pm 1 , \\ 0 & \text{for } l-l''=2k+1 ,\end{cases}$$

$$k=0,\pm 1,\dots . \quad (3.20)$$

The results obtained imply the following conclusions:

(i) Both the overlap integral (3.8) and the matrix elements of $\hat{W}$ given in Eq. (3.12) and calculated with the aid of (3.17) and (3.20) are the quantities proportional to $\delta_{\kappa'\kappa}$. Therefore, Eqs. (3.2) and (3.5) can be solved separately for each κ. The eigenvalues and the eigenvectors can be labeled by the quantum number κ and the branch index Λ and be determined from the equations

$$\sum_{\mu',l',m'}W_{\mu,\mu'}^{lm\kappa,l'm'\kappa}[j]a_{\mu'l'm'}^{\kappa\Lambda}=E_a^{\kappa\Lambda}\mathscr{C}(\kappa)a_{\mu lm}^{\kappa\Lambda} , \qquad (3.21a)$$

$$\sum_{\mu',l',m'}W_{\mu,\mu'}^{lm\kappa,l'm'\kappa}[n]\mathscr{b}_{\mu'l'm'}^{\kappa\Lambda}=E_{\mathscr{b}}^{\kappa\Lambda}\mathscr{C}(\kappa)\mathscr{b}_{\mu lm}^{\kappa\Lambda} . \qquad (3.21b)$$

(ii) The values of the overlap integrals (3.8) and the matrix elements (3.12) of $\hat{W}$ when calculated with the aid of n_l are the same as those calculated with the aid of j_l. Therefore the eigenvectors $a_{\mu lm}^{\kappa\Lambda}$ and $\mathscr{b}_{\mu lm}^{\kappa\Lambda}$ are the same—this also holds for the eigenvalues corresponding to these eigenvectors:

$$E_a^{\kappa\Lambda}=E_{\mathscr{b}}^{\kappa\Lambda}=E^{\kappa\Lambda} .$$

This makes the following conclusion possible:

(iii) Two approximate solutions of the eigenequation (2.11) of paper I, calculated for an ideal spherical crystal in which some volume around the crystal center is removed, are the following:

$$\mathscr{A}_\mu^{\kappa\Lambda}(\mathbf{R})=\sum_{l,m}a_{\mu lm}^{\kappa\Lambda}Y_{lm}\left[\frac{\mathbf{R}}{R}\right]j_l(\kappa R) , \qquad (3.22a)$$

$$\mathscr{B}_\mu^{\kappa\Lambda}(\mathbf{R})=\sum_{l,m}a_{\mu lm}^{\kappa\Lambda}Y_{lm}\left[\frac{\mathbf{R}}{R}\right]n_l(\kappa R) . \qquad (3.22b)$$

The coefficients $a_{\mu lm}^{\kappa\Lambda}$ which enter (3.22a) and (3.22b) may be determined from Eq. (3.21a).

(iv) Furthermore, the two solutions (3.22) are mutually orthogonal [cf. here Eq. (3.18) of paper I],

$$\sum_\mu \int_{R_s < R < R_b} d^3R \, \mathscr{A}_\mu^{*\kappa\Lambda}(\mathbf{R})\mathscr{B}_\mu^{\kappa'\Lambda'}(\mathbf{R}) = 0 , \quad (3.23)$$

i.e., they are linearly independent. This is so because the radial integral occurring on the left-hand side of (3.23) is

$$\int_{R_s}^{R_b} dR \, R^2 j_l(\kappa R) n_l(\kappa'R) = 0 . \quad (3.24)$$

For $\kappa \neq \kappa'$ the result (3.24) follows immediately from (3.6), (3.7), and the argument similar to that used in the calculation of (3.8). In the case of $\kappa = \kappa'$ the integrand in (3.24) is proportional to

$$\sin(\kappa R)\cos(\kappa R) = \tfrac{1}{2}\sin(2\kappa R) ,$$

so it is an oscillating function which, when integrated, leads to the result (3.24).

(v) Since the two solutions are linearly independent, the general solution that must be used for a perturbed crystal at positions $\mathbf{R}$, which are far from the perturbation region, is

$$\mathscr{A}_\mu^{\text{per},\kappa\Lambda}(\mathbf{R}) = \mathscr{A}_\mu^{\kappa'\Lambda}(\mathbf{R})\cos(\delta^{\kappa\Lambda}) - \mathscr{B}_\mu^{\kappa'\Lambda}(\mathbf{R})\sin(\delta^{\kappa\Lambda})$$
$$= \sum_l \left[\sum_m a_{\mu lm}^{\kappa\Lambda} Y_{lm}\left(\frac{\mathbf{R}}{R}\right) \right] j_l(\kappa'R + \delta^{\kappa\Lambda}) . \quad (3.25)$$

This expression is fully analogous to the result obtained for the case of a one-dimensional crystal, Eqs. (2.17) and (2.18). The phase shifts $\delta^{\kappa\Lambda}$ can be obtained, in principle, from the information regarding the perturbation potential.

(vi) The radial quantum number κ' of the perturbed state is related to the corresponding parameter κ of the unperturbed state by the requirement that the phase at the crystal boundary calculated either in the presence or the absence of impurities must remain unchanged. This gives the relation

$$\kappa R_b = \kappa'R_b + \delta^{\kappa\Lambda} , \quad (3.26)$$

and hence

$$\kappa' = \kappa - \delta^{\kappa\Lambda}/R_b . \quad (3.27)$$

(vii) The allowed values of the radial quantum number κ are to be determined from the zeros of the Bessel function. In the region of large R considered, this function is either a sine or cosine, Eq. (3.6). Therefore, $\kappa R_b = n\pi$ or $\kappa R_b = n\pi + \tfrac{1}{2}\pi$ for l even or odd, respectively. The number n is a positive integer. In each case the two consecutive allowed κ's are separated by the interval

$$\Delta\kappa = \pi/R_b , \quad (3.28)$$

which is the same as that obtained by Friedel in a free-electron case.

In general, Eq. (3.21a) represents a system of equations of a very high rank, so it is still too complicated for practical use. For this reason, in the next section we will construct a different set of the approximate solutions which rely, however, on the conclusions (i)—(vii) established above.

Nevertheless, an equation similar to Eq. (3.21a) has been solved before[20] under certain simplifying assumptions. These were (i) only a single atomic orbital (s-like one) present in the metal, and (ii) a very small number of the Bessel functions were considered ($l_0 \leq 20$). Taking the advantage of the symmetry of the crystal, spherical harmonics could be replaced by cubic harmonics. This reduced, for the Γ_1 representation, the size of the eigenequation to values not exceeding 14. In spite of this very limited basis, the density of states obtained in these calculations was quite accurate. Another conclusion which followed from these papers concerned the energy dispersion curves. They were obtained there as the plots of energy versus κ for fixed Λ; so $E = E^{\kappa\Lambda}$. These curves resembled well the dispersion curves of the Bloch solutions, $E = E^{\mathbf{k}\lambda}$, calculated as the functions of $k = |\mathbf{k}|$ at fixed direction $\mathbf{k}/k$ and for a given branch of solution λ. This correspondence between the two kinds of dispersion curves for energy will be exploited in the next section.

IV. APPLICATION OF THE APPROXIMATE SOLUTIONS TO THE IMPURITY PROBLEM

The variational method for the calculation of the coefficient functions $\mathscr{A}_\mu(\mathbf{R})$ given in Sec. III seems impractical in its applications because of the very high rank of the matrices involved. To circumvent this difficulty, we now try to transform the SWLPC functions derived in Sec. III of paper I into the solutions that have had all their qualitative properties established in the preceding section.

The SWLPC function depends on $\mathbf{R}$ through the combination of $e^{i\mathbf{k}\cdot\mathbf{R}}$; see Eqs. (3.10) and (3.11) of paper I. Any plane-wave function has a well-known expansion in the series of the spherical Bessel functions:

$$e^{i\mathbf{k}\cdot\mathbf{R}} = \sum_{l=0}^\infty i^l(2l+1)P_l\left[\frac{\mathbf{k}\cdot\mathbf{R}}{kR}\right]j_l(kR) . \quad (4.1)$$

Let us denote by $e_{l_0}^{i\mathbf{k}\cdot\mathbf{R}}$ the series (4.1) truncated on some term $l = l_0$, so $e_{l_0}^{i\mathbf{k}\cdot\mathbf{R}}$ is a finite sum over l up to l_0. This truncated function is a good approximation to the original plane-wave function,

$$| e^{i\mathbf{k}\cdot\mathbf{R}} - e_{l_0}^{i\mathbf{k}\cdot\mathbf{R}} | \ll 1 ,$$

on the condition that the argument

$$kR \lesssim l_0/2 .$$

The same approximation is true for $A_{l_0\mu}^{\omega\mathbf{k}\lambda}(\mathbf{R})$, which is the modified SWLPC function (3.10) of paper I constructed according to Eq. (3.11) of I on the basis of the truncated plane waves $e_{l_0}^{i(\hat{T}\mathbf{k})\cdot\mathbf{R}_L}$ taken instead of $e^{i(\hat{T}\mathbf{k})\cdot\mathbf{R}_L}$. In a limiting situation of very large l_0, the approximate solutions $A_{l_0\mu}^{\omega\mathbf{k}\lambda}(\mathbf{R})$ are very close to the exact solutions $A_\mu^{\omega\mathbf{k}\lambda}(\mathbf{R})$. The parameter $k = |\mathbf{k}|$ present in $A_{l_0\mu}^{\omega\mathbf{k}\lambda}(\mathbf{R})$ plays the same role as the argument κ of the Bessel and Neumann functions given in (3.22). In addition to the symmetry index ω and the branch index λ, the approximate solution $A_{l_0\mu}^{\omega\mathbf{k}\lambda}(\mathbf{R})$ is characterized also by $\tau = \mathbf{k}/k$—the direction of the wave vector.

Now we will consider the function proportional to $A_{l_0\mu}^{\omega k\tau\lambda}(\mathbf{R})$ as an approximate solution to the Wannier-Slater equation (2.11) of paper I, similar to the function $\mathscr{A}_\mu^{\kappa\Lambda}(\mathbf{R})$ discussed in Sec. III of the present paper. This approximation is supported also by the correspondence between the dispersion curves mentioned at the end of Sec. III. In order to account properly for the number of states represented by the approximate solutions, many different directions τ_i must be taken into account. Let their number be denoted by $i_{\max}$. We assume the directions are *uniformly* distributed in the solid angle corresponding to the irreducible part of the Brillouin zone [see Eq. (3.17a) of paper I]:

$$\tau_i = \mathbf{k}_i / k_i, \quad \mathbf{k}_i \in \mathsf{v}_{\text{IBZ}}, \quad i = 1, 2, \ldots, i_{\max} \quad (4.2)$$

(IBZ denotes the irreducible Brillouin zone). The approximate wave function must be normalized. Because of the mentioned proportionality, we postulate that the new SWLPC function, which is quantized in a spherical box, has the form

$$A_\mu^{\text{sph},\omega k\tau_i\lambda}(\mathbf{R}) = \left[\frac{S_{l_0}^k}{\sum\limits_{\omega',\mu'} |A_{\mu'}^{\omega' k\tau_i\lambda}(\mathbf{0})|^2}\right]^{1/2} A_{l_0\mu}^{\omega k\tau_i\lambda}(\mathbf{R}) .$$

$$(4.3)$$

Note that $A_{l_0\mu}^{\omega k\tau_i\lambda}(\mathbf{0}) = A_\mu^{\omega k\tau_i\lambda}(\mathbf{0})$. The eigenenergy corresponding to the function (4.3) is $E^{k\tau_i\lambda}$.

Let us now determine the factor $S_{l_0}^k$ and the number of directions $i_{\max}$. First we note that the radial quantum number κ and the length k of the wave vector $\mathbf{k}$ are identical: $\kappa = k$. This is so because the eigenvalue k^2 of the kinetic-energy operator calculated in the Cartesian-coordinate system and the eigenvalue κ^2 calculated in a spherical coordinate system must be the same. As was mentioned in Sec. III of paper I, index ω runs over d_g values and index λ runs over σ values, so the number of states represented by the solutions $A_\mu^{\text{sph},\omega k\tau_i\lambda}(\mathbf{R})$ taken for a given k is

$$d_g i_{\max} \sigma .$$

The number of states represented by the solutions $\mathscr{A}_\mu^{\kappa\Lambda}(\mathbf{R})$ for a given $\kappa = k$ is equal to the number of branches $\Lambda_{\max}$ obtained in the diagonalization process; therefore it must be equal to the number of possible sets of the indices μ, l, m which label the basis functions and the coefficients entering Eqs. (3.21). Because μ runs over σ values, l is an integer from 0 to l_0, and m has $2l+1$ possible values for each l, the total number of solutions is

$$\Lambda_{\max} = \sigma \sum_{l=0}^{l_0} (2l+1) = \sigma(l_0+1)^2 . \quad (4.4)$$

The requirement that the number of states is the same for the two kinds of solutions considered gives therefore

$$i_{\max} = (l_0+1)^2/d_g . \quad (4.5)$$

The next step toward $S_{l_0}^k$ is the calculation of the number

of all electron states characterized by the absolute value k of the wave vector $\mathbf{k}$ from the range $[k, k+dk]$. This can be done using the solutions (4.3) on one hand and the Bloch solutions $A_\mu^{\mathbf{k}\lambda}(\mathbf{R})$ given in Eq. (2.13) of paper I on the other. In both cases the contributions obtained per atomic site, say $\mathbf{R}_L = 0$, are taken into account. If both results are set equal we obtain the equation

$$\left[\frac{dk}{\pi/R_b}\right] \sum_{\omega,i,\lambda} \sum_\mu |A_\mu^{\text{sph},\omega k\tau_i,\lambda}(\mathbf{0})|^2$$

$$= \left[\frac{4\pi k^2 dk}{v_{\text{BZ}}/N}\right] \sum_\lambda \sum_\mu |A_\mu^{\mathbf{k}\lambda}(\mathbf{0})|^2 . \quad (4.6)$$

The factor within large parentheses on the left-hand side (lhs) of (4.6) represents the number of allowed values of the radial quantum parameter k in the range $[k, k+dk]$, calculated with the help of Eq. (3.28). The factor within large parentheses on the right-hand side of (4.6) represents the number of the wave vectors $\mathbf{k}$ whose ends point to the spherical shell of the radius k and the thickness dk. The volume per vector point is $(1/N)$th of the Brillouin-zone (BZ) volume, which is $v_{\text{BZ}} = (2\pi)^3/v_{\text{at}}$, where v_{at} is the crystal volume per atom. The application of the definition (4.3) to the lhs of (4.6) and the substitution of (2.13) of paper I, together with (2.19) of I, to the rhs of (4.6), gives

$$\frac{R_b}{\pi} \sum_{i=1}^{i_{\max}} \sum_{\lambda=1}^\sigma S_{l_0}^k = \frac{4\pi k^2 N}{v_{\text{BZ}}} \sum_{\lambda=1}^\sigma \frac{1}{N} ,$$

which leads to the following expression for the normalization factor:

$$S_{l_0}^k = \frac{\pi}{R_b} \frac{k^2}{v_{\text{BZ}}} \frac{4\pi}{i_{\max}} . \quad (4.7)$$

Similar to the function $A^{\text{sph},\omega k\tau_i\lambda}(\mathbf{R})$, we may introduce the function $B^{\text{sph},\omega k\tau_i\lambda}(\mathbf{R})$ as a second solution of Eq. (2.11) of paper I in the region far from the perturbation. Since the SWLPC function $A^{\text{sph},\omega k\tau_i\lambda}(\mathbf{R})$ is approximately equivalent to the function $\mathscr{A}_\mu^{\kappa\Lambda}(\mathbf{R})$, it is reasonable to assume that the function $B_\mu^{\text{sph},\omega k\tau_i\lambda}(\mathbf{R})$ is approximately equivalent to the function $\mathscr{B}_\mu^{\kappa\Lambda}(\mathbf{R})$ given in (3.22b). Following Sec. III, the function $B_\mu^{\text{sph},\omega k\tau_i\lambda}(\mathbf{R})$ can be obtained from the function $A_\mu^{\text{sph},\omega k\tau_i\lambda}(\mathbf{R})$ by means of replacement of any $j_l(kR)$ by $n_l(kR)$. Therefore the general solution in the crystal region far from impurities may be written as [cf. Eq. (3.25)]

$$A_\mu^{\text{per},\omega k\tau_i\lambda}(\mathbf{R}) = A_\mu^{\text{sph},\omega k'\tau_i\lambda}(\mathbf{R})\cos(\delta^{\omega k\tau_i\lambda})$$

$$- B_\mu^{\text{sph},\omega k'\tau_i\lambda}(\mathbf{R})\sin(\delta^{\omega k\tau_i\lambda}) . \quad (4.8)$$

According to the second part of Eq. (3.25), expression (4.8) should have the same form as the unperturbed solution $A_\mu^{\text{sph},\omega k\tau_i\lambda}(\mathbf{R})$, but the argument of each Bessel functions j_l is changed from kR to $k'R + \delta^{\omega k\tau_i\lambda}$. The boundary condition applied at the radius R_b of the spherical crystal gives the following relation between the phase shift $\delta^{\omega k\tau_i\lambda}$ and the change of the wave-vector length:

$$k'-k=-\delta^{\omega k \tau_i \lambda}/R_b \qquad (4.9)$$

[cf. Eq. (3.27)].

A rigorous way to obtain the phase shift is to solve the eigenequation (2.20) of paper I for the perturbed crystal in the region of impurities and then match this solution with the solution (4.8) valid outside the perturbed region. In the present paper we give a very simple, though very approximate, estimate of the phase shift. First, the eigenenergy of the crystal with impurities is calculated by means of the rigid-band approximation. This means that degeneracy among the states having different τ_i, ω, etc. is neglected. The energy is

$$E^{\mathrm{per},\omega k \tau_i \lambda}=E^{k \tau_i \lambda}+\sum_{L,\mu,L',\mu'} A_{\mu}^{*\,\mathrm{sph},\omega k \tau_i \lambda}(\mathbf{R}_L)$$
$$\times V_{\mu L,\mu'L'} A_{\mu}^{\mathrm{sph},\omega k \tau_i \lambda}(\mathbf{R}_{L'}) \ .$$

$$(4.10)$$

On the other hand, the perturbed crystal energy must be the same as the eigenenergy of the unperturbed crystal calculated at k shifted to k':

$$E^{\mathrm{per},\omega k \tau_i \lambda}=E^{k'\tau_i \lambda}=E^{k \tau_i \lambda}+\frac{\partial E^{k \tau_i \lambda}}{\partial k}(k'-k)+\cdots .$$

$$(4.11)$$

Taking into account in (4.11) and (4.10) only the terms linear in the perturbation potential and using (4.9) and (4.3), we obtain

$$\delta^{\omega k \tau_i \lambda}=-\widetilde{V}^{\omega k \tau_i \lambda}S_{l_0}^k R_b \bigg/ \frac{\partial E^{k \tau_i \lambda}}{\partial k} , \qquad (4.12)$$

where

$$\widetilde{V}^{\omega k \tau_i \lambda}=\sum_{L,\mu,L',\mu'} A_{\mu}^{*\,\omega k \tau_i \lambda}(\mathbf{R}_L)V_{\mu L,\mu'L'}A_{\mu'}^{\omega k \tau_i \lambda}(\mathbf{R}_{L'}) \bigg/ \left[\sum_{\omega',\mu''} |A_{\mu''}^{\omega' k \tau_i \lambda}(0)|^2\right]=\frac{V^{\omega k \tau_i \lambda,\omega k \tau_i \lambda}}{\rho^{k \tau_i \lambda}(0)} \qquad (4.13)$$

[cf. Eqs. (8.1) and (5.5) of paper I] is introduced to denote the expression whose meaning is the average perturbation energy over the state labeled by ω, k, τ_i, and λ. The subscript l_0 in the SWLPC functions has been omitted in (4.13) because at the lattice positions $\mathbf{R}=\mathbf{R}_L$, where the perturbation is important ($\mathbf{R}_L$ close to $\mathbf{R}=0$), the difference between $A_{l_0\mu}(\mathbf{R})$ and $A_{\mu}(\mathbf{R})$ is negligible. Expression (4.12) is the main result of the present paper: The phase shift is expressed in terms of (i) the matrix elements of the perturbation $V_{\mu L,\mu'L'}$, (ii) the eigenenergy $E^{k \tau_i \lambda}=E^{\mathbf{k}\lambda}$ of the Bloch solution, and (iii) the combinations of the corresponding eigenvectors $A_{\mu}^{\omega k \lambda}(\mathbf{R}_L)$, which form the SWLPC functions.

V. RELATION BETWEEN THE DENSITY OF STATES AND THE PHASE SHIFT

To establish the relation between the density of states and the phase shift, we recall several standard definitions. The total number of electrons which are in the band λ and have energy less than ε is

$$N_\lambda(\varepsilon)=2\frac{N}{v_{\mathrm{BZ}}}\int_{v_{\mathrm{BZ}}} d^3 k \,\Theta(\varepsilon-E^{\mathbf{k}\lambda}) , \qquad (5.1)$$

where $\Theta(x)$ is a Heaviside step function. If $D_\lambda(\varepsilon)$ is the density of states of the λth band calculated per one atom and one kind of spin, then

$$N_\lambda(\varepsilon)=2N\int_{-\infty}^{\varepsilon} D_\lambda(\varepsilon')d\varepsilon' . \qquad (5.2)$$

This gives

$$D_\lambda(\varepsilon)=\frac{1}{2N}\frac{d}{d\varepsilon}N_\lambda(\varepsilon)=\frac{1}{v_{\mathrm{BZ}}}\int_{v_{\mathrm{BZ}}}d^3 k \,\delta(\varepsilon-E^{\mathbf{k}\lambda})=\frac{1}{v_{\mathrm{BZ}}}\int_{4\pi}d^2\Omega_\tau\int_0^{k_{\mathrm{BZ}}(\tau)}dk\,k^2\delta(\varepsilon-E^{k\tau\lambda}) . \qquad (5.3)$$

Here, $k_{\mathrm{BZ}}(\tau)$ is the distance from the center of the BZ to the BZ surface taken along the direction τ. Let $k=k_j^{\tau\lambda}(\varepsilon)$ be the jth solution of the equation

$$\varepsilon-E^{k\tau\lambda}=0 \qquad (5.3a)$$

for k taken from the interval $[0,k_{\mathrm{BZ}}(\tau)]$. (If ε is outside the band λ, there is no solution.) Therefore the δ function occurring in (5.3) may be transformed

$$\delta(\varepsilon-E^{k\tau\lambda})=\sum_j\frac{1}{|\partial E^{k\tau\lambda}/\partial k|}\delta(k-k_j^{\tau\lambda}(\varepsilon)) . \qquad (5.4)$$

Using (5.4) and the point symmetry of the crystal, we obtain from (5.3),

$$D_\lambda(\varepsilon)=\frac{d_g}{v_{\mathrm{BZ}}}\int_{v_{\mathrm{IBZ}}}d^2\Omega_\tau$$
$$\times\sum_j\left[\frac{k^2}{|\partial E^{k\tau\lambda}/\partial k|}\right]_{k=k_j^{\tau\lambda}(\varepsilon)} . \qquad (5.5)$$

Here the integral over the solid angle is performed over $4\pi/d_g$ as it is limited by v_{IBZ}. A connection with expression (4.12) derived for the phase shift can be obtained if the solid-angle integral given in (5.5) is represented as a Riemann sum calculated over the uniformly distributed directions τ_i; see Eq. (4.2). Then,

$$D_\lambda(\varepsilon) = \frac{d_g}{v_{\text{BZ}}} \sum_{i=1}^{i_{\text{max}}} \Delta\Omega \sum_j \left[\frac{k^2}{|\partial E^{k\tau_i\lambda}/\partial k|} \right]_{k=k_j^{\tau_i\lambda}(\varepsilon)} ,$$

$$(5.6)$$

where

$$\Delta\Omega = \frac{4\pi}{d_g i_{\text{max}}} .$$

Finally,

$$D_\lambda(\varepsilon) = \sum_{i=1}^{i_{\text{max}}} \sum_j D_\lambda^{ij}(\varepsilon) ,$$

$$(5.7)$$

where

$$D_\lambda^{ij}(\varepsilon) = \frac{4\pi}{i_{\text{max}} v_{\text{BZ}}} \left[\frac{k^2}{|\partial E^{k\tau_i\lambda}/\partial k|} \right]_{k=k_j^{\tau_i\lambda}(\varepsilon)} .$$

$$(5.8)$$

Expression (5.8) is the contribution to the density of states connected with the ith direction within v_{IBZ} and the jth isoenergetic sheet of $E^{k\lambda}$ within the λth band. Comparing (5.8) with (4.12) and (4.7), we arrive at the relation

$$\delta^{\omega k\tau_i\lambda} = -\tilde{V}^{\omega k\tau_i\lambda} \pi D_\lambda^{ij}(\varepsilon) \text{sgn} \left[\frac{\partial E^{k\tau_i\lambda}}{\partial k} \right] .$$

$$(5.9)$$

The energy ε and index j are related to i and k through Eq. (5.3a) taken for $\tau = \tau_i$, since k must be the jth solution of this equation.

We see that the phase shift is represented as a product of two factors: (i) $\tilde{V}^{\omega k\tau_i\lambda}$, which depends on the perturbation matrix elements due to impurities and the properties of the state being perturbed according to Eq. (4.13); and (ii) $D_\lambda^{ij}(\varepsilon)$, which represents the properties of the λth band of the ideal crystal, namely its (i,j)th contribution to the density of states. This proportionality of the phase shift to a component of the density of states can be compared with a similar result obtained earlier for the free-electron case.[21,22]

VI. CHANGE OF THE ELECTRON CHARGE DUE TO AN IMPURITY

Friedel[6] has shown that the change of the electron number in a metal due to an impurity is

$$\delta n_l = \frac{1}{R_b} \left[\frac{\partial \delta_l(k)}{\partial k} + \cdots \right]$$

$$(6.1)$$

where the ellipsis represents additional oscillatory terms. This change is calculated per electron state labeled by the quantum numbers k,l,m; the calculation has been done for the simplest model of a metal, where the free electrons enclosed in a spherical box are scattered on a spherically symmetric potential. The approximate solution (4.8) is a generalization of the Friedel solution since both functions $A_\mu^{\text{sph},\omega k'\tau_i\lambda}(\mathbf{R})$ and $B_\mu^{\text{sph},\omega k'\tau_i\lambda}(\mathbf{R})$ happen to be the eigenfunctions of the kinetic-energy operator with the same eigenvalue $(k')^2$. At large $|\mathbf{R}|$ the unperturbed solution $A_\mu^{\text{sph},\omega k\tau_i\lambda}(\mathbf{R})$ and the perturbed solution (4.8) can be factorized into an angular and a radial part, the last part going into

$$R^{-1}\sin[kR + (n/2)\pi]$$

and

$$R^{-1}\sin[k'R + (n/2)\pi + \delta^{\omega k\tau_i\lambda}] ,$$

respectively. This allows us to consider $A_\mu^{\text{sph},\omega k\tau_i\lambda}$ and the function (4.8) on the same footing as the free-electron solutions as far as the reasoning given originally by Friedel is applied. Therefore, in analogy with (6.1), we postulate

$$\delta n^{\omega k\tau_i\lambda} = \frac{1}{R_b} \frac{\partial \delta^{\omega k\tau_i\lambda}}{\partial k} .$$

$$(6.2)$$

The oscillatory terms are discarded because we are interested in the average change of charge and the averaging process is performed over a set of crystals having slightly different R_b.

The total number of electrons, characterized by symmetry index ω and band λ, changed by the presence of impurities, is obtained by a summation of (6.2) over all occupied states, i.e., having their energy less than the Fermi energy ε_F:

$$\Delta N_\lambda^\omega(\varepsilon_F) = 2 \sum_{i=1}^{i_{\text{max}}} \int_0^{k_{\text{BZ}}(\tau_i)} \frac{dk}{\pi/R_b} \Theta(\varepsilon_F - E^{k\tau_i\lambda}) \delta n^{\omega k\tau_i\lambda} .$$

$$(6.3)$$

In this expression, factor 2 accounts for the spin summation, whereas the summation over the allowed values of the radial quantum number k is represented as an integral weighted by the factor $1/\Delta\kappa$; see Eq. (3.28). The integral limit $k_{\text{BZ}}(\tau_i)$ is defined below Eq. (5.3). When (6.2) is substituted into (6.3), the integration done by parts gives

$$\Delta N_\lambda^\omega(\varepsilon_F) = \frac{2}{\pi} \sum_i \left[[\delta^{\omega k\tau_i\lambda} \Theta(\varepsilon_F - E^{k\tau_i\lambda})] \Big|_{k=0}^{k=k_{\text{BZ}}(\tau_i)} - \int_0^{k_{\text{BZ}}(\tau_i)} dk\, \delta^{\omega k\tau_i\lambda} \frac{\partial}{\partial k} \Theta(\varepsilon_F - E^{k\tau_i\lambda}) \right] .$$

$$(6.4)$$

The first term does not contribute at $k=0$ because $\delta^{\omega k\tau_i\lambda}$ is zero there [see Eq. (4.12)], $S^k \sim k^2$ because of (6.7), and $\partial E^{k\tau_i\lambda}/\partial k \sim k$ at small k. Furthermore, the term at $k = k_{\text{BZ}}(\tau_i)$ may be disregarded for the following reason. In the course of evaluation of Eq. (6.3), it is also possible to extend the integration region to include a great number of BZ's; simultaneously, the result is divided by the number of BZ's. In this case the point $k = k_{\text{BZ}}(\tau_i)$ does not contribute, because—as it belongs to the first BZ—it is inner. The arising contribution at the surface of the last BZ will be negligible compared to contributions coming from many BZ's which are represented by the second term in (6.4).

Now, in order to calculate the second term in (6.4), we

must account for the fact that

$$\frac{\partial}{\partial k}\Theta(\varepsilon_F - E^{k\tau_i\lambda}) = \delta(\varepsilon_F - E^{k\tau_i\lambda})(-1)\frac{\partial E^{k\tau_i\lambda}}{\partial k} \ .$$

Together with Eq. (5.4) this gives

$$\Delta N_\lambda^\omega(\varepsilon_F) = -\frac{2}{\pi}\sum_{i,j}\left[-\delta^{\omega k\tau_i\lambda}\text{sgn}\left[\frac{\partial E^{k\tau_i\lambda}}{\partial k}\right]\right]_{k=k_j^{\tau_i\lambda}(\varepsilon_F)} \ .$$

$$(6.5)$$

If Eq. (5.9) is substituted into the last equation, then it becomes

$$\Delta N_\lambda^\omega(\varepsilon_F) = -2\sum_{i,j}D_\lambda^{ij}(\varepsilon_F)(\tilde{V}^{\omega k\tau_i\lambda})_{k=k_j^{\tau_i\lambda}(\varepsilon_F)} \ . \qquad (6.6)$$

The quantity $\tilde{V}^{\omega k\tau_i\lambda}$ was defined by Eq. (4.13).

The expression obtained may be rewritten in a more compact form if the sum over directions τ_i is represented as an integral over a solid angle; finally an integral over d^3k can be performed [compare the transformations from (5.3) to (5.6) taken in reverse order]:

$$\Delta N_\lambda^\omega(\varepsilon_F) = -2\frac{d_g}{v_{\text{BZ}}}\int_{v_{\text{IBZ}}}d^3k\,\delta(\varepsilon_F - E^{k\lambda})\tilde{V}^{\omega k\lambda} \ . \quad (6.7)$$

The wave vector **k** is equivalent to the vector $k\tau$ given previously. The above example of the calculation done for $\Delta N_\lambda^\omega(\varepsilon_F)$ demonstrates that the formalism developed in the present paper is a useful tool for the investigation of the properties of transition metals with impurities. Other applications will be published separately.

In conclusion, we would like to show that formula (6.7) represents a meaningful expression not only for a localized perturbation, which is due to an impurity, but that it also holds for the perturbation which is spread out over the entire crystal volume. Let us assume, for instance, that

$$V_{\mu L,\mu'L'} = V_0\delta_{LL'}\delta_{\mu\mu'} \ , \qquad (6.8)$$

where L and L' are any crystal sites. This perturbation shifts all the eigenenergies of the crystal by an amount V_0; at the same time the eigenvectors remain unchanged. Therefore the number of electrons occupying the states below energy ε_F in the perturbed crystal is the same as in an unperturbed crystal, but below the energy $\varepsilon_F - V_0$:

$$\sum_\omega N_\lambda^{\text{per},\omega}(\varepsilon_F) = \sum_\omega N_\lambda^\omega(\varepsilon_F - V_0) \ . \qquad (6.9)$$

We may obtain the change of the electron number due to the perturbation by expanding the right-hand side of (6.9) in the Taylor series with respect to small V_0. We get

$$\sum_\omega \Delta N_\lambda^\omega(\varepsilon_F) = \sum_\omega \frac{dN_\lambda^\omega(\varepsilon)}{d\varepsilon}\bigg|_{\varepsilon=\varepsilon_F}(-V_0)+O(V_0^2) = -V_0\frac{dN_\lambda(\varepsilon)}{d\varepsilon}\bigg|_{\varepsilon=\varepsilon_F} = -V_0\frac{2N}{v_{\text{BZ}}}\int_{v_{\text{BZ}}}d^3k\,\delta(\varepsilon_F-E^{k\lambda}) \ . \qquad (6.10)$$

In the second step we used the relation

$$\sum_\omega N_\lambda^\omega(\varepsilon) = N_\lambda(\varepsilon) \ ,$$

and in the last step we used Eq. (5.3).

Now let us calculate the same change using formula (6.7). We apply the mean perturbation energy defined in (4.13). For the perturbation matrix (6.8) it gives

$$\sum_\omega \tilde{V}^{\omega k\lambda} = V_0\sum_L\left[\sum_{\omega,\mu}|A_\mu^{\omega k\lambda}(\mathbf{R}_L)|^2\right]\bigg/\left[\sum_{\omega',\mu'}|A_{\mu'}^{\omega'k\lambda}(0)|^2\right] = V_0 N \ ,$$

because the contribution to the electron density at each lattice site $\mathbf{R}_L$ is the same as that calculated at $\mathbf{R}_L = 0$. Therefore formula (6.7) gives

$$\sum_\omega \Delta N_\lambda^\omega(\varepsilon_F) = -V_0 2N\frac{d_g}{v_{\text{BZ}}}\int_{v_{\text{IBZ}}}d^3k\,\delta(\varepsilon_F-E^{k\lambda}) \ , \quad (6.11)$$

which is exactly the same result as given in (6.10); the integral in (6.11) is confined to v_{IBZ} by symmetry. The agreement obtained may be regarded as independent proof that we were correct in our disregard of the contributions which come at $k = k_{\text{BZ}}(\tau)$ in the course of the evaluation of $\Delta N_\lambda^\omega(\varepsilon_F)$; see Eq. (6.4) and the inferences below it.

[1]F. Gautier, Ann. Phys. (Paris) **10**, 275 (1964).

[2]F. Gautier, J. Phys. Chem. Solids **24**, 387 (1963).

[3]J. Kanamori, J. Appl. Phys. Suppl. **36**, 929 (1965).

[4]J. Friedel, Adv. Phys. **3**, 446 (1954); J. Phys. F **3**, 784 (1973).

[5]J. Friedel, Philos. Mag. **43**, 153 (1952).

[6]J. Friedel, Nuovo Cimento Suppl. **7**, 287 (1958).

[7]G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954).

[8]G. F. Koster, Phys. Rev. **95**, 1436 (1954).

[9]G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954).

[10]J. Callaway, J. Math. Phys. **5**, 783 (1964); D. A. Goodings and

B. Mozer, Phys. Rev. **136**, A1093 (1964); R. E. Turner and D. A. Goodings, Proc. Phys. Soc. London, Sect. A **86**, 87 (1965); G. J. Morgan, *ibid.* **89**, 365 (1966); J. Callaway, Phys. Rev. **154**, 515 (1967); J. Callaway and A. J. Hughes, *ibid.* **156**, 860 (1967); E. Mann, Phys. Status Solidi **13**, 293 (1966); F. Bassani, G. Iadonisi, and B. Preziosi, Phys. Rev. **186**, 735 (1969); M. Jaros and S. Brand, *ibid.* B **14**, 4494 (1976); G. A. Baraff and M. Schlüter, Phys. Rev. Lett. **41**, 892 (1978); N. O Lipari and S. T. Pantelides, *ibid.* **41**, 895 (1978).

[11]A. Holas, S. Olszewski, and A. Wierzbicki, preceding paper,

Phys. Rev. B **32**, 7890 (1985).

[12]J. L. Beeby, Proc. R. Soc. London, Ser. A **279**, 82 (1964); **302**, 113 (1967).

[13]R. Harris, J. Phys. C **3**, 172 (1970); J. W. Blaker and R. Harris, *ibid.* **4**, 569 (1971).

[14]N. A. W. Holzwarth, Phys. Rev. B **11**, 3718 (1975).

[15]R. Podloucky, R. Zeller, and P. H. Dederichs, Phys. Rev. B **22**, 5777 (1980).

[16]P. H. Dederichs and R. Zeller, in *Festkörperprobleme (Advances in Solid State Physics)*, edited by J. Treusch (Vieweg, Braunschweig, 1981), Vol. 21, p. 243.

[17]C. Koenig and E. Daniel, J. Phys. (Paris) Lett. **42**, L193 (1981).

[18]C. Koenig, P. Leonard, and E. Daniel, J. Phys. (Paris) **42**, 1015 (1981).

[19]O. Gunnarson, O. Jepsen, and O. K. Andersen, Phys. Rev. B **27**, 7144 (1983).

[20]S. Olszewski, Phys. Rev. B **24**, 4515 (1981); P. Modrak and S. Olszewski, *ibid.* **14**, 2387 (1976); cf. also Refs. 30—32 in paper I.

[21]N. Fukuda and R. G. Newton, Phys. Rev. **103**, 1558 (1956).

[22]B. S. DeWitt, Phys. Rev. **103**, 1565 (1956).