PHYSICAL REVIEW B VOLUME 11, NUMBER 10 15 MAY 1975

Theory of impurity scattering in dilute metal alloys based on the muffin-tin model*†

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(Received 27 June 1974)

The exact electronic eigenstates of a single substitutional impurity in an otherwise perfect lattice of muffin-tin potentials are developed for the purpose of investigating impurity scattering in dilute metal alloys. The impurity eigenfunctions are determined by an extension of the Green's-function method of band-structure calculation. Expressions are derived for the transition and scattering matrices describing impurity-induced elastic scattering between two Bloch states. These results are then related to a number of experimental situations; namely to measurements of residual resistivity, Dingle temperatures, Knight-shift satellites, and spin-lattice relaxation in conduction-electron spin resonance. The formal expressions depend upon the impurity and host atomic scattering phase shifts and upon the band structure of the host lattice through Bloch-wave amplitude coefficients and Brillouin-zone integrals of the inverse of the Green's-function secular matrix. The atomic scattering phase shifts can be determined from *ab initio* calculations of the muffin-tin potentials or can be inferred from semiempirical analysis of experimental data.

I. INTRODUCTION

The purpose of this paper is to present a theoretical study of impurity scattering in dilute metal alloys based on an expression for the exact electronic eigenstates of a single substitutional impurity in an otherwise perfect lattice of muffin-tin potentials. The expression for the eigenstates of this system was first derived by Dupree[1] by extending the Green's-function method of band-structure calculation.[2-5] Morgan[6] later showed formally how such a treatment can be used to calculate the transition matrix which describes impurity-induced scattering between Bloch states of the host lattice. In this paper explicit expressions for the transition matrix as well as the related scattering matrix are derived. The transition matrix depends upon the atomic potentials of the host and impurity through their respective scattering phase shifts, and upon the "band structure" of the host lattice through the Bloch-wave amplitude coefficients and the Brillouin-zone integral of the inverse of the Green's-function secular matrix. In addition to a nonrelativistic treatment, consideration is also given to systems which have strong spin-orbit interactions for which a relativistic treatment is needed. The general expressions for the eigenstates and transition matrices are then related, within the independent scattering approximation, to a variety of experimentally accessible quantities for dilute metal alloys. Specifically, expressions are derived for the (relativistic) impurity-induced spin-lattice relaxation rate of conduction-electron spin resonance and for the host-metal Knight-shift satellites induced by single impurities. Residual-resistivity and Dingle-temperature anisotropies are discussed only briefly, as a full account of these properties will be presented elsewhere.[7,8]

The muffin-tin model is expected to be an adequate description of the lattice potential in metallic systems having close-packed structures and negligible lattice distortions. It is expected to be most accurate for the description of electronic states near the Fermi level, for which the independent-quasiparticle approximation is valid and for which the mean electronic kinetic energies exceed the interstitial potential fluctuations that are neglected in the muffin-tin approximation.

The initial motivation of the present work was provided by recent Dingle-temperature anisotropy measurements in noble-metal alloys.[9-11] The Dingle temperature measures the scattering rate for electrons of a given Bloch state at the Fermi level, averaged around the k-space orbit induced by the applied magnetic field. The anisotropy of the Dingle temperature can be expressed as a product of a factor which represents variations in the host-metal Bloch-wave amplitude components over the Fermi surface, and a factor which involves information about the impurity. Scattering anisotropies may be studied theoretically by means of *ab initio* calculations, or semiempirically, determining the basic parameters of the theory, namely the host and impurity scattering phase shifts evaluated at the Fermi energy, from the experimental data. The latter approach has been followed by Coleridge and Lee.[7,12-14] They have interpreted noble-metal Dingle-temperature data to obtain a set of effective ("Friedel") phase shifts. The Friedel phase shifts may be further interpreted, either by making appropriate assumptions about host backscattering,[14] or by evaluating the expressions derived in the present paper, to determine scattering phase shifts associated with the impurity wave functions.[8]

This paper is organized as follows. In Sec. II, general expressions for the nonrelativistic wave functions of a muffin-tin lattice with a single substitutional impurity are derived. The wave functions are written in such a form that they may be readily compared with the corresponding wave functions appropriate for free-space potential scattering from the analogous perturbation. The latter form was used by Friedel[15,16] and others[17-19] in early studies of impurity scattering based on the free-electron model of the host lattice. Within the muffin-tin model, the role of the host lattice may be characterized in terms of a "backscattering" matrix defined by Morgan.[6] This backscattering matrix is related to the Brillouin-zone integral matrix of the present approach, and to the "renormalization" of the wave function amplitude on the impurity site.[14,20] In addition to a discussion of scattering states, a prescription for finding the bound states of the muffin-tin potential is also given. In Sec. III, the corresponding discussion is given for the relativistic wave functions. Expressions for the transition matrix are derived in Sec. IV. In the presence of spin-orbit interactions, the possibility of "spin-flip" scattering is introduced, in addition to ordinary potential scattering. In Sec. V, the eigenvalues of the scattering matrix are derived and the Friedel sum rule[21] is generalized. In Sec. VI, the role of the electron-phonon interaction and the effects of finite impurity concentration are discussed qualitatively. Then, the results of the preceding sections are used to derive expressions for various experimentally accessible quantities to which this analysis is applicable. It is found that the present approach is most easily applied to the interpretation of experiments that involve electrons on a single surface of constant energy. Experimental quantities involving electrons throughout the conduction band of the host metal could also be evaluated within this model, but with increased computational effort. In Sec. VII, the results of the present paper are summarized and compared with other recent theoretical treatments of impurity scattering. This paper is concluded with a brief discussion of possible extensions of the present work.

II. SPIN-INDEPENDENT (NONRELATIVISTIC) IMPURITY WAVE FUNCTIONS

The Schrödinger equation for the electronic eigenstates of a single substitutional impurity in an otherwise perfect lattice of muffin-tin potentials was solved by Dupree[1] by extending the Green's-function method of band-structure calculations.[2-5] The same problem was later solved by Beeby[22] to determine the local electronic density, using a transition-matrix formalism. The bulk density of states induced by the impurity atom has been determined by Lasseter and Soven,[23] using a Green's-function approach. In this section, the focus is on the nature of the electronic wave function in the vicinity of the impurity site. This is developed, following the work of Dupree,[1] but using the Green's-function conventions of Kohn and Rostoker (KR).[4] A derivation of expressions for the electronic wave functions is given from the viewpoint of a simple wave matching procedure as discussed by Korringa.[3] A similar approach has been used by Johnson,[24] and by Keller and Smith,[25] to describe scattering from small clusters of atoms. For simplicity, the host lattice will be assumed to be cubic, and to have one atom per primitive unit cell.

The wave function in the interstitial region (i.e., exterior to any muffin-tin sphere) of an infinite lattice, can be expressed quite generally as a coherent sum of scattered waves diverging from each lattice site:

$$\Psi_\epsilon(\vec{k},\vec{r}) = \sum_N \sum_{lm} w^N_{lm}(\vec{k},\epsilon)\,[i h_l(\kappa r_N)]\, Y_{lm}(\hat{r}_N) \;. \tag{2.1}$$

The electron energy $\epsilon = \hbar^2\kappa^2/2m$ is measured with respect to the muffin-tin zero; $\vec{R}_N$ denotes the position of the Nth lattice site; $\vec{r}_N \equiv \vec{r} - \vec{R}_N$; $h_l(\kappa r_N)$ is a spherical Hankel function[26]; $Y_{lm}(\hat{r}_N)$ is a spherical harmonic[27]; and $w^N_{lm}(\vec{k},\epsilon)$ are the "interstitial" amplitude coefficients. The wave vector $\vec{k}$ labels the eigenstates of translation for a perfect lattice. The translational symmetry is broken when an impurity is substituted for a host atom in the lattice; in this case, the label $\vec{k}$ denotes those impurity states which exist in one-to-one correspondence with the Bloch states of the ideal lattice.

The wave function inside the Nth muffin-tin sphere may be expressed in terms of a single-center expansion:

$$\Psi_\epsilon(\vec{k},\vec{r}) = \sum_{lm} i^l z^N_{lm}(\vec{k},\epsilon)\, R^{(N)}_{\epsilon l}(r_N)\, Y_{lm}(\hat{r}_N) \;, \tag{2.2}$$

where $R^{(N)}_{\epsilon l}(r_N)$ denotes the radial wave function of angular momentum l which pertains to the spherical potential of the host $[(N)=h]$ or impurity $[(N)=i]$ depending on whether the Nth site is occupied by a host or an impurity atom. It is convenient to normalize the radial wave function so that outside the muffin-tin sphere it takes the form

$$R_{\epsilon l}^{(N)}(r_N) = j_l(\kappa r_N) + i \sin\eta_l^{(N)} e^{i\eta_l^{(N)}} h_l(\kappa r_N), \quad r_N \geqslant s^{(N)} \tag{2.3}$$

where $j_l(\kappa r_N)$ is a spherical Bessel function, $s^{(N)}$ is the appropriate muffin-tin radius, and $\eta_l^{(N)}(\epsilon)$ is the appropriate "atomic" scattering phase shift. For convenience in notation, the factor multiplying the Hankel function will be termed the "atomic scattering parameter" and denoted

$$t_l^{(N)} \equiv \sin\eta_l^{(N)} e^{i\eta_l^{(N)}} . \tag{2.4}$$

To determine the muffin tin $[z_{lm}^N(\vec{k}, \epsilon)]$ and interstitial $[w_{lm}^N(\vec{k}, \epsilon)]$ amplitude coefficients, one must match the two expansions of the wave function [(2.1) and (2.2)] and the corresponding normal derivatives at the surface of each muffin-tin sphere. In order to do so, the sum of the scattered waves diverging from each lattice site (2.1) must be expanded about a single lattice site. A spherical wave diverging from a center at $\vec{R}_{N'}$ can be expressed in terms of spherical waves diverging from a different center $\vec{R}_N$ by the expansion[28]

$$i h_{l'}(\kappa r_{N'}) Y_{l'm'}(\hat{r}_{N'}) = \sum_{lm} j_l(\kappa r_N) Y_{lm}(\hat{r}_N) H_{lm\,l'm'}^{NN'} . \tag{2.5}$$

The convergence of this expansion and the exact form of the two-center transformation matrix $H_{lm\,l'm'}^{NN'}$ are discussed in Appendix A.

The wave-matching conditions determine the following relationships between the amplitude coefficients. Firstly, the interstitial amplitude is directly proportional to the corresponding muffin-tin amplitude and atomic scattering parameter:

$$w_{lm}^N(\vec{k}, \epsilon) = i^l t_l^{(N)}(\epsilon) z_{lm}^N(\vec{k}, \epsilon) . \tag{2.6}$$

Secondly, the muffin-tin amplitude coefficients of a given cell (N) are related to the coefficients of all the other cells of the lattice (N') and those of the impurity cell (I) in the following way:

$$i^l z_{lm}^N - \sum_{N' \neq N} \sum_{l'm'} H_{lm\,l'm'}^{NN'} t_{l'}^h i^{l'} z_{l'm'}^{N'} = \sum_{l'm'} H_{lm\,l'm'}^{NI} (t_{l'}^i - t_{l'}^h) i^{l'} z_{l'm'}^I . \tag{2.7}$$

Provided that the otherwise undefined two-center transformation matrix elements having identical site indices, $H_{lm\,l'm'}^{NN}$, are set equal to zero, this expression is valid for N equal to a host cell index *or* to the impurity cell index I. The solution of the Schrödinger equation for the muffin-tin impurity problem has thus been cast in the form of an infinite set of algebraic linear equations. Further relationships between Eqs. (2.6) and (2.7) and their convergence properties are discussed in Appendix A.

For a perfect crystal, the right-hand side of Eq. (2.7) vanishes and it is natural to seek solutions by taking the muffin-tin amplitudes to be of Bloch form:

$$z_{lm}^{N(0)}(\vec{k}, \epsilon) = a_{lm}(\vec{k}, \epsilon) e^{i\vec{k}\cdot\vec{R}_N} , \tag{2.8}$$

or correspondingly for the interstitial amplitudes,

$$w_{lm}^{N(0)}(\vec{k}, \epsilon) = [\mathfrak{N}(\vec{k}, \epsilon)]^{-1} v_{lm}(\vec{k}, \epsilon) e^{i\vec{k}\cdot\vec{R}_N} . \tag{2.9}$$

Here superscript 0 is used to denote coefficients pertaining to the Bloch waves $\Psi_\epsilon^{(0)}(\vec{k}, \vec{r})$ of the pure host metal, and $\mathfrak{N}(\vec{k}, \epsilon)$ is a normalizing factor. Substituting the interstitial amplitude coefficients (2.9) into the homogeneous form of Eq. (2.7), one obtains the following secular equations for the $v_{lm}(\vec{k}, \epsilon)$ coefficients:

$$\sum_{l'm'} \left[(\cot\eta_l - i) \delta_{ll'} \delta_{mm'} - \sum_{N' \neq N} H_{lm\,l'm'}^{NN'} e^{i\vec{k}\cdot(\vec{R}_{N'} - \vec{R}_N)} \right] v_{l'm'}(\vec{k}, \epsilon) = 0 . \tag{2.10}$$

These are the familiar Green's-function secular equations as can be seen by noting that the structure matrix $A_{lm,l'm'}(\vec{k}, \epsilon)$ defined by Kohn and Rostoker[4] is related to the Fourier transform of the two-center transformation matrix [Eq. (2.5)]:

$$(1/\kappa) A_{lm,l'm'} + i\delta_{ll'} \delta_{mm'} = -\sum_{N' \neq N} H_{lm\,l'm'}^{NN'} e^{i\vec{k}\cdot(\vec{R}_{N'} - \vec{R}_N)} . \tag{2.11}$$

Thus, the bracketed term in Eq. (2.10) is just the KR Green's-function secular matrix,[4]

$$M_{lm,l'm'}(\vec{k}, \epsilon) \equiv \cot\eta_l^h \delta_{ll'} \delta_{mm'} + (1/\kappa) A_{lm,l'm'}(\vec{k}, \epsilon) , \tag{2.12}$$

and the $v_{lm}(\vec{k}, \epsilon)$ coefficients are components of its zero eigenvector (corresponding to the eigenvalue equal to zero). More generally, the eigenvalue equations for the KR secular matrix can be written

$$\sum_{l'm'} M_{lm,l'm'}(\vec{k}, \epsilon) v_{l'm'}^n(\vec{k}, \epsilon) = \lambda^n(\vec{k}, \epsilon) v_{lm}^n(\vec{k}, \epsilon) . \tag{2.13}$$

The eigenvector v written without superscript will be assumed to correspond to the zero eigenvalue $\lambda(\vec{k}, \epsilon) = 0$. The implicit relationship $\lambda(\vec{k}, \epsilon) = 0$ defines the surface of constant electron energy $\epsilon(\vec{k}) = \epsilon$ of the host lattice. For convenience, it will be assumed that all eigenvectors are normalized to unity:

$$\sum_{lm} |v^{n}_{lm}(\vec{k}, \epsilon)|^2 = 1 \ . \tag{2.14}$$

Using the above definitions, the wave function for the pure host metal in the interstitial region can be expressed in the Bloch form obtained from Eq. (2.1)

$$\Psi^{(0)}_{\epsilon}(\vec{k}, \vec{r}) = e^{i\vec{k}\cdot\vec{r}}\,[\mathfrak{N}(\vec{k}, \epsilon)]^{-1} \sum_{N} \sum_{lm} v_{lm}(\vec{k}, \epsilon)\, e^{-i\vec{k}\cdot\vec{r}_N} \times [ih_l(\kappa r_N)]\, Y_{lm}(\hat{r}_N) \ . \tag{2.15}$$

A more convenient expression for evaluating the wave function within the Nth cell is obtained from Eq. (2.2):

$$\Psi^{(0)}_{\epsilon}(\vec{k}, \vec{r}) = e^{i\vec{k}\cdot\vec{R}_N} \sum_{lm} i^{\,l}\, a_{lm}(\vec{k}, \epsilon)\, R^{h}_{\epsilon l}(r_N)\, Y_{lm}(r_N) \ . \tag{2.16}$$

It is shown in Appendix B that the normalization constant $\mathfrak{N}(\vec{k}, \epsilon)$ can be evaluated in terms of the energy derivative of the zero eigenvalue of the KR secular matrix. For a Bloch wave function normalized to unity within the volume Ω of the unit cell [i.e., $\int_{\Omega} d^3r\, |\Psi^{(0)}_{\epsilon}(\vec{k}, \vec{r})|^2 = 1$], the constant is given by

$$\mathfrak{N}(\vec{k}, \epsilon)^2 = \frac{\epsilon}{\kappa^3}\left(-\frac{\partial \lambda(\vec{k}, \epsilon)}{\partial \epsilon}\right) \ . \tag{2.17}$$

In the presence of the impurity, there are two types of solutions to the amplitude equation (2.7). Bound states and continuum states occur, respectively, for energies outside and inside the bands of the host lattice. In either case, as the impurity site is characterized by the full point symmetry of the lattice, it is convenient to discuss the solutions in terms of a "lattice harmonic" expansion.[29–31] A lattice harmonic is a linear combination of spherical harmonics of a given order l which transforms according to an irreducible representation Γ:

$$Y_{l\Gamma\gamma}(\hat{r}) = \sum_{m} U^{l\Gamma\gamma}_{lm}\, Y_{lm}(\hat{r}) \ . \tag{2.18}$$

The transformation U between spherical and lattice harmonics is unitary. The index γ denotes the specific member of the representation Γ.[32] In the lattice harmonic basis the amplitude coefficients transform according to the inverse matrix

$$z^{N}_{l\Gamma\gamma}(\vec{k}, \epsilon) = \sum_{m} (U^{l\Gamma\gamma}_{lm})^{-1}\, z^{N}_{lm}(\vec{k}, \epsilon) \ . \tag{2.19}$$

Dupree[1] has shown that the solution of the amplitude equation (2.7) in the presence of the impurity in the Ith unit cell proceeds most easily by expressing the spatial dependence of the amplitude coefficients $z^{N}_{l\Gamma\gamma}$ in terms of a Fourier integral over the first Brillouin zone. The corresponding "Fourier transform" of Eq. (2.7) may be expressed in terms of structure factors, which for a substitutional impurity considered here, are identical to the structure factors of the pure host and may be written in terms of the KR secular matrix (2.12). The details of the solution are presented in Appendix A.

The solutions can be expressed in terms of the inverse Fourier transform of the reciprocal KR secular matrix:

$$\chi_{l\Gamma\gamma,\, l'\Gamma'\gamma'}(\epsilon, \vec{R}_N - \vec{R}_I) \equiv \frac{\Omega}{(2\pi)^3} \int_{\mathrm{Bz}} d^3q\, e^{i\vec{q}\cdot(\vec{R}_N - \vec{R}_I)}\, [M(\vec{q}, \epsilon)]^{-1}_{l\Gamma\gamma,\, l'\Gamma'\gamma'} \ . \tag{2.20}$$

Before discussing the nature of the solutions themselves, the properties of this Brillouin-zone integral will be briefly investigated. The integrand of the χ matrix is singular on the surface of constant energy which corresponds to the locus of Bloch states of the host lattice; $\lambda(\vec{q}, \epsilon) = 0$. In order for the general impurity wave functions to be consistent with the "outgoing" scattered wave condition as well as the optical theorem, the singular integral (2.20) must be evaluated in the following way:

$$P\int_{\mathrm{Bz}} d^3q\, e^{i\vec{q}\cdot(\vec{R}_N - \vec{R}_I)}\, [M(\vec{q}, \epsilon)]^{-1}_{l\Gamma\gamma,\, l'\Gamma'\gamma'} + i\pi \int_{\mathrm{Bz}} d^3q\, \delta(\lambda(q, \epsilon))\, e^{i\vec{q}\cdot(\vec{R}_N - \vec{R}_I)} \times \mathrm{Res}\,\{[M(\vec{q}, \epsilon)]^{-1}_{l\Gamma\gamma,\, l'\Gamma'\gamma'}\} \ . \tag{2.21}$$

Here P denotes principal-parts integral. The residue is nonzero for energies inside the bands of the host lattice and may be evaluated according to

$$\lim_{\lambda(\vec{q}, \epsilon) \to 0} \{\lambda(\vec{q}, \epsilon)\, [M(\vec{q}, \epsilon)]^{-1}_{l\Gamma\gamma,\, l'\Gamma'\gamma'}\} = v_{l\Gamma\gamma}(\vec{q}, \epsilon)\, v^{*}_{l'\Gamma'\gamma'}(\vec{q}, \epsilon) \ , \tag{2.22}$$

since $M(\vec{q}, \epsilon)$ is a Hermitian matrix. In particular, the Brillouin-zone integral evaluated at the impurity site $\chi(\epsilon, 0)$, has special symmetry properties. It is diagonal in the irreducible representation $\Gamma\gamma$ and is identical for each member γ. Hence, it is convenient to introduce the shorthand notation:

$$\chi_{l\Gamma\gamma,\, l'\Gamma'\gamma'}(\epsilon, 0) = \chi^{\Gamma}_{ll'}(\epsilon)\, \delta_{\Gamma\Gamma'}\, \delta_{\gamma\gamma'} \ . \tag{2.23}$$

Continuum solutions to the amplitude equations (2.7) may be expressed in terms of a linear combination of the corresponding Bloch amplitudes. The amplitudes for the impurity site take the form

$$i^l z^I_{l\Gamma\gamma}(\vec{k},\epsilon)=\sum_{l'}\mathcal{A}^\Gamma_{ll'}(\epsilon)\,i^{l'}a_{l'\Gamma\gamma}(\vec{k},\epsilon)\,e^{i\vec{k}\cdot\vec{R}_I}\ , \tag{2.24}$$

where the matrix

$$(\mathcal{A}^\Gamma)^{-1}_{ll'}=\frac{t^i_l(\epsilon)}{t^h_l(\epsilon)}\,\delta_{ll'}-\frac{\chi^\Gamma_{ll'}(\epsilon)[t^i_{l'}(\epsilon)-t^h_{l'}(\epsilon)]}{t^h_l(\epsilon)\,t^h_{l'}(\epsilon)} \tag{2.25}$$

determines the extent to which the impurity amplitudes have been "renormalized" with respect to their corresponding Bloch amplitudes. For this reason $\mathcal{A}^\Gamma_{ll'}(\epsilon)$ is termed the "renormalization matrix." Alternatively, using relation (2.6), the interstitial amplitudes for the impurity cell can be written in the form

$$\begin{aligned}w^I_{l\Gamma\gamma}(\vec{k},\epsilon)&\\&=[\mathfrak{N}(\vec{k},\epsilon)]^{-1}\,\xi_l\sum_{l'}(\xi-\chi^\Gamma)^{-1}_{ll'}\,v_{l'\Gamma\gamma}(\vec{k},\epsilon)\,e^{i\vec{k}\cdot\vec{R}_I}\ ,\end{aligned} \tag{2.26}$$

where ξ is a real diagonal matrix with elements given by

$$\begin{aligned}\xi_l(\epsilon)&\equiv t^i_l(\epsilon)\,t^h_l(\epsilon)\,[t^i_l(\epsilon)-t^h_l(\epsilon)]^{-1}\\&=[\cot\eta^h_l(\epsilon)-\cot\eta^i_l(\epsilon)]^{-1}\ .\end{aligned} \tag{2.27}$$

From either expression (2.24) or (2.26), it is evident that the comparison between the impurity amplitude and the corresponding amplitude for the pure metal depends upon both the impurity and host scattering phase shifts η^i_l and η^h_l, and the Brillouin-zone integral $\chi^\Gamma_{ll'}$. The physical significance of these contributions is most easily understood in terms of the partial-wave backscattering matrix T^M defined by Morgan.[6] The T^M matrix describes the contribution to the amplitude at the impurity site due to "backscattering" from all the host sites, of a scattered wave diverging from the impurity. It is related to the renormalization matrix (2.25) according to[6,14]

$$\mathcal{A}^\Gamma_{ll'}(\epsilon)=i^{l-l'}\sum_{l''}(I-iT^M_\Gamma t^i)^{-1}_{ll''}\,(I-iT^M_\Gamma t^h)_{l''l'}\ . \tag{2.28}$$

The backscattering matrix T^M can be evaluated in terms of the Brillouin-zone integrals; it satisfies the same symmetry relations as does $\chi(\epsilon,0)$ and is related to it in the following way:

$$i^{l-l'}\,T^M_{\Gamma;ll'}(\epsilon)=i\{[\chi^\Gamma(\epsilon)]^{-1}_{ll'}-(t^h_l)^{-1}\delta_{ll'}\}\ . \tag{2.29}$$

It is interesting to compare the results obtained above with the corresponding results for a free-electron model of the host metal. In that case, there is no backscattering by the host lattice: $T^M\equiv 0$. The "free electron" value of the Brillouin zone integral matrix χ^Γ is thus inferred to be

$$\chi^{\Gamma(\text{free})}_{ll'}=t^h_l\,\delta_{ll'}\ , \tag{2.30}$$

and the free-electron value of the renormalization matrix $\mathcal{A}^\Gamma$ is seen to be the identity matrix.

For many alloy systems of interest, such as for several types of impurities in noble metal hosts,[7,8,14] it is reasonable to assume that only scattering phase shifts through $l\leq 2$ are significantly different from zero. As each representation of the cubic point group is associated with only one angular momentum for $l\leq 2$, the block of the $\chi(\epsilon,0)$ matrix needed in the calculation of the amplitude coefficients is diagonal. Consequently the partial-wave backscattering matrix T^M and the renormalization matrix $\mathcal{A}^\Gamma$ are also diagonal. Then, the impurity muffin-tin amplitude coefficient is directly proportional to the corresponding Bloch-amplitude coefficient, but renormalized by a scalar factor[14,20]:

$$\begin{aligned}\mathcal{A}^\Gamma_{ll}(\epsilon)&\equiv\frac{1-iT^M_{\Gamma;ll}\,t^i_l}{1-iT^M_{\Gamma;ll}\,t^h_l}\\&=\frac{e^{-i(\eta^i_l-\eta^h_l)}\sin^2\eta^h}{\sin\eta^i_l\,\sin\eta^h_l-\chi^\Gamma_{ll}\sin(\eta^i_l-\eta^h_l)}\ ,\end{aligned} \tag{2.31}$$

which is independent of $\vec{k}$.

Once the impurity amplitudes have been determined, Eq. (2.7) can be solved for the amplitudes on neighboring host sites, which can be expressed as a linear combination of the amplitudes at the impurity site as follows:

$$i^l z^N_{l\Gamma\gamma}(\vec{k},\epsilon)=i^l a_{l\Gamma\gamma}(\vec{k},\epsilon)\,e^{i\vec{k}\cdot\vec{R}_N}+\frac{1}{t^h_l}\sum_{l'\Gamma'\gamma'}\chi_{l\Gamma\gamma,l'\Gamma'\gamma'}(\epsilon,\vec{R}_N-\vec{R}_I)\left(\frac{t^i_{l'}-t^h_{l'}}{t^h_{l'}}\right)i^{l'}z^I_{l'\Gamma'\gamma'}(\vec{k},\epsilon)\quad(N\neq I) \tag{2.32}$$

or explicitly in terms of the interstitial Bloch amplitudes:

$$w^N_{l\Gamma\gamma}(\vec{k},\epsilon)=[\mathfrak{N}(\vec{k},\epsilon)]^{-1}\left[v_{l\Gamma\gamma}(\vec{k},\epsilon)\,e^{i\vec{k}\cdot\vec{R}_N}+\sum_{l'\Gamma'\gamma';l''}\chi_{l\Gamma\gamma,l'\Gamma'\gamma'}(\epsilon,\vec{R}_N-\vec{R}_I)\,(\xi-\chi^\Gamma)^{-1}_{l'l''}\,v_{l''\Gamma'\gamma'}(\vec{k},\epsilon)\,e^{i\vec{k}\cdot\vec{R}_I}\right]$$

$$(N\neq I)\ \ (2.33)$$

For host sites far from the impurity site, the Brillouin-zone integral $\chi_{l\Gamma\gamma,l'\Gamma'\gamma'}(\epsilon,\vec{R}_N-\vec{R}_I)$ may be evaluated approximately by the method of stationary phase as discussed by Dupree.[1]

Bound-state solutions to the amplitude equation (2.7) can be determined by a procedure similar to the one discussed above. A bound state contains no admixture of the Bloch wave function of the pure metal; the amplitude coefficient is given only by the "scattered wave" contribution. Consequently, for this case Eq. (A6) is a homogeneous equation for the impurity amplitude $z^I_{l\Gamma\gamma}\equiv z^{I(s)}_{l\Gamma\gamma}$ which may be written in the more convenient form

$$\sum_{l'}(\xi_l\delta_{ll'}-\chi^\Gamma_{ll'})\frac{1}{\xi_{l'}}w^I_{l'\Gamma\gamma}(\epsilon)=0\ . \tag{2.34}$$

Since $\xi(\epsilon)$ is a real diagonal matrix and $\chi^\Gamma(\epsilon)$ is a symmetric matrix, $(\xi-\chi^\Gamma)$ can have a zero eigenvalue only if $\chi^\Gamma(\epsilon)$ is real. Because the imaginary contributions to χ^Γ, according to Eq. (2.21), come from the Bloch states of the host lattice at energy ϵ, bound-state solutions exist only for those energies ϵ outside the bands of the host lattice. In general, an impurity bound state will be characterized by a unique representation Γ_0 for which (2.34) is satisfied with nonzero coefficients $w^I_{l'\Gamma_0\gamma'}(\epsilon)$. The amplitude coefficients on other sites are then given by

$$w^N_{l\Gamma\gamma}(\epsilon)=\sum_{l'\gamma'}\chi_{l\Gamma\gamma,l'\Gamma_0\gamma'}(\epsilon,\vec{R}_N-\vec{R}_I)\frac{1}{\xi_{l'}(\epsilon)}w^I_{l'\Gamma_0\gamma'}(\epsilon)\ . \tag{2.35}$$

One is assured that such states are spatially localized because the inverse Fourier integral $\chi_{l\Gamma\gamma,l'\Gamma'\gamma'}(\epsilon,\vec{R}_N-\vec{R}_I)$ decreases in amplitude with increasing distance from the impurity. Such states $\Psi_{\epsilon\Gamma_0}(\vec{r})$ are conveniently normalized to unity within the entire volume of the crystal.

III. RELATIVISTIC IMPURITY WAVE FUNCTIONS

When the conduction electrons in a metal are treated in the independent-particle approximation, the wave function amplitudes can depend upon spin through the spin-orbit interaction. In addition to introducing a new degree of freedom, the spin affects the symmetry properties of the wave functions. Relativistic effects are expected to be important for heavy atoms, such as gold, since the associated strong atomic core potentials can induce extremely large local electron velocities. Fortunately, the relativistic generalization of the Green's-function method of band-structure calculation[33] is straightforward, as is the relativistic treatment of the impurity problem.

The Dirac wave function has two components $\Psi=\binom{\Psi^U}{\Psi^L}$ which satisfy two coupled first-order differential equations[34]

$$\begin{aligned} c\vec{\sigma}\cdot\vec{p}\Psi^U(\vec{r})&=[\epsilon+2mc^2-V(\vec{r})]\Psi^L(\vec{r})\ ,\\ c\vec{\sigma}\cdot\vec{p}\Psi^L(\vec{r})&=[\epsilon-V(\vec{r})]\Psi^U(\vec{r})\ . \end{aligned} \tag{3.1}$$

Here c is the speed of light, $\vec{\sigma}$ is a Pauli matrix, $\vec{p}$ denotes momentum operator, $V(\vec{r})$ denotes the potential, and the energy ϵ is the total energy of the electron *minus its rest energy*, measured with respect to the muffin tin zero. The scalar wavevector κ is related to ϵ according to the relativistic kinematic relation

$$\hbar\kappa\equiv p=[\epsilon(2m+\epsilon/c^2)]^{1/2}\ . \tag{3.2}$$

The upper component Ψ^U is larger in magnitude than the lower component Ψ^L by a factor proportional to the electronic velocity divided by the speed of light. Two convenient quantum numbers for labelling solutions of the Dirac equations in a central field are the component μ of the total angular momentum (j), measured along the direction of quantization, and the "spin angular" quantum number[35] Λ which is related to the projection of the spin angular momentum onto the orbital angular momentum[34] $\vec{L}$:

$$\begin{aligned} \vec{\sigma}\cdot\vec{L}\Psi^U&=-(\Lambda+1)\hbar\Psi^U\ ,\\ \vec{\sigma}\cdot\vec{L}\Psi^L&=(\Lambda-1)\hbar\Psi^L\ . \end{aligned} \tag{3.3}$$

The single quantum number Λ, which takes positive and negative integer values, represents the pair of quantum numbers lj for a given electronic "partial wave." The relationship between these quantum numbers can be written[34] $|\Lambda|=j+\frac{1}{2}$ and $\mathrm{sgn}(\Lambda)\equiv S_\Lambda=2(l-j)$. In the following sections, the notations $\Lambda=-1,1,-2,2,-3,\ldots$ and $lj=0\frac{1}{2},1\frac{1}{2},1\frac{3}{2},2\frac{3}{2},2\frac{5}{2},\ldots$ will be used interchangeably.

The Dirac wave function in the interstitial region of the lattice can be written in analogy with Eq. (2.1):

$$\Psi_\epsilon(\vec{k},\vec{r})=\sum_N\sum_{\Lambda\mu}w^N_{\Lambda\mu}(\vec{k},\epsilon)[i\mathcal{H}_{\Lambda\mu}(\kappa,\vec{r}_N)]\ . \tag{3.4}$$

Here the two-component Hankel function, which is a solution to the Dirac equation (3.1) in absence of the potential $V(\vec{r})$, is given by

$$\mathcal{H}_{\Lambda\mu}(\kappa,\vec{r})\equiv\begin{bmatrix} h_l(\kappa r)\mathcal{Y}^l_{j\mu}(\hat{r})\\ \\ \dfrac{iS_\Lambda pc}{\epsilon+2mc^2}h_{\bar{l}}(\kappa r)\mathcal{Y}^{\bar{l}}_{j\mu}(\hat{r}) \end{bmatrix}\ . \tag{3.5}$$

The orbital angular momenta for the upper and lower components are, respectively, $l=|\Lambda|+\frac{1}{2}(S_\Lambda-1)$ and $\bar{l}=l-S_\Lambda$. The spin angular functions $\mathcal{Y}^l_{j\mu}(\hat{r})$ are formed from a linear combination of products of spherical harmonics and two-component spinors X_{m_s} multiplied by the appropriate Clebsch-Gordan coefficients,[34]

$$\mathcal{Y}^{l}_{j\mu}(\hat{r}) = \sum_{m_s=\pm 1/2} C^{lj\mu}_{m_s} Y_{l\mu-m_s}(\hat{r}) X_{m_s} , \qquad (3.6)$$

where

$$C^{lj\mu}_{m_s} \equiv [-2(l-j)]^{m_s+1/2} \times \{[l-4m_s(l-j)\,\mu+1/2]/(2l+1)\}^{1/2} .$$

In the Nth unit cell, the wave function can be written, in analogy with Eq. (2.2)

$$\Psi_{\epsilon}(\vec{k},\vec{r}) = \sum_{\Lambda\mu} i^{l} z^{N}_{\Lambda\mu}(\vec{k},\epsilon)\, \mathcal{R}^{(N)}_{\epsilon,\Lambda\mu}(\vec{r}_N) , \qquad (3.7)$$

where the two-component "partial wave" $\mathcal{R}^{(N)}_{\epsilon,\Lambda\mu}(\vec{r}_N)$ is normalized so that outside the muffin tin sphere it takes the form:

$$\mathcal{R}^{(N)}_{\epsilon,\Lambda\mu}(\vec{r}_N) = \mathcal{J}_{\Lambda\mu}(\kappa,\vec{r}_N) + it^{(N)}_{\Lambda}(\epsilon)\ \mathcal{H}_{\Lambda\mu}(\kappa,\vec{r}_N), \qquad r_N \geqslant s^{(N)} . \qquad (3.8)$$

Here the two-component spherical Hankel function $\mathcal{H}_{\Lambda\mu}$ is defined in Eq. (3.5) and the two-component spherical Bessel function $\mathcal{J}_{\Lambda\mu}$ is defined in a similar way, with $j_l(\kappa r_N)$ replacing the $h_l(\kappa r_N)$. Because of the spin-orbit interaction, the relativistic wave function is characterized by an atomic scattering parameter $t^{(N)}_{\Lambda} \equiv \sin\eta^{(N)}_{\Lambda} e^{i\eta^{(N)}_{\Lambda}}$ for each spin angular quantum number Λ; that is, for $l>0$, there are twice as many parameters as for the corresponding nonrelativistic wave function.

The two-center expansion (2.5) can be applied to the upper component of the Dirac scattered wave:

$$ih_{l'}(\kappa r_{N'})\mathcal{Y}^{l'}_{j'\mu'}(\hat{r}_{N'}) = \sum_{lj\mu} j_l(\kappa r_N)\mathcal{Y}^{l}_{j\mu}(\hat{r}_N)\tilde{H}^{NN'}_{lj\mu,l'j'\mu'} , \qquad (3.9)$$

where the relativistic transformation matrix is given by

$$\tilde{H}^{NN'}_{lj\mu,l'j'\mu'} = \sum_{m_s=\pm 1/2} C^{lj\mu}_{m_s} H^{NN'}_{l\mu-m_s\,l'\mu'-m_s} C^{l'j'\mu'}_{m_s} . \qquad (3.10)$$

For the lower component of the scattered wave, the corresponding two-center expansion can be obtained by application of the identity[34]:

$$\vec{\sigma}\cdot\vec{p}\,\zeta_l(\kappa r)\mathcal{Y}^{l}_{j\mu}(\hat{r}) = i\hbar\kappa S_{\Lambda}\zeta_{\bar{l}}(\kappa r)\mathcal{Y}^{\bar{l}}_{j\mu}(\hat{r}) \qquad (3.11)$$

to both sides of Eq. (3.9). Here ζ_l denotes either a spherical Bessel or spherical Hankel function. The relativistic amplitude coefficients $w^{N}_{\Lambda\mu}$ and $z^{N}_{\Lambda\mu}$ are then determined by matching the upper and lower components of the interstitial (3.4) and muffin tin (3.7) expansions of the wave function at each muffin-tin sphere. The resulting relations between the amplitude coefficients are identical to Eqs. (2.6) and (2.7) of Sec. II, but with the spin angular indexes $\Lambda\mu$ or $lj\mu$ replacing the spherical harmonic indexes lm, the transformed two-center expansion matrix $\tilde{H}^{NN'}_{\Lambda\mu\Lambda'\mu'}$ replacing its nonrelativistic analog, and the relativistic kinematic relation (3.2) determining the relationship between energy and momentum. The entire discussion of Sec. II following Eq. (2.7) can be similarly translated into the relativistic version. That is, any formal expression for the relativistic amplitude coefficients can be easily determined from the corresponding expression for the nonrelativistic coefficients by using the simple translation procedure described above.

Although the relativistic and nonrelativistic amplitude coefficients are formally very similar, there are some qualitative differences between them due to the dependence on the electronic spin. In the first place, for a lattice with inversion symmetry, as considered here, the relativistic Green's-function secular matrix $\tilde{M}_{\Lambda\mu,\Lambda'\mu'}(\vec{k},\epsilon)$ for each energy ϵ and wave vector $\vec{k}$, has doubly degenerate eigenvalues $\lambda^{n}(\vec{k},\epsilon)$. The double degeneracy of the zero eigenvalue $\lambda(\vec{k},\epsilon)=0$ corresponds to the so-called Kramer's degeneracy of the energy eigenstates of the lattice and reflects the invariance of the Hamiltonian of the system under time-reversal symmetry.[36] The time-reversal symmetry relation of the Green's-function secular matrix (as well as of the relativistic two-center transformation matrix) can be written in the form

$$\tilde{M}_{lj\mu,l'j'\mu'}(\vec{k},\epsilon) = (-1)^{l-\mu}(-S_{\Lambda}) \times\tilde{M}^{*}_{lj-\mu,l'j'-\mu'}(\vec{k},\epsilon)(-1)^{-l'+\mu'}(-S_{\Lambda'}) . \qquad (3.12)$$

Consequently, if $v^{n\uparrow}_{lj\mu}(\vec{k},\epsilon)$ denotes a component of a given eigenvector of the secular matrix, the corresponding component of the time-reversed eigenvector is given by

$$v^{n\downarrow}_{lj\mu}(\vec{k},\epsilon) = (-S_{\Lambda})(-1)^{l-\mu}[v^{n\uparrow}_{lj-\mu}(\vec{k},\epsilon)]^{*} . \qquad (3.13)$$

Because of the double degeneracy of the secular matrix, the evaluation of the residue of its inverse is no longer given by Eq. (2.22), but by a sum of contributions from both zero eigenvectors:

$$\mathrm{Res}\{[\tilde{M}(\vec{q},\epsilon)]^{-1}_{\Lambda\Gamma\gamma,\Lambda'\Gamma'\gamma'}\} = v^{\uparrow}_{\Lambda\Gamma\gamma}(\vec{q},\epsilon)\,v^{\uparrow *}_{\Lambda'\Gamma'\gamma'}(\vec{q},\epsilon) + v^{\downarrow}_{\Lambda\Gamma\gamma}(\vec{q},\epsilon)\,v^{\downarrow *}_{\Lambda'\Gamma'\gamma'}(\vec{q},\epsilon) . \qquad (3.14)$$

In the absence of spin-orbit interaction, the two time reversed states correspond to the two possible spin orientations of the electron in the presence of a magnetic field. In the presence of the spin-orbit interaction, the two time-reversed states of the electron correspond to the two possible "generalized spin" orientations of the electron in the presence of a magnetic field. The generalized spin orientation is characterized by a combination of actual spin and orbital contributions. In addition, the spin-orbit interaction of the impurity atom is usually different from that of the host atom, so that the presence of the impurity in the lattice generally induces transitions between Bloch states of opposite generalized spin orientation as well as between those of the same orientation. The former process is called "spin-flip" scattering and will be discussed in Sec. VI for cases in which the spin-orbit interaction of the host atom is negligible.

The diagonalization of the Hamiltonian representing the effects of an external magnetic field on the host lattice with significant spin-orbit interactions is in general quite complicated.[37] This is not attempted in the present paper; in the following discussions, the notations $v^{\uparrow}$ and $v^{\downarrow}$ will be taken to mean two orthonormal eigenvectors corresponding to arbitrary generalized spin orientations of the electron, which are not necessarily those which would occur in the presence of a magnetic field. Consequently, in the presence of significant spin-orbit interaction, considerations will be limited to those quantities which do *not* depend upon a knowledge of exact generalized spin orientations in a magnetic field.

A second qualitative difference between the relativistic amplitude coefficients and their corresponding nonrelativistic amplitude coefficients is that their symmetry properties are dictated by the double point group. One can introduce lattice spin angular functions $\mathcal{Y}_{\Lambda\Gamma\gamma}(\vec{r})$ for the lattice double group. For cubic symmetry, these have been described by Onodera and Okazaki.[38] When discussing the amplitude coefficients $z^{N}_{\Lambda\Gamma\gamma}$, the irreducible representation Γ refers to the symmetry of the upper component of the Dirac wave function. The corresponding lower component has the opposite parity. One finds that for cubic double group symmetry, the Brillouin-zone integrals $\chi(\epsilon, 0)$ are no longer diagonal when $l = 2$, since both the partial waves $lj = 2\frac{3}{2}$ and $lj = 2\frac{5}{2}$ include the representation Γ_8^+. The $\chi^{\Gamma}_{lj,l'j'}$ coefficients for cubic double-group symmetry are listed in Table I in terms of their $\frac{1}{48}$th Brillouin-zone integrals $x_{lj\mu,l'j'\mu'}$ for $l \leq 2$. One notices that, as is characteristic of the cubic double group, expressions differing only in parity and $lj \to (l+1)j$ are formally identical.

IV. TRANSITION MATRIX

In order to derive formal expressions for the T matrix applicable to systems with weak and strong spin-orbit interactions at the same time, a generalized spin-orientation index $\theta = \uparrow$ or $\downarrow$ will be introduced. In the absence of spin-orbit interactions, transitions between states of opposite generalized spin orientation are forbidden and the appropriate amplitude coefficients $z^{N\theta}_{l\Gamma\gamma}(\vec{k}, \epsilon)$ and $w^{N\theta}_{l\Gamma\gamma}(\vec{k}, \epsilon)$, are equal to those derived in Sec. II without consideration of the spin degree of freedom. The partial-wave index Λ will be used with the understanding that in expressions for nonrelativistic systems, Λ must be identified with the orbital angular momentum index l.

The transition matrix $\mathcal{T}^{\theta'\theta}_{k'k}(\epsilon)$ describes the rate

TABLE I. Evaluation of $\chi^{\Gamma}_{lj,l'j'}$ coefficients for a cubic lattice in terms of their partial Brillouin-zone integrals $x_{lj\mu,l'j'\mu'}$. Lattice spin-orbital conventions are those of Onodera and Okazaki (Ref. 38).

$$\chi^{6+}_{0\,1/2,0\,1/2} = 24(x_{0\,1/2\;1/2,0\,1/2\;1/2} + x_{0\,1/2\;-1/2,0\,1/2\;-1/2})$$

$$\chi^{6-}_{1\,1/2,1\,1/2} = 24(x_{1\,1/2\;1/2,1\,1/2\;1/2} + x_{1\,1/2\;-1/2,1\,1/2\;-1/2})$$

$$\chi^{8-}_{1\,3/2,1\,3/2} = 12(x_{1\,3/2\;3/2,1\,3/2\;3/2} + x_{1\,3/2\;1/2,1\,3/2\;1/2} + x_{1\,3/2\;-1/2,1\,3/2\;-1/2} + x_{1\,3/2\;-3/2,1\,3/2\;-3/2})$$

$$\chi^{8+}_{2\,3/2,2\,3/2} = 12(x_{2\,3/2\;3/2,2\,3/2\;3/2} + x_{2\,3/2\;1/2,2\,3/2\;1/2} + x_{2\,3/2\;-1/2,2\,3/2\;-1/2} + x_{2\,3/2\;-3/2,2\,3/2\;-3/2})$$

$$\begin{aligned}\chi^{8+}_{2\,5/2,2\,5/2} = {} & 10(x_{2\,5/2\;5/2,2\,5/2\;5/2} + x_{2\,5/2\;-5/2,2\,5/2\;-5/2}) + 2(x_{2\,5/2\;3/2,2\,5/2\;3/2} + x_{2\,5/2\;-3/2,2\,5/2\;-3/2}) \\ & + 12(x_{2\,5/2\;1/2,2\,5/2\;1/2} + x_{2\,5/2\;-1/2,2\,5/2\;-1/2}) + 2\sqrt{5}\,(x_{2\,5/2\;5/2,2\,5/2\;-3/2} \\ & + x_{2\,5/2\;3/2,2\,5/2\;-5/2} + x_{2\,5/2\;-3/2,2\,5/2\;5/2} + x_{2\,5/2\;-5/2,2\,5/2\;3/2})\end{aligned}$$

$$\begin{aligned}\chi^{8+}_{2\,3/2,2\,5/2} = {} & -2\sqrt{30}\,(x_{2\,3/2\;3/2,2\,5/2\;-5/2} - x_{2\,3/2\;-3/2,2\,5/2\;5/2}) - 2\sqrt{6}\,(x_{2\,3/2\;3/2,2\,5/2\;3/2} \\ & - x_{2\,3/2\;-3/2,2\,5/2\;-3/2}) + 12(x_{2\,3/2\;1/2,2\,5/2\;1/2} - x_{2\,3/2\;-1/2,2\,5/2\;-1/2})\end{aligned}$$

$$\begin{aligned}\chi^{7+}_{2\,5/2,2\,5/2} = {} & 20(x_{2\,5/2\;3/2,2\,5/2\;3/2} + x_{2\,5/2\;-3/2,2\,5/2\;-3/2}) + 4(x_{2\,5/2\;5/2,2\,5/2\;5/2} + x_{2\,5/2\;-5/2,2\,5/2\;-5/2}) \\ & -4\sqrt{5}\,(x_{2\,5/2\;5/2,2\,5/2\;-3/2} + x_{2\,5/2\;3/2,2\,5/2\;-5/2} + x_{2\,5/2\;-3/2,2\,5/2\;5/2} \\ & + x_{2\,5/2\;-5/2,2\,5/2\;3/2})\end{aligned}$$

of change of the probability amplitude for finding an electron in the Bloch state $\Psi_\epsilon^{(0)\theta'}(\vec{k}', \vec{r})$, under the influence of a perturbing potential given that it was initially in the Bloch state $\Psi_\epsilon^{(0)\theta}(\vec{k}, \vec{r})$. In this case the perturbing potential is the potential difference $\Delta V(\vec{r})$ of the system with and without the impurity, and the transition matrix is given by[39]

$$\mathcal{T}_{k'k}^{\theta'\theta}(\epsilon) \equiv \frac{1}{N_c} T_{k'k}^{\theta'\theta}(\epsilon) = \frac{1}{N_c} \int d^3r [\Psi_\epsilon^{(0)\theta'}(\vec{k}', \vec{r})]^* \Delta V(\vec{r}) \Psi_\epsilon^{\theta}(\vec{k}, \vec{r}) . \tag{4.1}$$

Here $\Psi_\epsilon^{\theta}(\vec{k}, \vec{r})$ is the wave function of the defected lattice associated with the Bloch function of the pure host lattice $\Psi_\epsilon^{(0)\theta}(\vec{k}, \vec{r})$. The factor N_c, the total number of unit cells in the crystal, appears in the denominator of (4.1) because the Bloch waves (as well as their associated impurity wave functions in the limit $N_c \to \infty$) have been normalized to a primitive unit cell. The T matrix is important for calculating electronic transition rates and lifetimes. The transition rate per unit time induced by incoherent scattering from an atomic fraction c_I of impurities, given that the initial state is occupied and the final state is not, is given by the Golden rule[39]

$$\mathcal{P}_{k'k}^{\theta'\theta}(\epsilon) = \frac{2\pi}{\hbar} \frac{c_I}{N_c} | T_{k'k}^{\theta'\theta}(\epsilon) |^2 \delta(\epsilon(k) - \epsilon(k')) . \tag{4.2}$$

As the number of electrons scattered out of the initial state by a given impurity atom must be equal to the number of electrons scattered into all final states, the T matrix satisfies a sum rule called the optical theorem[39]:

$$\operatorname{Im} T_{kk}^{\theta\theta}(\epsilon) = - \frac{\Omega}{8\pi^2} \int_{\mathrm{Bz}} d^3k' \sum_{\theta'} | T_{k'k}^{\theta'\theta}(\epsilon) |^2 \delta(\epsilon - \epsilon(k')) . \tag{4.3}$$

Consequently, the inverse lifetime of the Bloch state $\Psi_\epsilon^{(0)\theta}(\vec{k}, \vec{r})$, with respect to impurity scattering, is given by

$$\frac{1}{\tau(\vec{k}, \epsilon)} = - \frac{2}{\hbar} c_I \operatorname{Im} T_{kk}^{\theta\theta}(\epsilon) . \tag{4.4}$$

In the muffin-tin model, the perturbing potential $\Delta V(\vec{r})$ is confined within the Ith unit cell and has a spherical boundary. In order to evaluate the T matrix in terms of the exact wave functions derived in Secs. II and III, one can use the Schrödinger or Dirac equation to reduce the volume integral (4.1) to an integral over the surface of the muffin-tin sphere enclosing the perturbing potential $\Delta V(r) \equiv V^i(r) - V^h(r)$.[6] In terms of the muffin-tin amplitude coefficients (2.24), the T matrix then reduces to the form

$$T_{k'k}^{\theta'\theta}(\epsilon) = - \frac{\epsilon}{\kappa^3} e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_I} \times \sum_{\Lambda\Gamma\gamma;\Lambda'} \sin(\eta_\Lambda^i - \eta_\Lambda^h) e^{i(\eta_\Lambda^i - \eta_\Lambda^h)} a_{\Lambda\Gamma\gamma}^{\theta'*}(\vec{k}', \epsilon) \times \mathcal{A}_{\Lambda\Lambda'}^{\Gamma}(\epsilon) a_{\Lambda'\Gamma\gamma}^{\theta}(\vec{k}, \epsilon) . \tag{4.5}$$

This form of the T matrix is similar to that derived by Morgan[6] and utilized by Coleridge and Lee[7,14] for analysis of impurity scattering. However, in the earlier work, the explicit form of the renormalization matrix $\mathcal{A}_{\Lambda\Lambda'}^{\Gamma}(\epsilon)$ was not known.

Alternatively, the T matrix can be expressed in a more symmetric form:

$$T_{k'k}^{\theta'\theta}(\epsilon) = - \sum_{\Lambda\Gamma\gamma;\,\Lambda'} f_{\Lambda\Gamma\gamma}^{\theta'*}(\vec{k}', \epsilon) (\xi - \chi^{\Gamma})_{\Lambda\Lambda'}^{-1} f_{\Lambda'\Gamma\gamma}^{\theta}(\vec{k}, \epsilon) , \tag{4.6}$$

by introducing Bloch-amplitude basis functions proportional to the interstitial amplitude coefficients (2.9):

$$f_{\Lambda\Gamma\gamma}^{\theta}(\vec{k}, \epsilon) \equiv e^{i\vec{k}\cdot\vec{R}_I} \left(- \frac{\partial\lambda}{\partial\epsilon}(\vec{k}, \epsilon) \right)^{-1/2} v_{\Lambda\Gamma\gamma}^{\theta}(\vec{k}, \epsilon) . \tag{4.7}$$

In Appendix C it is demonstrated that these results for the forms of the T matrix are consistent with the optical theorem (4.3) as required.

As discussed in the introduction to this section, the expressions for the T matrix given above may be interpreted either for a nonrelativistic or for a relativistic treatment, where the irreducible representation indices $\Gamma\gamma$ refer, respectively, to the single or double point group of the lattice. Another case of interest occurs when the spin-orbit interaction of the host-metal atom is negligible but that of the impurity is significant. It is then convenient to evaluate the T matrix in terms of the single point group of the lattice, even though the amplitudes of the alloy wave function for the impurity cell are not diagonal in this representation. The host basis functions (4.7) corresponding to a definite spin orientation m_s can be written in the form (neglecting arbitrary phase factors)

$$f_{l\Gamma\gamma m_s}^{\theta}(\vec{k}, \epsilon) = f_{l\Gamma\gamma}(\vec{k}, \epsilon) \delta_{\theta m_s} , \tag{4.8}$$

where the right-hand side of the expression depends upon the amplitude coefficients calculated as described in Sec. II, without regard for the spin degree of freedom, and where throughout this paragraph $\Gamma\gamma$ refers to the irreducible representations of the single point group of the lattice. The T matrix then takes the form

$$T_{k'k}^{\theta'\theta}(\epsilon) = -\sum_{\substack{l'\Gamma'\gamma'; \\ l\Gamma\gamma}} f^*_{l'\Gamma'\gamma'}(\vec{k}', \epsilon) \times (\hat{\xi} - \hat{\chi})^{-1}_{l'\Gamma'\gamma'\theta', l\Gamma\gamma\theta} f_{l\Gamma\gamma}(\vec{k}, \epsilon) \; . \tag{4.9}$$

The evaluation of the nondiagonal kernel $(\hat{\xi} - \hat{\chi})^{-1}$ depends upon the unitary transformation between the single and double point group representations and will be given explicitly in a subsequent publication.

V. SCATTERING MATRIX AND THE FRIEDEL SUM RULE

The number of electronic states of energy less than ϵ, $N(\epsilon)$, introduced by a single impurity in an otherwise perfect lattice can be calculated quite generally from the scattering matrix $\mathcal{S}(\epsilon)$, as shown by Langer and Ambegaokar.[40] The relationship is given by

$$N(\epsilon) = \frac{1}{2\pi} \operatorname{Im}\{\operatorname{Tr}[\ln \mathcal{S}(\epsilon)]\} \; . \tag{5.1}$$

This expression is a generalization of that derived by Friedel[21] for free-electron impurity scattering. The energy derivative of $N(\epsilon)$ gives the change in the density of states induced by the impurity. The total number of electrons displaced in the vicinity of the impurity is given by (5.1) evaluated at the Fermi energy. Because the system must remain electrically neutral, the total amount of electronic charge displaced by the impurity $N(\epsilon_F)$, must exactly compensate the excess nuclear charge Z introduced by the impurity. The equality $Z = N(\epsilon_F)$ is known as the Friedel sum rule.[21]

In order to evaluate Eq. (5.1), one must find the eigenvalues of the scattering matrix $\mathcal{S}(\epsilon)$. This matrix is related to the transition matrix $\mathcal{T}(\epsilon)$ according to[39]

$$\mathcal{S}_{k'k}^{\theta'\theta}(\epsilon) = \frac{(2\pi)^3}{N_c \Omega} \delta(\vec{k} - \vec{k}')\, \delta_{\theta\theta'} - 2\pi i \delta(\epsilon - \epsilon(\vec{k}'))\, \mathcal{T}_{k'k}^{\theta'\theta}(\epsilon) \; . \tag{5.2}$$

From the form of the T matrix [Eqs. (4.5) and (4.6)], one may anticipate that an eigenvector of the $\mathcal{S}(\epsilon)$ matrix can be formed from a linear combination of Bloch-amplitude basis functions of the form:

$$s^\theta_{\nu\Gamma\gamma}(\vec{k}, \epsilon) = \sum_{\Lambda} Q^\Gamma_{\nu\Lambda}(\epsilon) f^\theta_{\Lambda\Gamma\gamma}(\vec{k}, \epsilon) \; . \tag{5.3}$$

Here, as in Sec. IV, Λ denotes the generalized partial-wave index, corresponding to the nonzero interstitial impurity amplitudes $w^I_{\Lambda\Gamma\gamma}(\vec{k}, \epsilon)$; ν labels the distinct eigenvalues of the $\mathcal{S}(\epsilon)$ matrix which exist in one-to-one correspondence with the Λ indexes. In this basis, the eigenvalue equation is given by

$$\sum_{\theta'} \frac{N_c \Omega}{(2\pi)^3} \int d^3k' \, \mathcal{S}_{k'k}^{\theta'\theta}(\epsilon)\, s^{\theta'}_{\nu\Gamma\gamma}(\vec{k}', \epsilon) = S_{\nu\Gamma}(\epsilon)\, s^\theta_{\nu\Gamma\gamma}(\vec{k}, \epsilon) \; . \tag{5.4}$$

Performing the integral over k' and the sum over θ', this reduces to the matrix equation

$$\sum_{\Lambda'} Q^\Gamma_{\nu\Lambda'} \left[\delta_{\Lambda\Lambda'} + 2i \sum_{\Lambda''} \operatorname{Im}\chi^\Gamma_{\Lambda'\Lambda''} (\xi - \chi^\Gamma)^{-1}_{\Lambda''\Lambda} \right] = \sum_{\Lambda'} Q^\Gamma_{\nu\Lambda'} \left[(\xi - \chi^{\Gamma *})(\xi - \chi^\Gamma)^{-1} \right]_{\Lambda'\Lambda} = S_{\nu\Gamma} Q^\Gamma_{\nu\Lambda} \; , \tag{5.5}$$

where ξ is given by Eq. (2.27). The kernel

$$\sigma^\Gamma_{\Lambda\Lambda'} \equiv [(\xi - \chi^{\Gamma *})(\xi - \chi^\Gamma)^{-1}]_{\Lambda\Lambda'} \tag{5.6}$$

is not unitary, a result that is caused by the use of nonorthogonal basis functions $f_{l\Gamma\gamma}(\vec{k}, \epsilon)$. However, it can be related to a unitary matrix $\tilde{\sigma}^\Gamma$ by means of a similarity transformation:

$$\tilde{\sigma}^\Gamma_{\alpha\alpha'} \equiv (\omega^{\Gamma\alpha})^{-1/2} \sum_{\Lambda\Lambda'} (u^{\Gamma\alpha}_\Lambda)^* \sigma^\Gamma_{\Lambda\Lambda'} u^{\Gamma\alpha'}_{\Lambda'} (\omega^{\Gamma\alpha'})^{1/2} \; . \tag{5.7}$$

Here $\omega^{\Gamma\alpha}$ and $u^{\Gamma\alpha}$ denote the eigenvalues and eigenfunctions of the "overlap" matrices [Appendix Eq. (C2)]:

$$\frac{1}{\pi} \sum_{\Lambda'} \operatorname{Im}\chi^\Gamma_{\Lambda\Lambda'} (u^{\Gamma\alpha}_{\Lambda'})^* = \omega^{\Gamma\alpha} (u^{\Gamma\alpha}_\Lambda)^* \; . \tag{5.8}$$

Since a unitary matrix has eigenvalues of magnitude unity, the eigenvalues of the $\mathcal{S}$ matrix can be written in the familiar form

$$S_{\nu\Gamma}(\epsilon) = e^{2i\varphi_{\nu\Gamma}(\epsilon)} \; , \tag{5.9}$$

where $2\varphi_{\nu\Gamma}(\epsilon)$ is the phase angle of an eigenvalue of $\tilde{\sigma}^\Gamma$ or σ^Γ. The degeneracy $d_{\nu\Gamma}$ of the eigenvalue can be deduced from the form of the eigenvalue equation (5.4). In the absence of spin-orbit interactions, there is a distinct solution of Eq. (5.4) for each spin orientation θ, as well as for each member of the irreducible representation Γ. Thus, for a nonrelativistic treatment, the degeneracy is given by $d_{\nu\Gamma} = 2g(\Gamma)$, where $g(\Gamma)$ is the degeneracy of the Γth representation of the single-point group of the lattice. In the presence of spin-orbit interactions, the eigenvectors of Eq. (5.4) are no longer characterized by a specific "spin-orbital" orientation θ, so that the degeneracy is given by the degeneracy of the Γth representation of the double-point group of the lattice, i.e., by $d_{\nu\Gamma} = g(\Gamma)$. In either case, the number of impurity-induced states can be expressed by

$$N(\epsilon)=\frac{1}{\pi}\sum_{\nu\Gamma} d_{\nu\Gamma}\varphi_{\nu\Gamma}(\epsilon)\ . \tag{5.10}$$

The effective phase shifts $\varphi_{\nu\Gamma}$ will be termed "Friedel" phase shifts.

Whenever the Brillouin-zone integral $\chi^{\Gamma}(\epsilon)$ is diagonal (for $l \leqslant 2$ in a nonrelativistic treatment and $l \leqslant 1$ in a relativistic treatment), the eigenvalues of the scattering matrix can be written immediately. In this case $Q_{\nu\Lambda}=\delta_{\nu\Lambda}$ and the Friedel phase shift is given by

$$\varphi_{\Lambda\Gamma}=\tan^{-1}\left(\frac{\sin(\eta_{\Lambda}^{i}-\eta_{\Lambda}^{h})\,\mathrm{Im}\chi_{\Lambda\Lambda}^{\Gamma}}{\sin\eta_{\Lambda}^{i}\,\sin\eta_{\Lambda}^{h}-\sin(\eta_{\Lambda}^{i}-\eta_{\Lambda}^{h})\,\mathrm{Re}\chi_{\Lambda\Lambda}^{\Gamma}}\right)\ . \tag{5.11}$$

An equivalent expression has been derived by Lasseter and Soven.[23] Alternatively, the Friedel phase shift may be expressed in terms of the Bloch-amplitude renormalization coefficient $\mathcal{A}_{\Lambda\Lambda}^{\Gamma}(\epsilon)$:

$$\varphi_{\Lambda\Gamma}=(\eta_{\Lambda}^{i}-\eta_{\Lambda}^{h})+\arg\mathcal{A}_{\Lambda\Lambda}^{\Gamma}(\epsilon)\ . \tag{5.12}$$

VI. APPLICATIONS

The calculations described in Secs. II and III yield exact normalized wave functions for a single substitutional impurity in an otherwise perfect infinite lattice of muffin-tin potentials. In Secs. IV and V the corresponding expressions for the transition and scattering matrices are derived. In order to relate these ideal quantities to actual experimental situations, two modifications must be considered: namely, the effects of the electron-phonon interactions and the effects of finite impurity concentrations. A qualitative discussion of these points is given below.

First consider the effects of the electron-phonon interaction. In the previous discussion, it has been implicitly assumed that the atoms of the alloy are clamped at their lattice positions $\vec{R}_N$. In a real material, even for temperatures close to absolute zero, the electronic states near the Fermi level are coupled to the lattice vibrations.[41] Consequently, for electronic states near the Fermi level, the wave functions as calculated in Secs. II and III, and the corresponding scattering rates or lifetimes as calculated from Eqs. (4.2) or (4.4), must be modified in order that they may be compared with experimental data.[7,14] It is reasonable to assume that dominant electron- phonon effects are those of the pure host metal, which are described by the real part of the electron-phonon self-energy $\Sigma_{ep}(\vec{k},\epsilon^{(*)})$.[42] [Here the asterisk (*) is used to indicate that the quantity has been corrected for electron-phonon effects.] The real part of the electron-phonon self-energy gives the difference between the effective eigenenergy of the host system in the presence and in the absence of phonon interactions for given wave vector $\vec{k}$.

$$\epsilon^{(*)}(\vec{k})=\epsilon(\vec{k})+\Sigma_{ep}(\vec{k},\epsilon^{(*)})\ . \tag{6.1}$$

If the electronic eigenstates of the host renormalized by the electron-phonon interactions $\Psi_{\epsilon^{(*)}}^{(0)(*)}(\vec{k},\vec{r})$ satisfy the same boundary conditions as do the corresponding clamped lattice eigenstates $\Psi_{\epsilon}^{(0)}(\vec{k},\vec{r})$ it can be shown from Brillouin-Wigner perturbation theory that the overlap of the two corresponding eigenstates is related to the energy derivative of the real part of the self-energy[42,43]

$$\frac{1}{N_c}\int_{\text{crystal}} d^3r\,[\Psi_{\epsilon(*)}^{(0)(*)}(\vec{k},\vec{r})]^{*}\Psi_{\epsilon}^{(0)}(\vec{k},\vec{r}) =\left(1-\frac{\partial}{\partial\epsilon^{(*)}}\Sigma_{ep}(\vec{k},\epsilon^{(*)})\right)^{1/2}\ . \tag{6.2}$$

It can also be shown that this renormalization of the amplitude of the Fermi-level Bloch wave functions is simply related to the corresponding renormalization of the Fermi velocity in the presence of the electron-phonon interactions. The "renormalized" Fermi velocity can be determined by taking the gradient of Eq. (6.1) with respect to wave vector and evaluating it at the Fermi energy. Since the variation of the self-energy with respect to wave vector $\partial\Sigma_{ep}/\partial k$ is negligible compared with its variation with respect to energy $\partial\Sigma_{ep}/\partial\epsilon^{(*)}$,[42] the renormalized Fermi velocity is given accurately by

$$\vec{v}_{\epsilon_F^{(*)}}^{(*)}(\vec{k})\equiv\frac{1}{\hbar}\vec{\nabla}_k\,\epsilon_F^{(*)}(\vec{k})\simeq\frac{\vec{v}_{\epsilon_F}(\vec{k})}{1-\partial\Sigma_{ep}(\vec{k},\epsilon_F^{(*)})/\partial\epsilon_F^{(*)}}\ . \tag{6.3}$$

This relationship means that the ratio of the squared magnitude of a Fermi-level Bloch wave function to its corresponding Fermi velocity is nearly invariant under the effects of the electron-phonon interaction

$$\frac{|\Psi_{\epsilon_F}^{(0)}(\vec{k},\vec{r})|^2}{v_{\epsilon_F}(\vec{k})}\simeq\frac{|\Psi_{\epsilon_F^{(*)}}^{(0)(*)}(\vec{k},\vec{r})|^2}{v_{\epsilon_F^{(*)}}^{(*)}(\vec{k})}\ . \tag{6.4}$$

In the presence of the impurity, a similar argument can be made. If simultaneous phonon and impurity scattering processes, and changes in the phonon spectrum induced by the impurity, are neglected, then Eq. (6.4) remains valid if the impurity wave functions $\Psi_{\epsilon_F}(\vec{k},\vec{r})$ or $\Psi_{\epsilon_F^{(*)}}^{(*)}(\vec{k},\vec{r})$ replace their corresponding Bloch wave functions. It follows that the ratio of the squared T matrix to the corresponding Fermi velocities is, to a good approximation, the same for a clamped lattice as for a more realistic lattice including electron-phonon interactions:

$$\frac{|T_{k'k}(\epsilon_F)|^2}{v_{\epsilon_F}(\vec{\mathrm{k}}')\,v_{\epsilon_F}(\vec{\mathrm{k}})} \simeq \frac{|T^{(*)}_{k'k}(\epsilon_F^{(*)})|^2}{v^{(*)}_{\epsilon_F^{(*)}}(\vec{\mathrm{k}}')\,v^{(*)}_{\epsilon_F^{(*)}}(\vec{\mathrm{k}})} \,. \tag{6.5}$$

These results[42] are very convenient from the viewpoint of the analysis of experiments involving electrons at the Fermi level in terms of the impurity wave functions and transition matrices discussed in the preceding sections. As will be shown below, experimentally observed quantities such as impurity-induced Knight shifts or transition probabilities[12-14] involve Fermi-surface averages of these ratios (6.4) or (6.5). In any case, methods for evaluating the renormalization parameter $\partial\Sigma_{ep}(k,\epsilon^{(*)})/\partial\epsilon^{(*)}$ either semiempirically,[44,45] or from first principles[46,47] are well documented in the literature.

Secondly, consider the effects of finite-impurity concentrations. Realistic impurity concentrations are atomic fractions of the order of 10^{-6} to 10^{-3}. The formal extension of the amplitude equation (2.7) to include scattering from more than one impurity is straightforward, but its exact solutions then depend upon the relative locations of the impurities. Fortunately, the incoherent scattering approximation, in which each impurity scatters electrons independently of all other impurity sites, is valid for low impurity concentrations. In this approximation the expressions derived in the above sections may be used to describe impurity scattering at finite impurity concentrations, except for a concentration-dependent change in the normalization of the wave functions, or equivalently in the spectral weight function. Such effects can be observed experimentally as a change in the bulk density of states as discussed by Lasseter and Soven[23] (and briefly below). For the purposes of the present paper, it suffices to note that the expressions derived in the sections above are applicable for investigating incoherent scattering, and the resulting scattering rates (4.2) or inverse electron lifetimes (4.4) are accurate through terms linear in the impurity atomic fraction c. Similarly, the electron densities calculated from the squared magnitude of the impurity wave functions as calculated in Secs. II and III, are valid to zero order in the impurity atomic fraction.

Within this framework, a variety of experimental measurements can be analyzed. The approach followed in the present paper is especially suitable for the analysis of experiments which involve the eigenstates of the system at the Fermi level $\epsilon=\epsilon_F$. It has the advantage that the Brillouin-zone integrals (2.20) need be evaluated only at the Fermi energy, and it gives one the option of treating the basic parameters of the theory, namely the atomic scattering phase shifts $\eta_l^h(\epsilon_F)$ and $\eta_l^i(\epsilon_F)$, by semiempirical analysis of experimental data. data.[7,12-14] Moreover, one expects that the muffin-tin model best describes the dilute alloy potential close to the Fermi level. In this section, connections of the present approach with recent work of other authors are briefly discussed; two additional applications are then developed in detail.

The change in the electronic density of states induced in a dilute alloy, relative to that of the pure host, is proportional to the energy derivative of Eq. (5.10) multiplied by impurity atomic fraction c_I.[48] It affects experimental quantities such as the electronic specific heat and the static magnetic susceptibility. This was the subject of a recent paper by Lasseter and Soven.[23]

Residual resistivities of alkali metal alloys were calculated by Dupree[1] in his original treatment of the muffin-tin impurity problem. He estimated the scattering amplitude from the asymptotic form of the wave function amplitude coefficients (2.32), (2.33) for host lattice sites far from the impurity cell in order to calculate the resistivity by means of the usual approximation to the Boltzmann equation. Introducing explicit expressions for the T matrix (4.5-6) into the epxression for the impurity scattering rate (4.2) considerably simplifies the calculation of the residual resistivity. Such an approach has been followed by Coleridge and coworkers.[7,12,14]

The Dingle temperature is a measure of impurity scattering as it affects the damping of de Haas-van Alphen oscillations for a specific Landau orbit. It is often calculated by averaging the scattering rate $[\tau(\vec{\mathrm{k}},\epsilon_F)]^{-1}$ as determined from Eq. (4.4) around the corresponding Landau orbit in k space.[49] This approximation neglects the effects of magnetic field-dependent variations of the density of states at the Fermi level upon the scattering rate, and in the presence of spin-orbit interactions it assumes that the magnetic field does not affect the "spin-flip" scattering rate relative to the "no spin-flip" scattering rate. A justification of this approximation may be based on the fact that for the magnetic field strengths used in typical de Haas-van Alphen experiments ($<10^5$ G), the mean fractional variation in the electronic density of states with magnetic field is of the order of a few per cent and the magnitudes of the energy level shifts are of the order of 10^{-4} times the Fermi energy. Analyses of Dingle temperature anisotropies in various noble metal alloys have been discussed by Coleridge and Lee[7,13,14] and will also be the subject of further work.[8]

Spin-flip scattering rates

It is found experimentally that impurity-induced spin-flip scattering contributes to the spin-lattice relaxation rate and consequently to the widths of conduction-electron spin resonance signals. Such effects have been observed in dilute alloys of lithium and sodium by Asik *et al.*[19,50] The longitudinal spin-lattice relaxation rate T_1 is defined as the time constant for exponential decay of the magnetization of a sample, initially polarized by a dc magnetic field, when the magnetic field is removed. Since the magnetization is proportional to $\delta n(t)$, the population difference between electronic states of up and down spin, the spin-lattice relaxation rate can be calculated from the analysis of the expression[50]

$$\frac{d\delta n(t)}{dt}=-\frac{\delta n(t)}{T_1}\ . \tag{6.6}$$

For the reasons discussed in Sec. III above, only host metals having negligible spin-orbit interaction will be considered here. The appropriate T matrix describing the spin-flip scattering process at the impurity is thus given by Eq. (4.9), with $\theta' = -\theta$. The rate of change of the population difference $d\delta n/dt$ can be calculated from the corresponding transition rate [Eq. (4.2)] multiplied by the appropriate Fermi distribution factors and integrated over all possible final and initial wave vectors. In this way, the impurity scattering contribution to the longitudinal spin-lattice relaxation rate, for atomic fraction c_I of impurities, is related to the spin-flip T matrix according to

$$\frac{1}{T_1}=\frac{4\pi}{\hbar}\,\frac{c_I}{\mathfrak{D}(\epsilon_F)}\left(\frac{\Omega}{(2\pi)^3}\right)^2\iint\frac{d^2k}{|\nabla\epsilon(\vec{k})|_{\epsilon_F}} \times\frac{d^2k'}{|\nabla\epsilon(k')|_{\epsilon_F}}\;|T^{\uparrow\downarrow}_{k'k}(\epsilon_F)|^2\ . \tag{6.7}$$

Here $\mathfrak{D}(\epsilon_F)$ denotes the number of states of given spin per unit energy of the host metal at the Fermi level normalized to the volume of a unit cell Ω:

$$\mathfrak{D}(\epsilon_F)\equiv\frac{\Omega}{(2\pi)^3}\int\frac{d^2k}{|\nabla\epsilon(\mathrm{k})|_{\epsilon_F}}\ . \tag{6.8}$$

Evaluating this expression with the T matrix of Eq. (4.9), the following result is obtained:

$$\frac{1}{T_1}=\frac{4c_I}{\pi\hbar\,\mathfrak{D}(\epsilon_F)}\sum_{\substack{l\Gamma\gamma;l_1\\ l'\Gamma'\gamma';l'_1}}\mathrm{Im}\chi^{\Gamma}_{ll_1}(\epsilon_F) \times\mathrm{Im}\chi^{\Gamma'}_{l'l'_1}(\epsilon_F)\,(\hat{\xi}-\hat{\chi})^{-1}_{l\Gamma\gamma\uparrow,\,l'\Gamma'\gamma'\downarrow} \times(\hat{\xi}^*-\hat{\chi}^*)^{-1}_{l_1\Gamma\gamma\uparrow,\,l'_1\Gamma'\gamma'\downarrow}\ . \tag{6.9}$$

The change in the density of states induced by the impurity has been neglected in this expression since it contributes terms of order c_I^2. Previous theoretical treatments of spin-flip scattering (Refs. 19, 50, 51) have been based on the analogous free-space scattering process, valid for free-electron-like hosts. The free-electron treatment may be justified for alkali metal host,[19] but the more accurate treatment given by Eq. (6.9) may be needed to describe relaxation in copper or silver hosts, for example. Unfortunately, to the knowledge of this author, conduction-electron resonance experiments for nonmagnetic hosts in Cu and Ag have yet to be performed. In principle, a similar analysis should hold in the more general case in which the impurity causes "flipping" between the two generalized spin orientation eigenstates of the host. However, spin-orbit interaction in the host metal causes additional experimental difficulties in measuring T_1; the resulting wave vector dependence of the conduction-electron g factor may contribute significantly to the linewidth of the signal.[52]

Host Knight shift due to an impurity at a specific neighbor site

In the presence of an external magnetic field, the electrons of the alloy are polarized so that the effective magnetic field "seen" by the host nucleus in the Nth unit cell of the crystal is shifted by an amount ΔK_N relative to that of the pure host metal K°. This effect is termed the Knight shift and is observed through nuclear magnetic resonance (NMR) measurements.[50] Because the magnitude of the Knight shift depends upon the location of the host cell relative to the impurity cell, one expects to see, in the NMR spectrum of the alloy, a series of satellites on either side of the resonance of the pure host.

The shift is proportional to the applied magnetic field, so the separation between satellites increases linearly with increasing applied field. In this way, Knight shifts can be distinguished experimentally from quadrupole interactions which also cause NMR satellites.[53,54] The magnitude of the Knight shift for a given satellite is only very weakly dependent upon the impurity concentration for sufficiently dilute alloys. Such satellites have recently been studied by Lang, Boyce, Lo, and Slichter[55] for magnetic impurities in Cu in external magnetic fields through 65 kG. These spectra are apparently dominated by the effects of the spin polarized impurity atoms which interact directly with the host nuclei via dipole-dipole interactions and which induce spin density oscillations of the conduction electrons through an exchange scattering mechanism. Such dipolar and exchange scattering contributions to the Knight shifts will not be considered here; the present analysis can be most easily applied to the calculation of the contact contribution to the hyperfine interaction when the conduction-electron charge distribution is determined by potential scattering. The contact contribution to the Knight shift due to potential scattering is expected to dominate for nonmagnetic impurities.[50] A free-electron calculation by Blandin and Daniel[17] suggests that it will be of the same order of magnitude as that quoted for magnetic impurities.[55] Furthermore, the contact interaction is isotropic whereas dipolar interactions depend upon the magnetic field direction; so that these two contributions can be distinguished experimentally through measurements on single crystals.

The Knight shift in the Nth unit cell of the lattice due to the contact interaction is given by[50]

$$\Delta K_N = -\frac{8\pi}{3}\left(\langle\mu_e\rangle_N - \langle\mu_e^0\rangle_N\right) , \tag{6.10}$$

where the term in parentheses denotes the average value of the electronic magnetic moment per unit volume parallel to the applied magnetic field H_0 evaluated at $\vec{r}=\vec{R}_N$, relative to that for the pure host metal. For simplicity, it will be assumed that spin-orbit interactions are negligible and that a nonrelativistic treatment sufficies. Contributions to Eq. (6.10) from polarization of core electrons due to exchange interaction with the valence electrons[50] will also be neglected. Then, evaluating the expectation values in Eq. (6.10), the Knight shift can be written

$$\Delta K_N = \frac{8\pi}{3}\,\overline{\chi}_s \Omega H_0\left[\langle|\Psi_{\epsilon_F}(\vec{k},\vec{R}_N)|^2\rangle - \langle|\Psi^{(0)}_{\epsilon_F}(\vec{k},\vec{R}_N)|^2\rangle\right] , \tag{6.11}$$

where

$$\langle|\Psi_{\epsilon_F}(\vec{k},\vec{R}_N)|^2\rangle \equiv [\mathfrak{D}(\epsilon_F)]^{-1}\frac{\Omega}{(2\pi)^3}\int\frac{d^2k}{|\nabla\epsilon(\vec{k})|_{\epsilon_F}}\,|\Psi_{\epsilon_F}(\vec{k},\vec{r}=\vec{R}_N)|^2 \tag{6.12}$$

and the electron spin susceptibility per unit volume is given by

$$\overline{\chi}_s = \tfrac{1}{2}\langle|g|^2\rangle\,\mu_B\,\mathfrak{D}(\epsilon_F)/\Omega . \tag{6.13}$$

Here g is the electron g factor and μ_B is the Bohr magneton. Evaluating the wave function averages in terms of the amplitude coefficients of Eq. (2.33), and noting that only the s-wave component ($l=0$) and therefore the totally symmetric representation Γ_1, are nonzero at $\vec{r}=\vec{R}_N$, one obtains the following relation for the Knight shift:

$$\Delta K_N = \frac{8\pi}{3}\,\overline{\chi}_s H_0\,\frac{\mathfrak{D}^0(\epsilon_F)}{\mathfrak{D}(\epsilon_F)}\,\frac{1}{\sin^2\eta_0^h}\,|R^{(h)}_{\epsilon_F 0}(r_N=0)|^2\sum_{l\Gamma\gamma;l'}\mathrm{Im}\left[\chi_{0\Gamma_1,l\Gamma\gamma}(\epsilon_F,\vec{R}_N-\vec{R}_I)\,(\xi-\chi^{\Gamma})^{-1}_{ll'}\chi_{0\Gamma_1,l'\Gamma\gamma}(\epsilon_F,\vec{R}_N-\vec{R}_I)\right] , \tag{6.14}$$

where $\mathfrak{D}^0(\epsilon_F)\equiv\Omega k_F^3/4\pi^2\epsilon_F$. In deriving this result the symmetry properties of the Brillouin-zone integral $\chi_{l\Gamma\gamma,l'\Gamma'\gamma'}(\epsilon,\vec{R}_N-\vec{R}_I)$ were used. From the symmetry properties of the KR secular matrix Eqs. (A8) and (A9) and using the cubic harmonic conventions of von der Lage and Bethe,[29,31] it can be shown that the real and imaginary parts of $\chi_{l\Gamma\gamma,l'\Gamma'\gamma'}(\epsilon,\vec{R}_N-\vec{R}_I)$ are determined from the principal part and residue contributions, respectively, of the Brillouin-zone integral (2.20). Also, $\chi_{l\Gamma\gamma,l'\Gamma'\gamma'}(\epsilon,\vec{R}_N-\vec{R}_I)=\chi_{l'\Gamma'\gamma',l\Gamma\gamma}(\epsilon,-(\vec{R}_N-\vec{R}_I))$. As in the evaluation of the T matrix of Sec. IV, the sum over partial-wave components l and l' in in this expression should include only those for which the phase-shift differences $(\eta_l^i-\eta_l^h)$ and $(\eta_{l'}^i-\eta_{l'}^h)$ are nonzero. Furthermore, as expected $\chi_{l\Gamma\gamma,l'\Gamma'\gamma'}(\epsilon,\vec{R}_N-\vec{R}_I)$ and therefore ΔK_N obtained from Eq. (6.14), is identical for all host sites N belonging to a given neighbor shell surrounding the impurity site I. It is also interesting to note that the position of the Knight-shift satellite is largely independent of impurity concentration; concentration-dependent corrections to Eq. (6.14) come from impurity-induced changes in the density of states. Experimentally, the fractional Knight shift is frequently measured. If K° denotes the Knight shift of an isolated host nucleus, the fractional Knight shift is given by

$$\frac{\Delta K_N}{\mathrm{K}^\circ} = \frac{1}{\mathrm{Im}\chi_{00}^{\Gamma_1}}\sum_{l\Gamma\gamma;l'}\mathrm{Im}\left[\chi_{0\Gamma_1,l\Gamma\gamma}(\epsilon_F,\vec{R}_N-\vec{R}_I)\right.$$
$$\left.\times(\xi-\chi^{\Gamma})^{-1}_{ll'}\,\chi_{0\Gamma_1,l'\Gamma\gamma}(\epsilon_F,\vec{R}_N-\vec{R}_I)\right] . \tag{6.15}$$

VII. DISCUSSION

In summary, the following results have been developed in the present paper. Following the work of Dupree,[1] expressions have been derived for the exact, nonrelativistic wave functions of an electron in a muffin-tin lattice containing a single substitutional impurity. These are given by (2.1) and (2.2), where the amplitude coefficients are given by (2.24)–(2.27) and (2.32)–(2.33). These amplitude coefficients depend upon the atomic scattering phase shifts of the host atom η_l^h and impurity atom η_l^i, upon the Bloch amplitude coefficients of the pure host (2.8)–(2.9), and upon the Brillouin-zone integrals (2.20). Expressions for the analogous relativistic wave functions are given by Eqs. (3.4) and (3.7). The relativistic amplitude coefficients may be determined by a procedure very similar to that for determining the coefficients for a nonrelativistic treatment, as explained at the end of Sec. III. Once the electronic wave functions are known, the transition and scattering matrices may be evaluated; the results are given by Eqs. (4.5)–(4.6) and (5.9), respectively. The phases $\phi_{\nu\Gamma}$ of the $\mathcal{S}$ matrix (Friedel phase shifts) determine the Friedel sum (5.10), as recently derived in less general form by Lasseter and Soven.[23] From the knowledge of the electronic wave functions, transition matrices, and scattering matrices of the model system, and with certain assumptions about the relationship of the model to real materials, one can calculate various experimentally accessible quantities. Five examples are discussed. The calculation of the change in the electronic density of states is mentioned as an application of the present approach which has been recently studied by Lasseter and Soven.[23] Residual resistivity and Dingle-temperature anisotropies are mentioned briefly; they are the subject of collaborative work of the present author with Coleridge and Lee.[7,8] Expressions for longitudinal spin-lattice relaxation rates in conduction-electron spin resonance (6.9) and for host Knight-shift satellites (6.14) are, however, developed in detail.

The difference between impurity scattering in a lattice and the analogous potential scattering problem in free space can be characterized in terms of the host backscattering matrix T^M_Γ, defined by Morgan,[6] and the related renormalization matrix $\mathfrak{A}^\Gamma$.[6,14,20] Morgan's backscattering matrix has been shown to be related to the Brillouin-zone integral according to (2.29). For a free-electron-like host, the Brillouin-zone integral is given by Eq. (2.30); the backscattering matrix vanishes and the renormalization matrix reduces to the identity matrix. Brillouin-zone integrals and backscattering matrix elements have been numerically evaluated for the three noble metals, copper, silver, and gold, at their Fermi energies. The numerical results will be given in a subsequent publication.[8] One finds that these hosts show significant deviation from free-electron-like behavior, and that an accurate procedure such as the present one is needed for a realistic analysis of experimental data for their dilute alloys.

Throughout the present treatment, the effects of the muffin-tin potentials enter only in terms of their "atomic" scattering phase shifts $\eta^h_\Lambda(\epsilon)$ and $\eta^i_\Lambda(\epsilon)$. If one is interested in impurity scattering at the Fermi level, the host atom scattering phase shifts can be calculated either from an *ab initio* calculation of the muffin-tin potential or from a phase shift analysis of the Fermi surface based on accurate de Haas–van Alphen frequency measurements.[56,57] The latter approach has several advantages. Because of the errors inherent in the independent-electron approximation, no *ab initio* calculation has yet been able to reproduce the Fermi surface of a metal as accurately as it is known from de Haas–van Alphen measurements. Such a semiempirical approach has been successfully adopted for use in the analysis of Dingle-temperature anisotropy data for dilute noble metal alloys by Coleridge, Lee, and Holzwarth.[7,8] The host phase shifts determined from fits to de Haas–van Alphen data[58] were comparable to those determined from *ab initio* calculations.[59–61]

Other treatments of impurity scattering which are more realistic than a free-electron treatment have appeared in the literature. Most of the competitive approaches are based on approximate eigenfunction expansions. Orthogonalized plane wave basis functions have been used for calculations involving free-electron-like hosts[62]; combined orthogonalized plane wave and tight-binding functions have been used for calculations involving noble[63–65] or transition metal hosts.[66] Such approaches have in principle two main advantages over the present exact muffin-tin solution approach. Firstly, non-muffin-tin potential treatments can take into account nonspherical contributions to the host and impurity potentials and can include long-range components of the effective impurity potentials. The approximate eigenfunction treatments listed above did not focus on these aspects of the problem. However, it should be possible to adapt some of the systematic procedures now being developed for correcting the muffin-tin potential model in pure metals[67] to the impruity problem. Secondly, electron-electron correlations, which are important for describing magnetic impurities or hosts, are perhaps more easily treated by use of an eigenfunction expansion procedure. This point is briefly elaborated below.

In the present work, attention has been focused on the Fermi surface properties of nonmagnetic substitutional impurities in nonmagnetic metallic hosts. It is evident that the general formalism developed here can be extended to other systems as well. Firstly, a very similar analysis can be used to study interstitial impurities. This was the subject of a recent paper.[68] Secondly, the present approach could be applied to analyze experimental measurements which probe electrons throughout the conduction band of the metal. This extension leads to a technical difficulty; the evaluation of the Brillouin-zone integrals at a single-electron energy involves lengthy computation, comparable to the construction of a density-of-states curve for the conduction band of the host metal. If the Brillouin-zone integral computations were streamlined, then one could use the present approach to analyze such experiments as the impurity-induced electric field gradients as measured by nuclear quadrupole resonance experiments[53,54] or optical spectra of the alloys.[69] The present approach is also relevant to x-ray spectra of the pure host metal in which relaxation effects of the absorbing or emitting atom may be represented in terms of the "impurity" phase shifts.[70] Thirdly, the treatment presented here need not be restricted to metals. Although one expects the muffin-tin approximation to be less accurate for insulators and semiconductors than for metals, the formalism of the present approach can describe impurity states in nonmetals. Since the muffin-tin approximation is unable to represent long-range Coulomb interactions induced by charged impurities, attention would have to be confined to neutral impurities. For bound states of these systems, Eqs. (2.34) and (2.35) are directly applicable. Finally, for the description of magnetic impurities or hosts in which electron-electron correlations are important, such as in the description of exchange scattering by a magnetic impurity, the present approach is not directly applicable. On the other hand, correlation behavior can be simulated within a modification of the present approach by assuming certain free-atom-like correlations (such as L-S coupling)[65] to exist within the muffin-tin spheres. Whether such an approach is feasible or whether correlations are better handled by approximate eigenfunction expansion procedures[62-66] needs to be the subject of further study. However, for the description of rigidly aligned magnetic systems that can be described simply in terms of a spin-dependent electronic potential, the present approach can be easily modified in analogy to the calculation of ferromagnetic band structures.[71] In the absence of spin-orbit interactions, the introduction of a spin-dependent electronic potential means that one merely has to solve the impurity scattering problem separately for each spin orientation. In the presence of spin-orbit interactions, the introduction of a spin-dependent electronic potential breaks the double-point group symmetry of the system, as described by Falicov and Ruvalds.[72] Aside from the introduction of new symmetry properties, it is anticipated that the relativistic treatment of spin-dependent impurity scattering can be carried out by a straightforward extension of the present treatment. Such a treatment may be appropriate for the study of such systems as dilute Au(Fe) alloys aligned in a magnetic field.

ACKNOWLEDGMENTS

The author is grateful to Professor Martin J. G. Lee for suggesting this problem and for his careful guidance throughout the progress of this work. The author would also like to thank Dr. Harold Myron for the use of his Korringa-Kohn-Rostoker computer programs and Dr. T. H. Dupree, Dr. N. E. Christensen, and Dr. R. H. Lasseter for sending copies of their unpublished work. Discussions with Professor D. Forster, Dr. P. T. Coleridge, Professor J. T. Waber, and with members of the solid state group at the University of Chicago, especially Dr. R. L. Bush and Dr. M. S. Jhon, are also gratefully acknowledged.

APPENDIX A: DETAILS OF THE NONRELATIVISTIC TREATMENT OF THE IMPURITY WAVE FUNCTIONS

The two-center transformation matrix introduced in Eq. (2.5) is given by

$$H^{NN'}_{lml'm'}(\epsilon) = 4\pi i^{l-l'} \sum_{LM} i^{-L}[ih_L(\kappa R_{NN'})]\, Y^*_{LM}(\hat{R}_{NN'}) \times \int d^2\hat{r}\, Y^*_{lm}(\hat{r})\, Y_{LM}(\hat{r})\, Y_{l'm'}(\hat{r}) \,. \tag{A1}$$

Expansion (2.5) converges provided that the distance between the point at which the wave is evaluated and the second center is smaller than the distance between centers, i.e., as long as $r_N < R_{NN'}$, where $\vec{R}_{NN'} \equiv \vec{R}_{N'} - \vec{R}_N$.

From Eq. (2.6), it is evident that the interstitial amplitude coefficient $w^N_{lm}(\vec{k}, \epsilon)$ vanishes whenever the corresponding atomic scattering parameter $t^{(N)}_l(\epsilon)$ is negligible. Since, for electronic energies in the range appropriate for the conduction band of a metal, $\eta^{(N)}_l(\epsilon)$ decreases rapidly with increasing l, the interstitial expansion of the wave function (2.1) generally contains only a few, low angular momentum, partial-wave contributions from each lattice site. In contrast, the muffin-tin amplitude coefficients z^N_{lm} given by Eq. (2.7) diverge for large angular momenta l because the two-center transformation matrix $H^{NN'}_{lml'm'}$ diverges. However, the condition for convergence of the two-center transformation (2.5) ensures that the single-center expansion for the wave function (2.2) converges with increasing l, not only inside the muffin-tin sphere, but also at any distance less than the nearest-neighbor distance of the lattice. As will be shown below, the technical difficulty caused by the divergence of the muffin-tin amplitude coefficients for large l can be avoided by solving Eq. (2.7) in terms of the finite number of interstitial amplitude coefficients $w^N_{lm}(\vec{k},\epsilon)$ corresponding to nonzero atomic scattering parameters $t^{(N)}_l(\epsilon)$. If needed, the muffin-tin amplitudes $z^N_{lm}(\vec{k},\epsilon)$ for higher angular momenta can then be determined from them according to

$$i^l z^N_{lm}=\sum_{N'\neq N}\sum_{l'm'} H^{NN'}_{lml'm'}w^{N'}_{l'm'}\,. \tag{A2}$$

The solution of Eq. (2.7) by means of Fourier transformation[1] proceeds by expressing the muffin-tin amplitude coefficients as a Brillouin-zone integral:

$$z^N_{l\Gamma\gamma}(\vec{k},\epsilon)=\int_{Bz} d^3q\, e^{i\vec{q}\cdot\vec{R}_N}\zeta_{l\Gamma\gamma}(\vec{q};\vec{k},\epsilon)\,. \tag{A3}$$

Substituting this relation into Eq. (2.7), one finds that for each value of q, the Fourier transform $\zeta_{l\Gamma\gamma}(q)$ must satisfy a relationship of the form

$$\sum_{l'\Gamma'\gamma'} M_{l\Gamma\gamma,l'\Gamma'\gamma'}(\vec{q},\epsilon)\,t^h_{l'}\,i^{l'}\zeta_{l'\Gamma'\gamma'}(\vec{q})\,e^{i\vec{q}\cdot\vec{R}_I}$$
$$=\frac{\Omega}{(2\pi)^3}\sum_{l'\Gamma'\gamma'}\left[(t^h_l)^{-1}\delta_{ll'}\delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'}-M_{l\Gamma\gamma,l'\Gamma'\gamma'}(\vec{q},\epsilon)\right](t^i_{l'}-t^h_{l'})\,i^{l'}z^I_{l'\Gamma'\gamma'}(\vec{k},\epsilon)\,. \tag{A4}$$

Continuum solutions to the Schrödinger equation are conveniently expressed as the sum of a Bloch wave and a scattered wave contribution:

$$\Psi_\epsilon(\vec{k},\vec{r})=\Psi^{(0)}_\epsilon(\vec{k},\vec{r})+\Psi^{(s)}_\epsilon(\vec{k},\vec{r})\,.$$

The Fourier transform of the muffin-tin amplitude coefficient then takes the form

$$\zeta_{l\Gamma\gamma}(\vec{q};\vec{k},\epsilon)=a_{l\Gamma\gamma}(\vec{k},\epsilon)\delta(\vec{q}-\vec{k})+\zeta^{(s)}_{l\Gamma\gamma}(\vec{q};\vec{k},\epsilon)\,. \tag{A5}$$

Substituting this form into Eq. (A4), one finds that the Bloch wave contribution on the left-hand side of the equation vanishes. The equation may then be solved for the scattered wave amplitude on the impurity site $z^{I(s)}_{l\Gamma\gamma}(\vec{k},\epsilon)$ by eliminating the KR secular matrix from the left-hand side of the equation and then performing the Brillouin-zone integral:

$$\begin{aligned} i^l z^{I(s)}_{l\Gamma\gamma}(\vec{k},\epsilon) &=\sum_{l'\Gamma'\gamma'}\Big[(t^h_l)^{-1}\chi_{l\Gamma\gamma,l'\Gamma'\gamma'}(\epsilon,0)(t^h_{l'})^{-1} \\ &\qquad -(t^h_l)^{-1}\delta_{ll'}\delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'}\Big] \\ &\qquad \times(t^i_{l'}-t^h_{l'})\,i^{l'}z^I_{l'\Gamma'\gamma'}(\vec{k},\epsilon)\,. \end{aligned} \tag{A6}$$

This equation contains apparent divergences if an impurity scattering parameter $t^i_{l_0}(\epsilon)$ is nonzero while the corresponding host scattering parameter $t^h_{l_0}(\epsilon)$ is negligible. However, one may show that for this case the product $\chi_{l_0\Gamma\gamma,l'\Gamma'\gamma'}(\epsilon,R_N-R_I)\times[t^h_{l'}(\epsilon)]^{-1}$ asymptotically becomes $\delta_{NI}\delta_{l_0l'}\delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'}$ as $t^h_{l_0}(\epsilon)$ tends to zero. Therefore the coefficients $i^{l_0}t^i_{l_0}(\epsilon)z^I_{l_0\Gamma\gamma}(\vec{k},\epsilon)\equiv w^I_{l_0\Gamma\gamma}(\vec{k},\epsilon)$ are indeterminate on the basis of Eq. (A6) and will be set equal to zero.

The Brillouin-zone integral evaluated at the impurity site, Eq. (2.23), can be expressed as an integral $x(\epsilon)$ over an "irreducible sector" of the Brillouin zone ($\frac{1}{48}$th of the total volume of the Brillouin zone for a cubic lattice) and a summation over all the symmetry operations of the lattice point group. It may be simply determined from a summation over the partial Brillouin-zone integrals $x(\epsilon)$:

$$\begin{aligned}\chi^\Gamma_{ll'}(\epsilon)&=\frac{n_0}{g(\Gamma)}\sum_\gamma x_{l\Gamma\gamma,l'\Gamma\gamma}(\epsilon) \\ &=\frac{n_0}{g(\Gamma)}\sum_\gamma\sum_{mm'}(U^{l\Gamma\gamma}_{lm})^{-1}x_{lm,l'm'}(\epsilon)\,U^{l'\Gamma\gamma}_{l'm'}\,.\end{aligned} \tag{A7}$$

Here, the total number of symmetry operations of the lattice point group is denoted by n_0 ($n_0=48$ for cubic symmetry) and $g(\Gamma)$ denotes the degeneracy of the irreducible representation Γ. The coefficients multiplying the partial integrals in the spherical harmonic expansion $x_{lm,l'm'}$ for Eq. (A7) are listed in Table II for the case of cubic symmetry and $l\leq 3$.

The symmetry properties of the nonrelativistic Green's-function secular matrix (2.12) are important in various contexts. For a lattice with inversion symmetry, it can be shown that the KR secular matrix (as well as the corresponding two-center transformation matrix) satisfies the symmetry relationship

$$M_{lm,l'm'}(\vec{k},\epsilon)=(-1)^{l-m}M^*_{l-m,l'-m'}(\vec{k},\epsilon)(-1)^{-l'+m'} \tag{A8}$$

It follows that the phases of the eigenvectors v^n can be chosen so that the components obey the relation

TABLE II. Expressions for nonrelativistic $\chi_{l,l'}^{\Gamma}$ coefficients for a cubic lattice in terms of the partial Brillouin-zone integrals $x_{lm,l'm'} \equiv \int_{1/48\text{th Bz}} d^3q[M(\vec{q},\epsilon)]^{-1}_{lm,l'm'}$. Lattice harmonic conventions are those of von der Lage and Bethe (Ref. 29).

$$\begin{aligned}
\chi_{00}^{\Gamma_1} &= 48x_{00,00}\\
\chi_{11}^{\Gamma_{15}} &= 16(x_{10,10}+x_{11,11}+x_{1-1,1-1})\\
\chi_{22}^{\Gamma_{12}} &= 24x_{20,20}+12(x_{22,22}+x_{2-2,2-2}+x_{22,2-2}+x_{2-2,22})\\
\chi_{22}^{\Gamma_{25}'} &= 16(x_{11,11}+x_{1-1,1-1})+8(x_{22,22}+x_{2-2,2-2}-x_{22,2-2}-x_{2-2,22})\\
\chi_{33}^{\Gamma_{15}} &= 16x_{30,30}+10(x_{33,33}+x_{3-3,3-3})+6(x_{31,31}+x_{3-1,3-1})\\
&\quad +2\sqrt{15}\,(x_{33,3-1}+x_{3-3,31}+x_{3-1,33}+x_{31,3-3})\\
\chi_{31}^{\Gamma_{15}} &= 16x_{30,10}-4\sqrt{6}\,(x_{31,11}+x_{3-1,1-1})-4\sqrt{10}\,(x_{33,1-1}+x_{3-3,11})\\
\chi_{33}^{\Gamma_2'} &= 24(x_{32,32}+x_{3-2,3-2}-x_{32,3-2}-x_{3-2,32})\\
\chi_{33}^{\Gamma_{25}'} &= 8(x_{32,32}+x_{3-2,3-2}+x_{32,3-2}+x_{3-2,32})\\
&\quad +6(x_{33,33}+x_{3-3,3-3})+10(x_{31,31}+x_{3-1,3-1})\\
&\quad -2\sqrt{15}\,(x_{33,3-1}+x_{3-3,31}+x_{31,3-3}+x_{3-1,33})
\end{aligned}$$

$$v_{lm}^{n}(\vec{k},\epsilon)=(-1)^{l-m}\,v_{l-m}^{n*}(\vec{k},\epsilon)\,. \tag{A9}$$

(For $m=0$ this means that $v_{l0}^{n}(\vec{k},\epsilon)$ is real if l is even and is imaginary if l is odd.) These relations are used in Appendix C for consideration of the optical theorem, as well as in deriving Eqs. (3.12) and (3.13), and (4.14) and (4.15).

APPENDIX B: NORMALIZATION OF THE BLOCH WAVE FUNCTIONS

If the potential within the muffin-tin sphere is raised by a uniform amount $\Delta\mathcal{V}$, the energy eigenvalue at wavevector $\vec{k}$ is raised by

$$\Delta\epsilon(\vec{k})=\frac{\Delta\mathcal{V}\int_{\text{muffin-tin sphere}}|\Psi_{\epsilon}^{(0)}(\vec{k},\vec{r})|^2\,d^3r}{\int_{\Omega}|\Psi_{\epsilon}^{(0)}(\vec{k},\vec{r})|^2 d^3r} \tag{B1}$$

according to first order perturbation theory.[5] Consequently, the normalization condition, $\int_{\Omega}|\Psi^{(0)}(\vec{k},\vec{r})|^2\,d^3r=1$ may be expressed in terms of the integral within the muffin-tin sphere

$$\int_{\text{muffin-tin sphere}}|\Psi_{\epsilon}^{(0)}(\vec{k},\vec{r})|^2\,d^3r=\frac{\partial\epsilon(k)}{\partial\mathcal{V}}\,, \tag{B2}$$

where

$$\frac{\partial\epsilon(\vec{k})}{\partial\mathcal{V}}=\lim_{\Delta\mathcal{V}\to 0}\left(\frac{\Delta\epsilon(\vec{k})}{\Delta\mathcal{V}}\right)_{\vec{k}}\,.$$

Consider first the evaluation of (B2) using nonrelativistic dynamics. The left-hand side may be converted to a surface integral over the muffin-tin sphere by using an identity involving the Schrödinger equation.[73,74] The result may be expressed in the form

$$\begin{aligned}
\frac{\epsilon}{\kappa^2}(s^{(h)})^2\int d^2\hat{r}_N\left(\frac{\partial\Psi_{\epsilon}^{0}}{\partial\epsilon}\,\nabla\Psi_{\epsilon}^{0\,*}-\Psi_{\epsilon}^{0\,*}\,\frac{\nabla\partial\Psi_{\epsilon}^{0}}{\partial\epsilon}\right)_{r_N=s^{(h)}} &= \sum_{l\Gamma\gamma}|a_{l\Gamma\gamma}(\vec{k},\epsilon)|^2\cos^2\eta_l^h(\epsilon)\\
&\quad\times\left(\frac{\epsilon}{\kappa^2}\,\frac{\partial\tan\eta_l^h}{\partial\epsilon}+\tfrac{1}{2}(s^{(h)})^3[(j_l'-\tan\eta_l^h n_l')^2-(j_l-\tan\eta_l^h n_l)(j_l''-\tan\eta_l^h n_l'')]\right)\,.
\end{aligned} \tag{B3}$$

Here j_l and n_l denote, respectively, spherical Bessel and Neumann functions evaluated at the argument $\kappa s^{(h)}$; prime denotes differentiation with respect to the argument. The right-hand side of (B2) may be evaluated by use of the identity

$$\frac{\partial\epsilon(\vec{k})}{\partial\mathcal{V}}=-\frac{\partial\lambda(\vec{k},\epsilon)}{\partial\mathcal{V}}\bigg/\frac{\partial\lambda(\vec{k},\epsilon)}{\partial\epsilon}\,, \tag{B4}$$

where, following the notation of Sec. II, $\lambda(\vec{k},\epsilon)$ is the zero eigenvector of the KR secular matrix $M(\vec{k},\epsilon)$. Its derivatives may be determined from the expectation value of the derivative of the secular matrix[57]:

$$\frac{\partial\lambda(\vec{k},\epsilon)}{\partial x}=\sum_{\substack{l\Gamma\gamma,\\ l'\Gamma'\gamma'}}v_{l\Gamma\gamma}^{*}(\vec{k},\epsilon)\,\frac{\partial M_{l\Gamma\gamma,l'\Gamma'\gamma'}(\vec{k},\epsilon)}{\partial x}\,v_{l'\Gamma'\gamma'}(\vec{k},\epsilon)\,, \tag{B5}$$

In particular, the derivative of the secular matrix with respect to a constant change in the muffin-tin potential is given by

$$\frac{\partial M_{l\Gamma\gamma,l'\Gamma'\gamma'}(\vec{k},\epsilon)}{\partial\mathcal{V}}=-\cot^2\eta_l^h\,\frac{\partial\tan\eta_l^h}{\partial\mathcal{V}}\,\delta_{ll'}\,\delta_{\Gamma\Gamma'}\,\delta_{\gamma\gamma'}\,. \tag{B6}$$

However, it is apparent from Sec. II that the normalized eigenvector components of the KR secular matrix are related to the muffin-tin expansion coefficients of the Bloch wave by

$$v_{l\Gamma\gamma}(\vec{k},\epsilon)=\mathfrak{N}(\vec{k},\epsilon)\,i^l\,a_{l\Gamma\gamma}(\vec{k},\epsilon)\sin\eta_l^h\,e^{i\eta_l^h}\,, \tag{B7}$$

where the normalization factor is to be determined. Consequently, the right-hand side of equation (B2) becomes

$$-\left[|\mathfrak{N}(\vec{k},\epsilon)|^2\Big/\left(-\frac{\partial\lambda(\vec{k},\epsilon)}{\partial\epsilon}\right)\right]$$

$$\times\sum_{l\Gamma\gamma}|a_{l\Gamma\gamma}(\vec{k},\epsilon)|^2\cos^2\eta_l^h\,\frac{\partial\tan\eta_l^h}{\partial\mathcal{V}}\,. \tag{B8}$$

It can furthermore be shown that the variation of the phase shift η_l^h with respect to a constant change in the muffin-tin potential and its variation with respect to a change in the energy ϵ of the eigenstate are related according to

$$-\frac{\tan\eta_l^h}{\partial\mathcal{V}}=\frac{\tan\eta_l^h}{\partial\epsilon}+\frac{\kappa^3}{2\epsilon}(s^{(h)})^3[(j_l'-\tan\eta_l^h n_l')^2$$

$$-(j_l-\tan\eta_l^h n_l)(j_l''-\tan\eta_l^h n_l'')]\,. \tag{B9}$$

Equating (B3) and (B8), the normalization constant is determined to be

$$[\mathfrak{N}(\vec{k},\epsilon)]^2=\frac{\epsilon}{\kappa^3}\left(-\frac{\partial\lambda(\vec{k},\epsilon)}{\partial\epsilon}\right)$$

$$=\frac{\epsilon}{\kappa^3}\,\frac{\partial\lambda(\vec{k},\epsilon)}{\partial k}\Big/\hbar v_\epsilon(\vec{k})\,. \tag{B10}$$

The second form of the renormalizing constant in Eq. (B10) follows from the fact that the velocity of the Bloch state is given by

$$\hbar v_\epsilon(\vec{k})=\frac{\partial\lambda(\vec{k},\epsilon)}{\partial k}\Big/\left(-\frac{\partial\lambda(\vec{k},\epsilon)}{\partial\epsilon}\right).$$

For relativistic dynamics, a similar analysis follows. Now the normalization integrals involve a sum of the contributions from the upper and lower components of the Dirac wave function. The left-hand side of Eq. (B2) can then also be expressed in terms of a surface integral with the result

$$\sum_{\Lambda\Gamma\gamma}|a_{\Lambda\Gamma\gamma}(\vec{k},\epsilon)|^2\cos^2\eta_\Lambda^h\left(\frac{\epsilon}{\kappa^3}\,\frac{\partial\tan\eta_\Lambda^h}{\partial\epsilon}+\frac{\epsilon(\epsilon+mc^2)}{(pc)^2}(s^{(h)})^3[(j_l'-\tan\eta_\Lambda^h n_l')S_\Lambda(j_{\bar{l}}-\tan\eta_\Lambda^h n_{\bar{l}})\right.$$

$$\left.-(j_l-\tan\eta_\Lambda^h n_l)S_\Lambda(j_{\bar{l}}'-\tan\eta_\Lambda^h n_{\bar{l}}')]-\frac{\epsilon mc^2(s^{(h)})^2}{(pc)^2\kappa}S_\Lambda(j_{\bar{l}}-\tan\eta_\Lambda^h n_{\bar{l}})(j_l-\tan\eta_\Lambda^h n_l)\right)\,. \tag{B11}$$

Relations (B4)–(B8) remain valid in the relativistic treatment, with the spin-orbital index Λ replacing the index l. Relation (B9) is modified according to

$$-\frac{\partial\tan\eta_\Lambda^h(\epsilon)}{\partial\mathcal{V}}=\frac{\partial\tan_\Lambda^h(\epsilon)}{\partial\epsilon}+\frac{\kappa^3(\epsilon+mc^2)}{(pc)^2}(s^{(h)})^3[(j_l'-\tan\eta_\Lambda^h n_l')S_\Lambda(j_{\bar{l}}-\tan\eta_\Lambda^h n_{\bar{l}})-(j_l-\tan\eta_\Lambda^h n_l)S_\Lambda(j_{\bar{l}}'-\tan\eta_\Lambda^h n_{\bar{l}}')]$$

$$+\frac{\kappa^2mc^2}{(pc)^2}(s^{(h)})^2S_\Lambda(j_{\bar{l}}-\tan\eta_\Lambda^h n_{\bar{l}})(j_l-\tan\eta_\Lambda^h n_l)\,. \tag{B12}$$

Substituting this result into the relativistic equivalent of (B8) and equating it to expression (B11), the normalization constant is found to be again given by Eq. (B10).

APPENDIX C: OPTICAL THEOREM

In this appendix it will be demonstrated that the expression for the T matrix (4.6) is consistent with the optical theorem (4.3). It follows from symmetry relationships discussed in Appendix A that the phases of the amplitude coefficients can be chosen so that products of the form $f_{\Lambda\Gamma\gamma}^{\theta *}(\vec{k},\epsilon)f_{\Lambda'\Gamma\gamma}^{\theta}(\vec{k},\epsilon)$ are real numbers and that the χ^Γ matrices are symmetric. The imaginary part of the diagonal element of the T matrix is then

$$\operatorname{Im}T_{kk}^{\theta\theta}=-\sum_{\Lambda\Gamma\gamma;\Lambda'}f_{\Lambda\Gamma\gamma}^{\theta *}(\vec{k},\epsilon)f_{\Lambda'\Gamma\gamma}^{\theta}(\vec{k},\epsilon)\operatorname{Im}(\zeta-\chi^\Gamma)_{\Lambda\Lambda'}^{-1}\,. \tag{C1}$$

The right-hand side of the optical theorem (4.3) may be evaluated by noting that the overlap integral between basis functions $f_{\Lambda\Gamma\gamma}^{\theta}(\vec{k},\epsilon)$ is given by the residue term of the Brillouin-zone integral (2.20) evaluated at the impurity site:

$$[\Omega/(2\pi)^3]\int d^3k\, \delta(\epsilon-\epsilon(k))\sum_{\theta}[f^{\theta}_{\Lambda\Gamma\gamma}(\vec{k},\epsilon)]^* f^{\theta}_{\Lambda',\Gamma'\gamma'}(\vec{k},\epsilon)=(1/\pi)\,\mathrm{Im}\chi^{\Gamma}_{\Lambda\Lambda'}\,\delta_{\Gamma\Gamma'}\,\delta_{\gamma\gamma'}\,. \tag{C2}$$

The right-hand side of Eq. (4.3) is thus

$$-\frac{\Omega}{8\pi^2}\int d^3k'\,\delta(\epsilon-\epsilon(k'))\sum_{\theta'}|T^{\theta',\theta}_{k',k}(\epsilon)|^2$$

$$=\sum_{\Lambda\Gamma\gamma;\Lambda'} f^{\theta *}_{\Lambda\Gamma\gamma}(\vec{k},\epsilon) f^{\theta}_{\Lambda',\Gamma\gamma}(\vec{k},\epsilon)\sum_{\Lambda_1\Lambda_2}(\xi-\chi^{\Gamma^*})^{-1}_{\Lambda\Lambda_2}\,\mathrm{Im}\chi^{\Gamma^*}_{\Lambda_2\Lambda_1}(\xi-\chi^{\Gamma})^{-1}_{\Lambda_1\Lambda'}\,. \tag{C3}$$

The equality of (C1) and (C3) follows from the matrix identity $[\mathrm{Im}(B^{-1})]B=B^{*-1}[\mathrm{Im}(B^*)]$, which is valid for any complex matrix B.

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*Submitted in partial fulfillment of Ph.D. requirements to the Physics Department of the University of Chicago.

†Work supported by the National Science Foundation through the Materials Research Laboratory of the University of Chicago. The computations were supported by the Louis Block Fund at the University of Chicago. A preliminary report of this work was presented at the meeting of the American Physical Society [Bull. Am. Phys. Soc. 19, 363 (1974)].

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