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Phase-shift analysis of the impurity problem in cubic metals. I.

S. Olszewski
Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw, Poland

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The original phase-shift analysis of the impurity problem in metals, done first by Friedel, was confined mainly to crystals having spherical energy band. The present paper extends the phase-shift approach to any band of a cubic metal. At the first step the band of states *s* is considered but then the method is generalized to states *p* and *d*. The electron wave functions are the non-Bloch linear combinations of atomic orbitals extended throughout the crystal volume which is a large but finite sphere. It is shown that the electron density of a crystal perturbed by an isolated impurity can be represented by the wave functions of the perfect crystal whose coefficient functions are changed in their argument by a phase shift. The approach done in terms of phase shifts is shown to be equivalent to the Green's-function approach. For an impurity potential which is weak and confined to one lattice site the phase shift of any wave function is equal to the density of states contributed by this function at the position of the impurity times the potential strength. Therefore phase shifts depend on the position of the impurity. An analog of Friedel's sum rule can be derived also in the present theory. The total number of charge displaced in the crystal is proportional to the total density of states at the Fermi level. The scattering cross section due to an impurity can be expressed with the aid of phase shifts and in terms of parameters which define the unperturbed coefficient functions.

I. INTRODUCTION

The phase shifts introduced to the crystal wave functions by Friedel[1] are important because they allowed the prediction, or explanation, of several experimental effects in solids which are due to the oscillations of the perturbed crystal charge. Most of these effects are connected with the nuclear magnetic resonance in alloys (the Knight shift, the quadrupole effects), the lattice dilatation in alloys, the interaction between impurities and the ordering effects at short distances, the coupling effects with phonons (Kohn's anomaly), and the accumulation of defects in compact structures. When the spin density is considered, the charge oscillations due to an impurity cooperate in the formation of the local magnetic moments and lead to the interaction between impurities which is characteristic for spin-glasses.[2]

The use of the phase shifts is convenient in any problem in which we like to calculate the change of electron number per energy interval. In principle this task requires us to sum the contributions coming from any perturbed wave function which is extended over the whole crystal. Then any state within the energy interval has to be taken into account. In a formalism which does not use phase shifts, e.g., the method of the linear combination of atomic orbitals (LCAO) by Koster and Slater,[3–5] this means that the Green's function for any pair of the lattice vectors, one of which points to a site within the impurity area and the other to a site outside this area, has to be calculated. This makes the formalism enormously complicated. Even assuming that only large distances from the impurity give important contributions to the change of the density of states, the calculation of the Green's function for these distances remains tedious; see Sec. II.

Friedel's original approach was based on the free-electron approximation.[1] Though there exist attempts towards incorporating phase shifts in the methods where the periodic potential of the matrix is taken into account,[6–8] their success seems to be rather far from being complete. The purpose of the present paper is to make a step in this area. Our considerations are limited to electron states, but they can be generalized to phonons and spin waves. The formalism applied to the pure crystal taken as a starting point is different from Bloch's. The present electron wave functions are nonitinerant (standing) waves classified according to the symmetry species of the crystal point group. If the impurity potential has the point-group symmetry of the matrix, the selection rules between the potential and the wave functions can be easily established.[6] The wave functions of this kind were proposed before,[6] but their calculation has been limited to a small area composed of few lattice sites.[6,9] The present approach resembles that given originally by Friedel because the wave functions are delocalized over the whole crystal volume which is assumed to be a large, but finite, sphere. In effect, the phase shifts can be obtained more easily than on the basis of Bloch's wave functions. At the first step the cubic crystals having only s-like electrons on each atom are thoroughly examined; next the formalism is extended to crystals having p- and d-like atomic states.

II. LCAO METHOD AND THE FRIEDEL'S APPROACH

The present approach is a fusion of the LCAO method and Friedel's method. The LCAO approximation is a very useful tool in the calculation of the electron properties of solids, especially transition metals.[10] But the main object of the method was pure materials. This is so because of the difficulties involved in the application of the method to the impurity problem. In fact, for the nonspherical energy band of the host metal the calculation has been completed only for one special case characterized by (i) a single band of s electrons; (ii) the simple cubic structure of the lattice having the nearest-neighbor atomic interaction; and (iii) the potential of the substitutional impurity restricted to only one lattice site.[11] The other approach usually assumes a special, preferably spherical, shape of the energy band of the matrix or confines the calculation to the distances very far from the impurity center. But also for these distances, if the band is not spherical, the question arises which is the wavelength and the amplitude of the oscillation of the perturbed part of the original Bloch's function. The question cannot be answered unless the curvature of the Fermi surface for a given energy is calculated at the cross-section points of this surface with the vector which is parallel to the lattice vector entering the Green's function.[4, 12–14] Then the perturbed wave function usually becomes a very complicated function of the components of Bloch's wave vector and the lattice vector[4, 13, 14] although the method assumes only a very limited expansion of the exponent of the Green's function into the Taylor series.[4, 13, 14]

Friedel's approach, restricted to free electrons, assumes very convenient geometric conditions for the crystal. The crystal is a large sphere and the impurity potential, which is also of spherical symmetry, is located near the sphere center. Then instead of the plane waves the unperturbed wave functions are

$$P_l^m(\cos\theta)e^{im\phi}j_l(\kappa r) \quad . \tag{1}$$

θ and ϕ are angular coordinates, $P_l^m(\cos\theta)e^{im\phi}$ is a spherical harmonic, and j_l is a spherical Bessel function. If the impurity potential is added, its effect outside the potential area is that Eq. (1) has to be combined with

$$P_l^m(\cos\theta)e^{im\phi}n_l(\kappa r) \quad , \tag{2}$$

where n_l is a spherical Neumann function. Because of the asymptotic form of j_l and n_l for large r (Ref. 15) we obtain phase shifts. The coefficient with which Eq. (2) combines is dictated by the strength and the size of the perturbation. If this size is small, the coefficient of Eq. (2), hence the phase shift, tends to zero for any $l \gg 0$.

Clogston[7] combined the LCAO and the Friedel's approaches into one method, however, his method was restricted only to spherical bands. Furthermore, the impurity potential has been confined to one lattice site. In subsequent sections we try to extend the models by Friedel and Clogston to metals having the nonspherical energy bands.

II. OUTLINE OF THE PRESENT METHOD

A. Perfect crystal

The well known way of solving the impurity problem is to satisfy the set of the linear homogeneous equations for the coefficients $U(\vec{R}_l)$ with which the localized orbitals $\phi(\vec{r} - \vec{R}_l)$ combine into the LCAO wave function of the perturbed crystal

$$\psi^p = \sum_{\vec{R}_l} U(\vec{R}_l)\phi(\vec{r} - \vec{R}_l) \quad . \tag{3}$$

Vectors $\vec{R}_l$ label the positions of the lattice sites. At the first step we assume that only one kind of ϕ, for example those of spherical symmetry (type s), are present in the crystal. The sum (3) is extended over all sites of the lattice.

For the perfect crystal (the perturbation potential $V^p \rightarrow 0$)

$$\psi^p \rightarrow \psi \tag{4}$$

and

$$U(\vec{R}_l) \rightarrow A(\vec{R}_l) \quad . \tag{5}$$

In the case of the Bloch's wave functions

$$A(\vec{R}_l) = N^{-1/2}e^{i\vec{k}\cdot\vec{R}_l} \tag{6}$$

provided $\phi(\vec{r} - \vec{R}_l)$ form an orthonormal set; $\vec{k}$ is the wave vector and N is number of atoms in the lattice. The set of the linear homogeneous equations for $A(\vec{R}_l)$ can be transformed into the differential eigenequation[15–18]

$$\hat{W}A = \epsilon A \quad . \tag{7}$$

This is satisfied at any lattice site which is far from the crystal boundary. $\hat{W}$ is the differential operator dependent on the structure of the (perfect) lattice and the strength of the atomic interactions and ϵ is the energy parameter. Equation (7) can be obtained independently of the symmetry and the boundary conditions imposed on $A(\vec{R}_l)$.[18] In particular, Eq. (7) is satisfied by $A(\vec{R}_l)$ of Eq. (6).

To meet Friedel's boundary conditions we try to satisfy Eq. (7) with the aid of the combinations of Eq. (1). We are led to a secular problem which is simplified if Eqs. (1) are replaced by their projections on the rows μ of the irreducible representations Γ_i of the point group. These are called lattice harmonics. Taking the cubic point group as an example we can solve the secular problem

$$\begin{vmatrix} \langle (H)_{l',t'}^{\Gamma_i,\mu} j_{l'}(\kappa R) | \hat{W} | (H)_{l',t'} j_{l'}(\kappa R) \rangle - \epsilon, & \langle (H)_{l',t'}^{\Gamma_i,\mu} j_{l'}(\kappa R) | \hat{W} | (H)_{l'',t''}^{\Gamma_i,\mu} j_{l''}(\kappa R) \rangle & \cdots \\ \langle (H)_{l'',t''}^{\Gamma_i,\mu} j_{l''}(\kappa R) | \hat{W} | (H)_{l',t'} j_{l'}(\kappa R) \rangle & \langle (H)_{l'',t''}^{\Gamma_i,\mu} j_{l''}(\kappa R) | \hat{W} | (H)_{l'',t''}^{\Gamma_i,\mu} j_{l''}(\kappa R) \rangle - \epsilon & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix} = 0 \qquad (8)$$

separately for any Γ_i. The radial coordinate r in Eq. (1) is replaced by R because $A(\vec{R})$ is calculated in the space of the lattice sites; $\kappa = |\vec{k}|$. The $(H)_{l,t}^{\Gamma_i,\mu}$ are cubic harmonics, index t labels the harmonics which belong to a given Γ_i and μ and have the same l. Solving Eq. (8) we get the coefficient function

$$A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R}) = \sum_l \sum_t C_{l,t}^{\Gamma_i,\mu,\lambda}(\kappa)(H)_{l,t}^{\Gamma_i,\mu} j_l(\kappa R) \qquad (9)$$

and the wave function of the perfect crystal

$$\psi(\vec{r}) = \sum_{\vec{R}_l} A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R}_l)\phi(\vec{r}-\vec{R}_l) \ . \qquad (10)$$

Because $\phi(\vec{r}-\vec{R}_l)$ have spherical symmetry, any $\psi(\vec{r})$ is, like $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$, a basis function of Γ_i, and μ. The index λ labels different solutions of the secular problem. Outside the area of the impurity potential ($R \approx 0$) Eq. (7) can be satisfied also by

$$B^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R}) = \sum_l \sum_t D_{l,t}^{\Gamma_i,\mu,\lambda}(\kappa)(H)_{l,t}^{\Gamma_i,\mu} n_l(\kappa R) \ . \qquad (11)$$

If the crystal is large we have

$$D_{l,t}^{\Gamma_i,\mu,\lambda}(\kappa) = C_{l,t}^{\Gamma_i,\mu,\lambda}(\kappa) \qquad (12)$$

owing to the equality

$$\langle (H)_{l',t'}^{\Gamma_i,\mu} n_{l'}(\kappa R) | \hat{W} | (H)_{l'',t''}^{\Gamma_i,\mu} n_{l''}(\kappa R) \rangle$$

$$\approx \langle (H)_{l',t'}^{\Gamma_i,\mu} j_{l'}(\kappa R) | \hat{W} | (H)_{l'',t''}^{\Gamma_i,\mu} j_{l''}(\kappa R) \rangle \ , \qquad (13)$$

which holds for any l', t', l'', and t'', because: (i) the area where $n_l(\kappa R)$ are singular (small $R < R_a$) can be discarded in comparison with the whole crystal volume $\frac{4}{3}\pi R_d^3$, (ii) in the overwhelming part of the crystal volume the asymptotic formulas[15]

$$j_l(\kappa R) \underset{\kappa R \gg 1}{\approx} (\kappa R)^{-1} \cos[\kappa R - \tfrac{1}{2}(l+1)\pi] \ , \qquad (14)$$

$$n_l(\kappa R) \underset{\kappa R \gg 1}{\approx} (\kappa R)^{-1} \sin[\kappa R - \tfrac{1}{2}(l+1)\pi] \ , \qquad (15)$$

are valid, and (iii) we have

$$\int_{R_a}^{R_d} \sin^2\kappa R \, dR \approx \int_{R_a}^{R_d} \cos^2\kappa R \, dR$$

$$\approx \tfrac{1}{2}(R_d - R_a) \qquad (16)$$

providing that $R_d - R_a$ is large in comparison with the period of sine and cosine. In a perfect crystal the functions $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$ and $B^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$ do not combine because the matrix elements of $\hat{W}$ between these functions vanish. The coefficients (12) for different cubic lattices have been calculated elsewhere.[18–20] It has been shown that $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$ and the corresponding eigenenergies $\epsilon^{\Gamma_i,\lambda}(\kappa)$ can reproduce the density of states in the matrix metal.[20,25]

B. Crystal perturbed by an impurity

We approach the problem of the perturbed crystal on the basis of solutions given in Sec. III A. In general

$$U(\vec{R}) = \int V^P(\vec{R}_{\rm imp}) G_E(\vec{R},\vec{R}_{\rm imp}) U(\vec{R}_{\rm imp}) \, d\vec{R}_{\rm imp} \ . \qquad (17)$$

$G_E(\vec{R},\vec{R}_{\rm imp})$ is the Green's function of a crystal, $\vec{R}_{\rm imp}$ is the position of the impurity, and $V^P(\vec{R}_{\rm imp})$ is the perturbation potential at $\vec{R} = \vec{R}_{\rm imp}$. We have

$$G_E(\vec{R},\vec{R}_{\rm imp}) = \sum_{\Gamma_i} \sum_{\mu} \sum_{\lambda} \sum_{\kappa} \frac{A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R}) A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R}_{\rm imp})}{\epsilon^{\Gamma_i,\lambda}(\kappa) - E}$$

$$= \sum_{\lambda} \sum_{\kappa} \frac{A^{\Gamma_1,\lambda}(\kappa,\vec{R}) A^{\Gamma_1,\lambda}(\kappa,\vec{0})}{\epsilon^{\Gamma_1,\lambda}(\kappa) - E} \ , \qquad (18)$$

where at the second step we assumed that $\vec{R}_{\rm imp}$ is confined to one site, say $\vec{0}$. In this case $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{0}) = 0$ unless $\Gamma_i = \Gamma_1$ and Γ_1 is the one-dimensional irreducible representation. The sum over κ can be replaced by an integral (R_d is the crystal radius)

$$\sum_{\kappa} \to \int_0^{\kappa_m^\lambda} \frac{R_d}{\pi} \, d\kappa \ , \qquad (19)$$

where $\kappa_m^\lambda = \kappa_{\rm min}^\lambda$ is the value of κ at the limit of the λth subband[20,21]; see also inferences below Fig. 1. R_d/π is the density of states per unit of κ; cf. Ref. 1. Providing E is an energy within the band, at least for some λ we have certain κ_E^λ for which

$$E = \epsilon^{\Gamma_1,\lambda}(\kappa_E^\lambda) \ , \qquad (20)$$

where $\kappa_E^\lambda < \kappa_m^\lambda$; for the remainder of λ the contributions to Eq. (18) can be neglected.[20] The summands in Eq. (18) are the largest in the range of $\kappa \approx \kappa_E^\lambda$ therefore

$$\epsilon^{\Gamma_1,\lambda}(\kappa) - E \cong [\kappa^2 - (\kappa_E^\lambda)^2] \lim_{\kappa \to \kappa_E^\lambda} f_\lambda^{-1}(E,\kappa) \;, \tag{21}$$

where

$$f_\lambda^{-1}(E,\kappa) = \frac{\epsilon^{\Gamma_1,\lambda}(\kappa) - E}{\kappa^2 - (\kappa_E^\lambda)^2} \tag{22}$$

is a slowly varying function of κ. This is so because the behavior of $\epsilon^{\Gamma_1,\lambda}(\kappa)$ is very similar to parabolic.[20] At very large $R = |\vec{R}|$ the function $A^{\Gamma_1,\lambda}(\kappa,\vec{R})$ take the form [cf. Eq. (14); representation Γ_1 combines j_l and n_l having only even l]

$$A^{\Gamma_1,\lambda}(\kappa,\vec{R}) \underset{R\to\infty}{\longrightarrow} N^{\Gamma_1,\lambda}(\kappa)[1 + c_4^{\Gamma_1,\lambda}(\kappa)(H)_4^{\Gamma_1} - c_6^{\Gamma_1,\lambda}(\kappa)(H)_6^{\Gamma} + \cdots]\frac{\sin\kappa R}{\kappa R} \;, \tag{23}$$

where

$$N^{\Gamma_1,\lambda}(\kappa) = C_0^{\Gamma_1,\lambda}(\kappa) \;;$$
$$c_0^{\Gamma_1,\lambda}(\kappa) = \frac{C_0^{\Gamma_1,\lambda}(\kappa)}{C_0^{\Gamma_1,\lambda}(\kappa)} = 1 \;; \tag{24}$$
$$c_4^{\Gamma_1,\lambda}(\kappa) = \frac{C_4^{\Gamma_1,\lambda}(\kappa)}{C_0^{\Gamma_1,\lambda}(\kappa)}; \quad \cdots .$$

A similar asymptotic expression holds for $B^{\Gamma_1,\lambda}(\kappa,\vec{R})$. This expression for $B^{\Gamma_1,\lambda}(\kappa,\vec{R})$ is Eq. (23) having $\sin\kappa R$ replaced by $-\cos\kappa R$, viz.,

$$B^{\Gamma_1,\lambda}(\kappa,\vec{R}) \underset{R\to\infty}{\longrightarrow} -\cot(\kappa R) A^{\Gamma_1,\lambda}(\kappa,\vec{R}) \;; \tag{25}$$

cf. Eqs. (12) and (15). At $|\vec{R}| = 0$

$$A^{\Gamma_1,\lambda}(\kappa,\vec{0}) = N^{\Gamma_1,\lambda}(\kappa) \;, \tag{26}$$

whereas $B^{\Gamma_1,\lambda}(\kappa,\vec{0})$ diverges;

$$N^{\Gamma_1,\lambda}(\kappa) = \frac{\kappa v_a^{1/2}}{(2\pi R_d)^{1/2}} \{1 + [c_4^{\Gamma_1,\lambda}(\kappa)]^2 I_4 + [c_6^{\Gamma_1,\lambda}(\kappa)]^2 I_6 + \cdots \}^{-1/2} \;, \tag{27}$$

cf. Ref. 18; v_a is the volume of the elementary cell,

$$I_{l,t} = (4\pi)^{-1} \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi [(H)_{l,t}^{\Gamma_1}]^2 \;. \tag{28}$$

In virtue of Eqs. (18), (19), (21), (23), and (26) the $G_E(\vec{R},\vec{0})$ for large R is

$$\begin{aligned} \mathcal{G}_E(\vec{R},\vec{0}) \underset{R\to\infty}{\longrightarrow} & \sum_\lambda f_\lambda(E,\kappa_E^\lambda) \int_0^{\kappa_m^\lambda} \frac{R_d}{\pi} d\kappa \frac{\sin(\kappa R)}{\kappa R} [N^{\Gamma_1,\lambda}(\kappa_E^\lambda)]^2 \\ & \times [1 + c_4^{\Gamma_1,\lambda}(\kappa_E^\lambda)(H)_4^{\Gamma_1} - c_6^{\Gamma_1,\lambda}(\kappa_E^\lambda)(H)_6^{\Gamma_1} + \cdots] \\ \cong & \sum_\lambda f_\lambda(E,\kappa_E^\lambda) g_\lambda(\kappa_E^\lambda,\theta,\phi) \int_0^{\kappa_m^\lambda} d\kappa \frac{\kappa^2 \sin(\kappa R)}{R[\kappa^2 - (\kappa_E^\lambda)^2]} \;, \end{aligned} \tag{29}$$

where the last step is due to the fact that any

$$g_\lambda(\kappa,\theta,\phi) = \kappa^{-2}[N^{\Gamma_1,\lambda}(\kappa)]^2 \sum_{l\in\Gamma_1} \sum_{t\in\Gamma_1} (-1)^{l/2} c_{l,t}^{\Gamma_1,\lambda}(\kappa)(H)_{l,t}^{\Gamma_1} \tag{30}$$

is a slowly varying function of κ; the sum in Eq. (30) runs over l and t which label the cubic harmonics belonging to Γ_1. The principal value of the integral (29) is[9]

$$\begin{aligned} & \frac{1}{2R}\cos(\kappa_E^\lambda R)\{Si[(\kappa_m^\lambda - \kappa_E^\lambda)R] + Si[(\kappa_m^\lambda + \kappa_E^\lambda)R]\} \\ & + \frac{1}{2R}\sin(\kappa_E^\lambda R)\{Ci[(\kappa_m^\lambda - \kappa_E^\lambda)R] - Ci[(\kappa_m^\lambda + \kappa_E^\lambda)R]\} \cong \frac{\pi\cos(\kappa_E^\lambda R)}{R} \end{aligned} \tag{31}$$

providing R is very large. Since $C_l(0)\rightarrow\infty$ expression (31) does not apply when $\kappa_E^\lambda \rightarrow \kappa_m^\lambda$. Taking the principal value and the imaginary part of the integral (29) together we obtain for large R

$$G_E(\vec{R},\vec{0}) \cong \frac{\pi}{R}\sum_\lambda f_\lambda(E,\kappa_E^\lambda)g_\lambda(\kappa_E^\lambda,\theta,\phi) \times[\cos(\kappa_E^\lambda R)-i\sin(\kappa_E^\lambda R)] \;. \quad (32)$$

This term has to be added to any unperturbed coefficient function of Eq. (23) in which κ is replaced by one of κ_E^λ, if, in analogy to Koster method for the Bloch coefficient functions,[4] we put

$$U^{\Gamma_1,\lambda}(\vec{R}) = A^{\Gamma_1,\lambda}(\kappa,\vec{R}) + c(\vec{0})G_E(\vec{R},\vec{0}) \;. \quad (33)$$

[In order to avoid any confusion with the $c_{l,t}^{\Gamma_1,\lambda}(\kappa)$ used in Eqs. (23)–(30) the superscripts Γ_1 and λ at $c(\vec{0})$ are omitted.] We can calculate the coefficient $c(\vec{0})$ in the way similar to that used in Refs. 3 and 4. We have

$$\hat{W}A^{\Gamma_1,\lambda}(\kappa_E,\vec{R}) = \epsilon^{\Gamma_1,\lambda}(\kappa_E)A^{\Gamma_1,\lambda}(\kappa_E,\vec{R}) \;, \quad (34)$$

$$(\hat{W}+V^P)U^{\Gamma_1,\lambda}(R) = EU^{\Gamma_1,\lambda}(\vec{R}) \;. \quad (35)$$

The index λ for κ_E has been omitted. Substituting Eqs. (33) and (34) into Eq. (35) we have

$$(\hat{W}+V^P)[A^{\Gamma_1,\lambda}(\kappa_E,\vec{R})+c(\vec{0})G_E(\vec{R},\vec{0})] = \epsilon^{\Gamma_1,\lambda}(\kappa_E)A^{\Gamma_1,\lambda}(\kappa_E,\vec{R})+V^PA^{\Gamma_1,\lambda}(\kappa_E,\vec{R})+V^Pc(\vec{0})G_E(\vec{R},\vec{0})+c(\vec{0})\hat{W}G_E(\vec{R},\vec{0}$$

$$= EA^{\Gamma_1,\lambda}(\kappa_E,\vec{R}) + c(\vec{0})EG_E(\vec{R},\vec{0}) \;. \quad (36)$$

Because

$$\hat{W}G_E(\vec{R},\vec{0}) = \epsilon^{\Gamma_1,\lambda}(\kappa)G_E(\vec{R},\vec{0}) \quad (37)$$

and

$$\sum_\lambda\sum_\kappa \frac{[E-\epsilon^{\Gamma_1,\lambda}(\kappa)]A^{\Gamma_1,\lambda}(\kappa,\vec{R})A^{\Gamma_1,\lambda}(\kappa,\vec{0})}{\epsilon^{\Gamma_1,\lambda}(\kappa)-E} = -\delta(\vec{R},\vec{0}) \;, \quad (38)$$

which is the Kronecker's delta, we have

$$[-E+\epsilon^{\Gamma_1,\lambda}(\kappa_E)]A^{\Gamma_1,\lambda}(\kappa_E,\vec{R}) + V^PA^{\Gamma_1,\lambda}(\kappa_E,\vec{R}) + V^Pc(\vec{0})G_E(\vec{R},\vec{0}) = -c(\vec{0})\delta(\vec{R},\vec{0}) \;. \quad (39)$$

We multiply this equation by $A^{\Gamma_1,\lambda}(\kappa_E,\vec{R})$ and integrate over the crystal space. Taking into account that $V^P\neq 0$ only at $\vec{R}=\vec{0}$ we obtain

$$[-E+\epsilon^{\Gamma_1,\lambda}(\kappa_E)] + V^P(\vec{0})[A^{\Gamma_1,\lambda}(\kappa_E,\vec{0})]^2 + V^P(\vec{0})c(\vec{0})A^{\Gamma_1,\lambda}(\kappa_E,\vec{0})G_E(\vec{0},\vec{0}) = -c(\vec{0})A^{\Gamma_1,\lambda}(\kappa_E,\vec{0}) \;, \quad (40)$$

therefore

$$c(\vec{0}) = -\frac{A^{\Gamma_1,\lambda}(\kappa_E,\vec{0})V^P(\vec{0})}{1+V^P(\vec{0})G_E(\vec{0},\vec{0})} \;, \quad (41)$$

since $\epsilon^{\Gamma_1,\lambda}(\kappa_E)=E$ by hypothesis; see Eq. (20). For large R the dependence of $A^{\Gamma_1,\lambda}(\kappa,\vec{R})$ and $B^{\Gamma_1,\lambda}(\kappa,\vec{R})$ on the angles θ and ϕ is the same as the dependence of $g_\lambda(\kappa,\theta,\phi)$ on these angles. Then, because of the formula (32) and the asymptotic form of $A^{\Gamma_1,\lambda}(\kappa,\vec{R})$ and $B^{\Gamma_1,\lambda}(\kappa,\vec{R})$ [cf. Eqs. (23) and (25)], the $G_E(\vec{R},\vec{0})$ at large $|\vec{R}|$ is a linear combination of $A^{\Gamma_1,\lambda}(\kappa,\vec{R})$ and $B^{\Gamma_1,\lambda}(\kappa,\vec{R})$ taken for different λ. Therefore [Eq. (33)] the perturbed coefficient functions at large R are

$$\begin{aligned}
U^{\Gamma_1,\lambda'} &= (1+a^{\lambda'\lambda'})A^{\Gamma_1,\lambda'}(\kappa_E^{\lambda'}) + a^{\lambda'\lambda''}A^{\Gamma_1,\lambda''}(\kappa_E^{\lambda''}) + a^{\lambda'\lambda'''}A^{\Gamma_1,\lambda'''}(\kappa_E^{\lambda'''}) + \cdots \\
&\quad + b^{\lambda'\lambda'}B^{\Gamma_1,\lambda'}(\kappa_E^{\lambda'}) + b^{\lambda'\lambda''}B^{\Gamma_1,\lambda''}(\kappa_E^{\lambda''}) + b^{\lambda'\lambda'''}B^{\Gamma_1,\lambda'''}(\kappa_E^{\lambda'''}) + \cdots \;; \\
U^{\Gamma_1,\lambda''} &= (1+a^{\lambda''\lambda''})A^{\Gamma_1,\lambda''}(\kappa_E^{\lambda''}) + a^{\lambda''\lambda'}A^{\Gamma_1,\lambda'}(\kappa_E^{\lambda'}) + a^{\lambda''\lambda'''}A^{\Gamma_1,\lambda'''}(\kappa_E^{\lambda'''}) + \cdots \\
&\quad + b^{\lambda''\lambda'}B^{\Gamma_1,\lambda'}(\kappa_E^{\lambda'}) + b^{\lambda''\lambda''}B^{\Gamma_1,\lambda''}(\kappa_E^{\lambda''}) + b^{\lambda''\lambda'''}B^{\Gamma_1,\lambda'''}(\kappa_E^{\lambda'''}) + \cdots \;; \qquad (42) \\
&\cdots \\
U^{\Gamma_1,\lambda^{(n)}} &= (1+a^{\lambda^{(n)}\lambda^{(n)}})A^{\Gamma_1,\lambda^{(n)}}(\kappa_E^{\lambda^{(n)}}) + a^{\lambda^{(n)}\lambda'}A^{\Gamma_1,\lambda'}(\kappa_E^{\lambda'}) + a^{\lambda^{(n)}\lambda''}A^{\Gamma_1,\lambda''}(\kappa_E^{\lambda''}) + \cdots \\
&\quad + b^{\lambda^{(n)}\lambda'}B^{\Gamma_1,\lambda'}(\kappa_E^{\lambda'}) + b^{\lambda^{(n)}\lambda''}B^{\Gamma_1,\lambda''}(\kappa_E^{\lambda''}) + \cdots + b^{\lambda^{(n)}\lambda^{(n)}}B^{\Gamma_1,\lambda^{(n)}}(\kappa_E^{\lambda^{(n)}}) \;.
\end{aligned}$$

For any pair of the indices $\lambda^{(\mu)}$ and $\lambda^{(\nu)}$ the coefficients a and b depend on the strength of the perturbation potential and the energy; cf. Eq. (41). For the sake of simplicity the symbol $\vec{R}$ in the argument of $U^{\Gamma_1,\lambda}$, $A^{\Gamma_1,\lambda}$, and $B^{\Gamma_1,\lambda}$ in Eq. (42) has been omitted; the same applies to Eq. (46). We have assumed in Eqs. (42) that for a given E there are n values of κ_E^{λ}:

$$\kappa_E^{\lambda'}, \kappa_E^{\lambda''}, \ldots, \kappa_E^{\lambda^{(n)}} \tag{43}$$

for which

$$\epsilon^{\Gamma_1,\lambda'}(\kappa_E^{\lambda'}) = \epsilon^{\Gamma_1,\lambda''}(\kappa_E^{\lambda''}) = \cdots$$
$$= \epsilon^{\Gamma_1,\lambda^{(n)}}(\kappa_E^{\lambda^{(n)}}) = E \tag{44}$$

is satisfied. The important point is that $U^{\Gamma_1,\lambda'}$, $U^{\Gamma_1,\lambda''}, \ldots, U^{\Gamma_1,\lambda^{(n)}}$, which are solutions of the same eigenproblem, can be mutually orthogonalized. These solutions, however, are not of much use, because of the difficulties in the calculation of the coefficients $a^{\lambda^{(\mu)}\lambda^{(\nu)}}$ and $b^{\lambda^{(\mu)}\lambda^{(\nu)}}$. But there exists another set of functions, $\overline{U}^{\Gamma_1,\lambda}$, which are mutually orthogonal and are also the eigenfunctions of the energy operator $\hat{W}^p$ of the perturbed crystal outside the impurity area. For in this area

$$\hat{W}^p = \hat{W} \tag{45}$$

and the eigenfunctions are

$$\begin{aligned}
\overline{U}^{\Gamma_1,\lambda'} &= p^{(\lambda')}A^{\Gamma_1,\lambda'}(\kappa_E^{\lambda'}) + q^{(\lambda')}B^{\Gamma_1,\lambda'}(\kappa_E^{\lambda'}) \ ; \\
\overline{U}^{\Gamma_1,\lambda''} &= p^{(\lambda'')}A^{\Gamma_1,\lambda''}(\kappa_E^{\lambda''}) + q^{(\lambda'')}B^{\Gamma_1,\lambda''}(\kappa_E^{\lambda''}) \ ; \\
& \cdots \\
\overline{U}^{\Gamma_1,\lambda^{(n)}} &= p^{(\lambda^{(n)})}A^{\Gamma_1,\lambda^{(n)}}(\kappa_E^{\lambda^{(n)}}) + q^{(\lambda^{(n)})}B^{\Gamma_1,\lambda^{(n)}}(\kappa_E^{\lambda^{(n)}}) \ .
\end{aligned} \tag{46}$$

The energy of any function (46) satisfies Eq. (44) because of the validity of Eq. (12) in the considered area. The mutual orthogonality of the functions (46) can be easily checked if we note that for large R and any κ_E^{λ}

$$A^{\Gamma_1,\lambda}(\kappa_E^{\lambda}, \vec{R}) \propto R^{-1}\sin(\kappa_E^{\lambda}R) \ , \tag{47}$$

$$B^{\Gamma_1,\lambda}(\kappa_E^{\lambda}, \vec{R}) \propto R^{-1}\cos(\kappa_E^{\lambda}R) \ . \tag{48}$$

Any integral $\int \overline{U}^{\Gamma_1,\lambda^{(\mu)}}(\vec{R})\overline{U}^{\Gamma_1,\lambda^{(\nu)}}(\vec{R})\,d\Omega$ is a combination of

$$\begin{aligned}
\int \sin(\kappa_E^{\lambda^{(\mu)}}R)\sin(\kappa_E^{\lambda^{(\nu)}}R)\,dR &\approx \int \sin(\kappa_E^{\lambda^{(\mu)}}R)\cos(\kappa_E^{\lambda^{(\nu)}}R)\,dR \\
&\approx \int \cos(\kappa_E^{\lambda^{(\mu)}}R)\sin(\kappa_E^{\lambda^{(\nu)}}R)\,dR \\
&\approx \int \cos(\kappa_E^{\lambda^{(\mu)}}R)\cos(\kappa_E^{\lambda^{(\nu)}}R)\,dR \approx 0
\end{aligned} \tag{49}$$

providing $\mu \neq \gamma$. The result (49) holds because the interval of the integration over R is large in comparison with the period of sine and cosine and $\kappa_E^{\lambda^{(\mu)}} \neq \kappa_E^{\lambda^{(\nu)}}$; see Ref. 20. Since Eqs. (42) and (46) represent two sets of mutually orthogonal eigenfunctions of the same eigenproblem having one energy E there must exist a unitary transformation between these two sets of functions. As a result, the electron density given by a more complicated set (42) can be replaced by the density given by a simple set (46). This makes the impurity problem suitable to its further treatment with the aid of the phase shifts. For, if we put

$$p^{(\lambda)} = \cos\delta^{\lambda} \ , \tag{50}$$

$$q^{(\lambda)} = \sin\delta^{\lambda} \ , \tag{51}$$

and take into account Eqs. (47) and (48) we obtain $\overline{U}^{\Gamma_1,\lambda}$ equal to a phase-shifted $A^{\Gamma_1,\lambda}(\kappa_E, \vec{R})$. This is given by Eq. (23) in which $\kappa = \kappa_E^{\lambda}$ and the argument $\kappa_E^{\lambda}R$ is replaced by $\kappa_E^{\lambda}R + \delta^{\lambda}$. This can be done for any κ_E^{λ} which satisfies Eq. (44). We obtain one phase shift for any standing wave function whose energy is inside the band, in analogy with the result obtained earlier by Blandin for the Bloch state.[13]

IV. CALCULATION OF PHASE SHIFTS

This can be done on the basis of the rigid-band theorem. At the first step we assume the perturbation potential $V^p(\vec{r} - \vec{R}_p)$ centered on one lattice site, say $\vec{R}_p$. This site is close, but not necessarily equal to site $\vec{R}_p = \vec{0}$. The perturbation energy of the Bloch state is independent of the position $\vec{R}_p$, viz.,

$$\begin{aligned}
\Delta\epsilon^{\text{Bloch}} &= \frac{1}{N}V(\vec{R}_p) = \frac{1}{N}V(\vec{R}_{p'}) \\
&= \frac{1}{N}V(\vec{R}_{p''}) = \cdots = \frac{1}{N}V(\vec{0}) \ .
\end{aligned} \tag{52}$$

In Eq. (52) we assume that only

$$\begin{aligned}
V(\vec{R}_p) &= \int \phi^*(\vec{r} - \vec{R}_p)V^p(\vec{r} - \vec{R}_p)\phi(\vec{r} - \vec{R}_p)\,d\tau \\
&= V(\vec{R}_{p'}) \\
&= \int \phi^*(\vec{r} - \vec{R}_{p'})V^p(\vec{r} - \vec{R}_{p'})\phi(\vec{r} - \vec{R}_{p'})\,d\tau \\
&= \cdots
\end{aligned} \tag{53}$$

do not vanish.

Beyond the one-center integrals (53) we may also have

$$V(\vec{R}_p;\vec{R}_l,\vec{R}_l)=\int \phi^*(\vec{r}-\vec{R}_l)\,V^P(\vec{r}-\vec{R}_p)\,\phi(\vec{r}-\vec{R}_l)\,d\tau \ , \tag{54}$$

the two-center integrals, and

$$V(\vec{R}_p;\vec{R}_l,\vec{R}_m)=\int \phi^*(\vec{r}-\vec{R}_l)\,V^P(\vec{r}-\vec{R}_p)\,\phi(\vec{r}-\vec{R}_m)\,d\tau \ , \tag{55}$$

the three-center integrals. Their total effect on the standing wave function labeled by Γ_i, μ, λ, and κ is

$$\begin{aligned}\Delta\epsilon^{\Gamma_i,\lambda}&=V(\vec{R}_p)[A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R}_p)]^2+\sum_{\vec{R}_l}V(\vec{R}_p;\vec{R}_l,\vec{R}_l)\,[A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R}_l)]^2\\&\quad+\sum_{\vec{R}_l}\sum_{\vec{R}_m}V(\vec{R}_p;\vec{R}_l,\vec{R}_m)\,[A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R}_l)A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R}_m)] \ .\end{aligned} \tag{56}$$

The sums $\sum_{\vec{R}_l}$ and $\sum_{\vec{R}_m}$ run over these few centers near $\vec{R}_p\approx\vec{0}$ for which Eqs. (54) and (55) do not vanish. The superscript μ in $\epsilon^{\Gamma_i,\lambda}$ is omitted because energies of the wave functions belonging to different rows of an irreducible representation are degenerate.

Outside the region of the localized perturbation the energy operator of the perfect crystal is unchanged, hence the energy eigenvalue as a function of the quantum parameter κ must be unchanged, too. The energy change is due solely to the change of the allowed values of κ. If the condition of the vanishing of the coefficient function at the boundary of the metal sphere whose radius is R_d is satisfied by a particular κ before the impurity is introduced, the same boundary condition after the introduction of the impurity is satisfied by another value κ' such that[1,7,22]

$$\kappa' R_d+\delta^{\Gamma_i,\lambda}=\kappa R_d \ . \tag{57}$$

Therefore the shift of $\epsilon^{\Gamma_i,\lambda}$ given as a function of $\delta^{\Gamma_i,\lambda}$ is

$$\begin{aligned}\Delta\epsilon^{\Gamma_i,\lambda}&=\epsilon^{\Gamma_i,\lambda}(\kappa')-\epsilon^{\Gamma_i,\lambda}(\kappa)\\&\equiv(1+\alpha_1\kappa'^2+\alpha_2\kappa'^4+\cdots)^{\Gamma_i,\lambda}-(1+\alpha_1\kappa^2+\alpha_2\kappa^4+\cdots)^{\Gamma_i,\lambda}\\&=\alpha_1[(\kappa-\delta^{\Gamma_i,\lambda}/R_d)^2-\kappa^2]+\alpha_2^{\Gamma_i,\lambda}[(\kappa-\delta^{\Gamma_i,\lambda}/R_d)^4-\kappa^4]+\cdots\\&\cong-[\partial\epsilon^{\Gamma_i,\lambda}(\kappa)/\partial\kappa]\delta^{\Gamma_i,\lambda}/R_d \ .\end{aligned} \tag{58}$$

In the power expansion for $\epsilon^{\Gamma_i,\lambda}(\kappa')$ we took into account that $\delta^{\Gamma_i,\lambda}/R_d \ll 1$, so the terms $(\delta^{\Gamma_i,\lambda}/R_d)^n$ having $n>1$ can be neglected. The coefficients $\alpha_m^{\Gamma_i,\lambda}$ depend on the interaction integrals which define the potential of the perfect crystal:

$$\alpha_m^{\Gamma_i,\lambda}=\alpha_m^{\Gamma_i,\lambda}\left(\frac{\beta'}{\beta},\frac{\beta''}{\beta},\ \ldots\right) \ , \tag{59}$$

where $\beta,\beta',\beta'',\ \ldots\,$, are, respectively, the integrals of the nearest-neighbor, the second-nearest-neighbor, and the third-nearest-neighbor atomic interactions of a given atom. The coefficient $\alpha_1^{\Gamma_i,\lambda}$ is the same for any Γ_i and λ. Putting Eq. (56) equal to Eq. (58) we obtain $\delta^{\Gamma_i,\lambda}(\kappa)$.

The calculation of $\delta^{\Gamma_i,\lambda}$ can be simplified if the symmetry properties are used. For example, for $V^P(\vec{R}_p)$ confined to one point $\vec{R}_p=\vec{0}$ and neglected many-center integrals (54) and (55) only $\delta^{\Gamma_1,\lambda}$ do not vanish:

$$\delta^{\Gamma_1,\lambda}=R_d\left(-\frac{\partial\epsilon^{\Gamma_1,\lambda}}{\partial\kappa}\right)^{-1}V(\vec{0})[A^{\Gamma_1,\lambda}(\kappa,\vec{0})]^2 \ . \tag{60}$$

The density of states at energy ϵ coming from the λth wave function is[18]

$$\begin{aligned}D^{\Gamma_1,\lambda}(\epsilon)&=[A^{\Gamma_1,\lambda}(\kappa,\vec{0})]^2\frac{dn}{d\kappa}\left(-\frac{d\kappa}{d\epsilon^{\Gamma_1,\lambda}(\kappa)}\right)\\&=[N^{\Gamma_1,\lambda}(\kappa)]^2\frac{R_d}{\pi}\left(-\frac{d\kappa}{d\epsilon^{\Gamma_1,\lambda}(\kappa)}\right)\end{aligned} \tag{61}$$

providing κ satisfies the equation

$$\epsilon^{\Gamma_1,\lambda}(\kappa)=\epsilon \ . \tag{62}$$

Therefore

$$\delta^{\Gamma_1,\lambda}(\epsilon)=V(\vec{0})\pi D^{\Gamma_1,\lambda}(\epsilon) \ . \tag{63}$$

Tables I and II present the average $[V(\vec{0})\pi]^{-1}\delta^{\Gamma_1,\lambda}(\epsilon)$ calculated for the tightly-bound $(\beta'=\beta''=\cdots=0)$

TABLE I. Phase shifts $\delta^{\Gamma_1,\lambda}$ for the tightly-bound *s* electrons in the face-centered cubic lattice times the factor $[\pi V(\vec{0})]^{-1}$. The sum of $\bar{\delta}^{\Gamma_1,\lambda}=\delta^{\Gamma_1,\lambda}[\pi V(\vec{0})]^{-1}$ over λ approaches the density of states $D(\epsilon)$ in the crystal, therefore $D(\epsilon_i)\Delta\epsilon_i$ is the electron number within the energy interval $\Delta\epsilon_i$. The reduced electron energy of the band states is $\epsilon=(E-E_0^{(s)}-\gamma^{(s)})/12\beta(\vec{R}_j,\vec{R}_{vj})$, where E is the electron energy, $\beta(\vec{R}_j,\vec{R}_{vj})$ is the interaction integral of a lattice site $\vec{R}_j$ with any of its nearest neighbors $\vec{R}_{vj}$ and $E_0^{(s)}+\gamma^{(s)}$ is the value of β when $\vec{R}_j=\vec{R}_{vj}$. Energy ϵ is within the interval $(1,-\frac{1}{3})$ for the Bloch states and almost exactly the same interval holds for the states based on the standing wave functions; see Ref. 20. We choose $\Delta\epsilon_i=\frac{1}{30}$ for any i and assume $\lambda=1$, 2, 3, and 4 (four-subband model). The sum $Q=\sum_i D(\epsilon_i)\Delta\epsilon_i$ approaches the electron number per atom supplied by all states within the band, providing the spin degeneracy is neglected.

Energy interval	$\bar{\delta}^{\Gamma_1,1}$	$\bar{\delta}^{\Gamma_1,2}$	$\bar{\delta}^{\Gamma_1,3}$	$\bar{\delta}^{\Gamma_1,4}$	$\sum_{\lambda=1}^{4}\bar{\delta}^{\Gamma_1,\lambda}$	Bloch's $D(\epsilon)$
(1, 29/30)	0.009	0.008	0.011	0.005	0.033	0.033
(29/30, 28/30)	0.016	0.015	0.020	0.010	0.061	0.061
(28/30, 27/30)	0.022	0.020	0.025	0.012	0.079	0.078
(27/30, 26/30)	0.026	0.024	0.032	0.016	0.098	0.106
(26/30, 25/30)	0.030	0.028	0.040	0.018	0.116	0.110
(25/30, 24/30)	0.035	0.030	0.041	0.022	0.128	0.127
(24/30, 23/30)	0.039	0.038	0.049	0.022	0.148	0.152
(23/30, 22/30)	0.043	0.039	0.053	0.026	0.161	0.160
(22/30, 21/30)	0.049	0.041	0.061	0.027	0.178	0.177
(21/30, 20/30)	0.051	0.047	0.063	0.031	0.192	0.192
(20/30, 19/30)	0.057	0.052	0.065	0.035	0.209	0.215
(19/30, 18/30)	0.064	0.058	0.078	0.036	0.236	0.224
(18/30, 17/30)	0.070	0.059	0.079	0.039	0.247	0.256
(17/30, 16/30)	0.070	0.065	0.087	0.039	0.261	0.258
(16/30, 15/30)	0.077	0.070	0.095	0.046	0.288	0.301
(15/30, 14/30)	0.091	0.076	0.093	0.046	0.306	0.307
(14/30, 13/30)	0.090	0.083	0.110	0.055	0.338	0.320
(13/30, 12/30)	0.097	0.089	0.119	0.053	0.358	0.363
(12/30, 11/30)	0.114	0.096	0.116	0.057	0.383	0.399
(11/30, 10/30)	0.123	0.103	0.137	0.061	0.424	0.410
(10/30, 9/30)	0.132	0.110	0.146	0.066	0.454	0.457
(9/30, 8/30)	0.141	0.118	0.156	0.070	0.485	0.481
(8/30, 7/30)	0.150	0.137	0.167	0.082	0.536	0.533
(7/30, 6/30)	0.174	0.134	0.177	0.080	0.565	0.585
(6/30, 5/30)	0.201	0.156	0.188	0.093	0.638	0.632
(5/30, 4/30)	0.231	0.166	0.218	0.090	0.705	0.693
(4/30, 3/30)	0.247	0.177	0.232	0.105	0.761	0.777
(3/30, 2/30)	0.301	0.204	0.247	0.112	0.864	0.865
(2/30, 1/30)	0.362	0.235	0.284	0.119	1.000	1.01
(1/30, 0)	0.474	0.252	0.326	0.138	1.19	1.16
(0, −1/30)	0.673	0.289	0.347	0.147	1.46	1.56
(−1/30, −2/30)	1.476	0.333	0.396	0.169	2.37	1.53
(−2/30, −3/30)	· · ·	0.407	0.480	0.181	1.07	1.58
(−3/30, −4/30)	· · ·	0.499	0.546	0.223	1.27	1.63
(−4/30, −5/30)	· · ·	0.619	0.688	0.240	1.55	1.70
(−5/30, −6/30)	· · ·	0.927	0.893	0.312	2.13	1.73
(−6/30, −7/30)	· · ·	1.59	1.39	0.34	3.32	1.88
(−7/30, −8/30)	· · ·	3.99	3.00	0.46	7.45	2.00
(−8/30, −9/30)	· · ·	· · ·	· · ·	0.73	0.73	2.18
(−9/30, −10/30)	· · ·	· · ·	· · ·	1.82	1.82	2.77
Q	0.19	0.38	0.37	0.21	1.15	1.00

TABLE II. Phase shifts $\delta^{\Gamma_1,\lambda}$ for the almost-free s electrons in the face-centered cubic lattice times the factor $[\pi V(\vec{0})]^{-1}$. The sum of $\bar{\delta}^{\Gamma_1,\lambda}=\delta^{\Gamma_1,\lambda}[\pi V(\vec{0})]^{-1}$ over λ approaches the almost-free electron density of states $D^{n\,\text{free}}(\epsilon)$. Four-subband model ($\lambda=1$, 2, 3, and 4) has been considered. The bandwidth $\epsilon_t=\frac{1}{2}(\frac{1}{2}\sqrt{5}\pi)^2$ is divided into 40 intervals each having the length $\Delta\epsilon=\frac{1}{40}\epsilon_t$. The sum $Q=\sum_i D^{n\,\text{free}}(\epsilon_i)\Delta\epsilon_i$ over all i approaches the electron number per atom supplied by all states within the band providing the spin degeneracy is neglected.

Energy interval	$\bar{\delta}^{\Gamma_1,1}$	$\bar{\delta}^{\Gamma_1,2}$	$\bar{\delta}^{\Gamma_1,3}$	$\bar{\delta}^{\Gamma_1,4}$	$\sum_{\lambda=1}^{4}\bar{\delta}^{\Gamma_1,\lambda}$	Bloch's $D^{n\,\text{free}}(\epsilon)$
1	0.010	0.009	0.012	0.006	0.038	0.038
2	0.018	0.017	0.023	0.011	0.069	0.069
3	0.023	0.021	0.029	0.016	0.088	0.088
4	0.028	0.026	0.035	0.017	0.106	0.106
5	0.031	0.029	0.039	0.020	0.119	0.118
6	0.035	0.033	0.044	0.022	0.134	0.134
7	0.038	0.035	0.048	0.024	0.145	0.145
8	0.040	0.037	0.050	0.025	0.152	0.152
9	0.042	0.040	0.054	0.028	0.164	0.164
10	0.045	0.042	0.057	0.029	0.174	0.173
11	0.046	0.044	0.060	0.031	0.181	0.181
12	0.051	0.048	0.065	0.034	0.199	0.198
13	0.049	0.046	0.063	0.033	0.191	0.190
14	0.056	0.054	0.072	0.038	0.220	0.219
15	0.052	0.051	0.068	0.036	0.207	0.206
16	0.055	0.054	0.072	0.039	0.221	0.220
17	0.059	0.058	0.077	0.042	0.235	0.234
18	0.057	0.057	0.076	0.041	0.232	0.231
19	0.060	0.061	0.080	0.044	0.245	0.244
20	0.062	0.065	0.084	0.047	0.259	0.257
21	0.060	0.064	0.082	0.046	0.252	0.250
22	0.062	0.069	0.086	0.049	0.265	0.262
23	0.063	0.074	0.090	0.052	0.278	0.274
24	0.059	0.073	0.086	0.050	0.267	0.262
25	0.060	0.078	0.089	0.053	0.280	0.262
26	0.060	0.085	0.093	0.056	0.293	0.250
27	0.022	0.092	0.096	0.059	0.269	0.238
28	⋯	0.101	0.100	0.062	0.264	0.225
29	⋯	0.101	0.094	0.059	0.255	0.193
30	⋯	0.111	0.097	0.062	0.271	0.181
31	⋯	0.122	0.101	0.066	0.288	0.169
32	⋯	0.132	0.104	0.069	0.305	0.157
33	⋯	0.139	0.107	0.073	0.319	0.136
34	⋯	0.141	0.099	0.008	0.248	0.106
35	⋯	0.121	⋯	⋯	0.121	0.069
36	⋯	0.108	⋯	⋯	0.108	0.044
37	⋯	0.022	⋯	⋯	0.022	0.033
38	⋯	⋯	⋯	⋯	⋯	0.022
39	⋯	⋯	⋯	⋯	⋯	0.011
40	⋯	⋯	⋯	⋯	⋯	0.000
Q	0.19	0.38	0.37	0.21	1.15	1.00

and the almost free s electrons in the face-centered cubic lattice.

The $\delta^{\Gamma_i,\mu,\lambda}$ belonging to different Γ_i and μ depend on the size and the position of the perturbation, the structure of the matrix lattice, and the values of the integrals of the atomic interaction which enter $\epsilon^{\Gamma_i,\lambda}(\kappa)$. At the band bottom which is at $\kappa=0$ all $\delta^{\Gamma_i,\mu,\lambda}(\kappa)$ vanish because any $A^{\Gamma_i,\mu,\lambda}(0,\vec{R})$ is zero. It is easy to show for small κ and the perturbation integral confined to $V(\vec{0})$ that the phase shift given in Eq. (63) can be obtained also from the Green's-function method and the Born approximation.

V. USE OF PHASE SHIFTS

A. Total change of electron number and the sum rule for phase shifts

Phase shifts are very useful because one can calculate easily the change in the density of states due to an impurity. Assuming the main part of electron charge is coming from large distances, the change in the electron number due to a single wave function is

$$\Delta\rho^{\Gamma_i,\mu,\lambda}(\kappa) \cong \frac{1}{v_a}\int_0^{R_d} R^2 dR \int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi [N^{\Gamma_i,\mu,\lambda}(\kappa)]^2 \left(\frac{\sin^2(\kappa R + \delta^{\Gamma_i,\mu,\lambda} - \frac{1}{2}\Delta\pi)}{\kappa^2 R^2} - \frac{\sin^2(\kappa R - \frac{1}{2}\Delta\pi)}{\kappa^2 R^2} \right) \times \left[\sum_{l\in\Gamma_i} \sum_{t\in\Gamma_i} (-1)^q c^{\Gamma_i,\mu,\lambda}(\kappa)(H)_{l,t}^{\Gamma_i,\mu} \right]^2 \quad (64)$$

on condition that the angular part of the wave function remains unaltered;

$$\Delta = 0, \quad q = \tfrac{1}{2} l \text{ for } \Gamma_i = \Gamma_1,\ \Gamma_{12},\ \Gamma_{25'},\ \Gamma_{15'}, \text{ and } \Gamma_2 \quad (65)$$

and

$$\Delta = 1, \quad q = \tfrac{1}{2}(l-1) \text{ for } \Gamma_i = \Gamma_{1'},\ \Gamma_{2'},\ \Gamma_{12'},\ \Gamma_{15}, \text{ and } \Gamma_{25}\ . \quad (66)$$

Taking

$$\Phi = R^{-1}\sin[\kappa R + \delta^{\Gamma_i,\mu,\lambda}(\kappa) - \tfrac{1}{2}\Delta\pi] \quad (67)$$

and

$$\Phi_0 = R^{-1}\sin(\kappa R) \quad (68)$$

the functions Φ and Φ_0 can be regarded, respectively, as radial solutions of the perturbed and the unperturbed free-electron problem in a spherical potential box. Using the reasoning given by Friedel[1] as well as the fact that $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$ are normalized [cf. Eqs. (23) and (27) for $\Gamma_i = \Gamma_1$] we obtain

$$\Delta\rho^{\Gamma_i,\mu,\lambda}(\kappa) = \frac{1}{R_d}\left(\frac{d\delta^{\Gamma_i,\mu,\lambda}(\kappa)}{d\kappa} - \frac{1}{\kappa}\sin\delta^{\Gamma_i,\mu,\lambda}(\kappa) \times \cos[2\kappa R_d + \delta^{\Gamma_i,\mu,\lambda}(\kappa) - \Delta\pi] \right) . \quad (69)$$

Excepting for $\delta^{\Gamma_i,\mu,\lambda}(\kappa)$ which is not the free-electron phase shift, this formula is identical with Friedel's. The factor Δ replaces the azimuthal quantum number l of free electrons. Friedel has summed the free-electron contributions corresponding to a given l which gave the factor $2l+1$. In the present case this does not apply. To get the change of electron charge for a given E we have to sum expression (69) over all appropriate Γ_i and μ and over all $\kappa = \kappa_E^\lambda$ which satisfy Eq. (44). If $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$ are exact eigenfunctions, the $\epsilon^{\Gamma_i,\lambda}$ obtained for different Γ_i are degenerate (see Appendix for the proof); therefore we have the same set of κ_E^λ for any Γ_i. Neglecting the oscillating part in Eq. (69) we obtain a modified Friedel's sum rule (Z is the change of electron charge introduced to the metal by an impurity)

$$Z = \frac{2}{\pi}\sum_{\Gamma_i}\sum_{\mu}\sum_{\lambda}\int_0^{\kappa_F^\lambda} \frac{d\delta^{\Gamma_i,\mu,\lambda}(\kappa)}{d\kappa}\, d\kappa = \frac{2}{\pi}\sum_{\Gamma_i}\sum_{\mu}\sum_{\lambda}\delta^{\Gamma_i,\mu,\lambda}(\kappa_F^\lambda) \quad (70)$$

because $\delta^{\Gamma_i,\mu,\lambda}(0) = 0$. The κ_F^λ are obtained from Eq. (44) in which $E = E_F$ is the Fermi energy and

$$\frac{dn}{d\kappa} = \frac{R_d}{\pi} \quad (71)$$

is the density of states κ in a spherical potential box.[1] The factor 2 represents the spin degeneracy. Let us note that for a spherical energy band only a single value $\kappa = \kappa_E$ corresponds to a given E and only one phase shift was obtained for that E (Ref. 7); cf. also Sec. V C. A short numerical comparison of the present model with the Koster-Slater theory is given in the next paper.

For the impurity potential confined to one lattice site ($\vec{R}_p$)

$$Z = 2V(\vec{R}_p)\sum_{\Gamma_i}\sum_{\mu}\sum_{\lambda} D_{\vec{R}_p}^{\Gamma_i,\mu,\lambda}(E_F) = 2V(\vec{R}_p)D(E_F)\ , \quad (72)$$

where

$$D_{\vec{R}_p}^{\Gamma_i,\mu,\lambda}(E_F) = [A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R}_p)]^2 \frac{R_d}{\pi}\left(-\frac{d\kappa}{d\epsilon^{\Gamma_i,\lambda}(\kappa)} \right)\Bigg|_{\kappa=\kappa_F^\lambda} \quad (73)$$

is the component of the total density of states at the Fermi level of the matrix metal labeled by the indices Γ_i, μ, and λ. These components have been calculated before.[23] In distinction to the total density of states $D(E_F)$ expression (73) does depend on $\vec{\mathrm{R}}_p$; see Ref. 23.

Results given in Eqs. (63) and (70) can be obtained also in an elementary way. Since the change $\Delta\kappa$ of the interval of the quantum parameter due to the phase shift is $\delta^{\Gamma_i,\mu,\lambda}(\kappa_F^\lambda)/R_d$ the change Δn in the number of states labeled by Γ_i, μ, and λ is

$$\Delta n=\frac{dn}{d\kappa}\Delta\kappa=\frac{R_d}{\pi}\frac{\delta^{\Gamma_i,\mu,\lambda}}{R_d}=\left(\frac{dn}{d\epsilon}\right)_{\epsilon=E_F}\Delta\epsilon=D^{\Gamma_i,\mu,\lambda}(E_F)\,V(\vec{\mathrm{R}}_p) \tag{74}$$

because the density of states per unit of κ is that given in Eq. (71); at the second step we take into account the change of the density of states labeled by Γ_i, μ, and λ per unit of κ due to the presence of impurity. This is[7]

$$\frac{1}{\pi}\frac{d\delta^{\Gamma_i,\mu,\lambda}(\kappa)}{d\kappa} . \tag{75}$$

Therefore the total change in the number of states labeled by Γ_i, μ, and λ is

$$\frac{2}{\pi}\int_0^{\kappa_F^\lambda}\frac{d\delta^{\Gamma_i,\mu,\lambda}(\kappa)}{d\kappa}\,d\kappa=\frac{2}{\pi}\delta^{\Gamma_i,\mu,\lambda}(\kappa_F^\lambda) . \tag{76}$$

B. Local change of electron density

The total change of electron density at $\vec{\mathrm{R}}$, where $|\vec{\mathrm{R}}|$ is large, is

$$\Delta\rho(\vec{\mathrm{R}})=\frac{1}{R^2}\sum_{\Gamma_i}\sum_{\mu}\sum_{\lambda}\int_0^{\kappa_F^\lambda}\frac{R_d}{\pi}\,d\kappa\,\tilde{g}^{\Gamma_i,\mu,\lambda}(\kappa,\theta_{\vec{\mathrm{R}}},\phi_{\vec{\mathrm{R}}})[\sin^2(\kappa R+\delta^{\Gamma_i,\mu,\lambda}-\tfrac{1}{2}\Delta\pi)-\sin^2(\kappa R-\tfrac{1}{2}\Delta\pi)] , \tag{77}$$

where

$$\tilde{g}^{\Gamma_i,\mu,\lambda}(\kappa,\theta_{\vec{\mathrm{R}}},\phi_{\vec{\mathrm{R}}})=\frac{[N^{\Gamma_i,\mu,\lambda}(\kappa)]^2}{\kappa^2}\left[\sum_{l,t\in\Gamma_i}(-1)^q c_{l,t}^{\Gamma_i,\mu,\lambda}(\kappa)(H)_{l,t}^{\Gamma_i,\mu}\right]^2 \tag{78}$$

is another slowly varying function of κ. The term in the integrand in Eq. (77) can be transformed into

$$\begin{aligned}\sin^2(\kappa R+\delta^{\Gamma_i,\mu,\lambda}-\Delta\tfrac{1}{2}\pi)-\sin^2(\kappa R-\Delta\tfrac{1}{2}\pi)&=\sin(2\kappa R+\delta^{\Gamma_i,\mu,\lambda}-\Delta\pi)\sin\delta^{\Gamma_i,\mu,\lambda}\\&\approx(-1)^\Delta\tfrac{1}{2}\sin(2\kappa R)\sin(2\delta^{\Gamma_i,\mu,\lambda})\\&\approx(-1)^\Delta\sin(2\kappa R)\delta^{\Gamma_i,\mu,\lambda}\end{aligned} \tag{79}$$

providing all terms having $[V(\vec{0})]^2$ and higher powers $V(\vec{0})$ are neglected. The $\tilde{g}^{\Gamma_i,\mu,\lambda}(\kappa,\theta_{\vec{\mathrm{R}}},\phi_{\vec{\mathrm{R}}})$ can be approximated by a single value calculated for an argument $\kappa=\kappa_0$ which is within the interval $(0,\kappa_F^\lambda)$. Therefore

$$\Delta\rho(\vec{\mathrm{R}})\approx\frac{1}{R^2}\sum_{\Gamma_i}\sum_{\mu}\sum_{\lambda}\tilde{g}^{\Gamma_i,\mu,\lambda}(\kappa_0^\lambda,\theta_{\vec{\mathrm{R}}},\phi_{\vec{\mathrm{R}}})\frac{R_d}{\pi}(-1)^\Delta\int_0^{\kappa_F^\lambda}\sin(2\kappa R)\delta^{\Gamma_i,\mu,\lambda}(\kappa)\,d\kappa . \tag{80}$$

In a large interval of κ we have

$$\delta^{\Gamma_i,\mu,\lambda}(\kappa)\approx\tilde{C}^{\Gamma_i,\mu,\lambda}\kappa , \tag{81}$$

where $\tilde{C}^{\Gamma_i,\mu,\lambda}$ is a constant. Then

$$\int_0^{\kappa_F^\lambda} \sin(2\kappa R)\delta^{\Gamma_i,\mu,\lambda}(\kappa)\,d\kappa \approx -\frac{1}{2R}\cos(2\kappa R)\delta^{\Gamma_i,\mu,\lambda}(\kappa)\Big|_{\kappa=0}^{\kappa=\kappa_F^\lambda} + \frac{1}{2R}\int_0^{\kappa_F^\lambda}\cos(2\kappa R)\frac{d\delta^{\Gamma_i,\mu,\lambda}(\kappa)}{d\kappa}\,d\kappa$$

$$\cong -\frac{1}{2R}\cos(2\kappa_F^\lambda R)\delta^{\Gamma_i,\mu,\lambda}(\kappa_F^\lambda) + \frac{1}{(2R)^2}\tilde{C}^{\Gamma_i,\mu,\lambda}\sin(2\kappa_F^\lambda R)\ . \tag{82}$$

At large R the cosine term predominates; hence

$$\Delta\rho(\vec{R}) \approx -\frac{1}{2R^3}\sum_{\Gamma_i}\sum_{\mu}\sum_{\lambda}\cos(2\kappa_F^\lambda R)\delta^{\Gamma_i,\mu,\lambda}(\kappa_F^\lambda)\frac{R_d}{\pi}(-1)^\Delta \tilde{g}^{\Gamma_i,\mu,\lambda}(\kappa_0^\lambda,\theta_{\vec{R}},\phi_{\vec{R}})\ . \tag{83}$$

The dependence on R_d is canceled if the expression for $[N^{\Gamma_i,\mu,\lambda}(\kappa)]^2$ is taken into account; see Eqs. (78) and (27) for the special case of $\Gamma_i=\Gamma_1$. The charge oscillates, as it has been pointed out earlier, in the free-electron case[1]; but now the amplitude, which is proportional to R^{-3}, depends on the phase shift at the Fermi level and the direction in which the oscillation is going out. Only in the almost free-electron case for which all κ_F^λ are equal we have one length of the oscillation wave. In general the oscillation is a superposition of the waves whose lengths are reciprocals to the values of the quantum parameter taken at the Fermi level.

Instead of the intervals $(0,\kappa_F^\lambda)$ expression (77) can be referred to a small interval near κ and integrated over the surface of a sphere. Because of the form of $\tilde{g}^{\Gamma_i,\mu,\lambda}(\kappa,\theta_{\vec{R}},\phi_{\vec{R}})$ and the orthogonality of $(H)_{l,t}^{\Gamma_i,\mu}$ we obtain

$$\frac{1}{v_a}\frac{d}{d\kappa}\int_0^{\pi}\sin\theta\,d\theta\int_0^{2\pi}d\phi\,[\Delta\rho(\vec{R})]_{\kappa_F^\lambda=\kappa} = \frac{1}{v_a}\frac{1}{R^2}\sum_{\Gamma_i}\sum_{\mu}\sum_{\lambda}[N^{\Gamma_i,\mu,\lambda}(\kappa)]^2\frac{R_d}{\pi}\frac{1}{\kappa^2}$$

$$\times\sum_{l,t}[c_{l,t}^{\Gamma_i,\mu,\lambda}(\kappa)]^2 I_{l,t}(-1)^\Delta\sin(2\kappa R+\delta^{\Gamma_i,\mu,\lambda})\sin\delta^{\Gamma_i,\mu,\lambda}$$

$$=\frac{1}{R^2}\frac{(-1)^\Delta}{2\pi^2}\sum_{\Gamma_i}\sum_{\mu}\sum_{\lambda}\sin[2\kappa R+\delta^{\Gamma_i,\mu,\lambda}]\sin\delta^{\Gamma_i,\mu,\lambda}\ , \tag{84}$$

where the formula for $N^{\Gamma_i,\mu,\lambda}(\kappa)$ has been taken into account. Exactly the same result is obtained from Friedel's expression (69)

$$\frac{1}{4\pi R^2}\frac{\partial[\Delta\rho^{\Gamma_i,\mu,\lambda}(\kappa)]}{\partial R} = (-1)^\Delta\frac{1}{2\pi^2R^2}\sin(2\kappa R+\delta^{\Gamma_i,\mu,\lambda})\sin\delta^{\Gamma_i,\mu,\lambda} \tag{85}$$

providing Eq. (69) is multiplied by the density of states per unit of κ and we have put $R_d=R$.

C. Phase shifts for a spherical band

The result obtained in Eq. (63) can be compared with Clogston's.[7] He considered a spherical band and obtained one phase shift

$$\delta(E)=\arctan\left[-\frac{\pi D(E)V(\vec{0})}{1+V(\vec{0})I(E)}\right]\ , \tag{86}$$

where $I(E)$ is the principal value of the Green's function $G_E(\vec{R},\vec{R}_p)$ calculated at $\vec{R}=\vec{R}_p=\vec{0}$; the volume of the atomic cell is assumed equal to unity. If the powers of $V(\vec{0})$ higher than the first are neglected, Eq. (86) is simplified to

$$\delta(E)=-\pi V(\vec{0})D(E)\ ; \tag{87}$$

$D(E)$ is the density of states of the matrix metal at E. The identical result is obtained also in the model of this paper if we do not diagonalize the energy operator but apply the free-electron wave functions as the coefficient functions for the wave functions in a spherical band. Taking into account only one free-electron wave function, namely that which does not vanish at site $\vec{0}$, we obtain from Eq. (60)

$$\delta(E)=V(\vec{0})R_d\left[-\frac{\partial\kappa}{\partial\epsilon^{\text{free}}}\right]\left[\frac{\kappa}{(2\pi R_d)^{1/2}}j_0(\vec{0})\right]^2\Bigg|_{\kappa=\kappa_E}$$

$$=-\pi V(\vec{0})D^{\text{free}}(E)\ . \tag{88}$$

The superscript "free" refers to the fact that electrons are free in a spherical band. If the impurity is localized on site $\vec{R}_p\neq 0$ a similar result can be obtained but now we have many phase shifts

$$\delta^{l,m}(E)=-\pi V(\vec{0})D_{l,m}^{\text{free}}(E) \tag{89}$$

coming from the individual

$$D_{l,m}^{\text{free}}(E) \propto |P_l^m(\cos\theta_{\vec{R}_p})\exp(im\phi_{\vec{R}_p})j_l(\kappa R_p)|^2_{\kappa=\kappa_E} \tag{90}$$

which do not vanish at $\vec{R}=\vec{R}_p$ and can be added to $D^{\text{free}}(E)$:

$$\sum_l \sum_m D_{l,m}^{\text{free}}(E) = D^{\text{free}}(E) \ . \tag{91}$$

The eigenenergies of all $A = P_l^m(\cos\theta)e^{im\phi}j_l(\kappa R)$ are the same

$$\begin{aligned} \hat{W}A &\approx \Delta[P_l^m(\cos\theta)e^{im\phi}j_l(\kappa R)] \\ &= -\kappa^2 P_l^m(\cos\theta)e^{im\phi}j_l(\kappa R) \ . \end{aligned} \tag{92}$$

The total displacement of electron charge is obtained when Eq. (88) is multiplied by $2/\pi$ and calculated at the Fermi level[7]:

$$Z = -2V(\vec{0})D^{\text{free}}(E_F) \tag{93}$$

because $D^{\text{free}}(0)=0$. Now let us calculate the charge displacement in the present model. The coefficient functions diagonalize the energy operator. Since these operators commute independently of the strength of the atomic interaction taken into account, the accurate $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$ are the same for the tightly bound and nearly-free electrons. According to Eq. (70) we calculate a sum of all $\delta^{\Gamma_i,\mu,\lambda}(E)$ for $E=E_F$. Taking into account Eq. (63) we obtain

$$\begin{aligned} Z &= -2V(\vec{0}) \sum_\lambda D^{n\,\text{free}\Gamma_1,\lambda}(E_F)|_{\vec{R}=\vec{0}} \\ &= -2V(\vec{R}_p) \sum_{\Gamma_i} \sum_\mu \sum_\lambda D^{n\,\text{free}\Gamma_i,\mu,\lambda}(E_F)|_{\vec{R}=\vec{R}_p\neq\vec{0}} \\ &= -2V(\vec{0})D^{n\,\text{free}}(E_F) \end{aligned} \tag{94}$$

since, as it has been checked before for several cases,[23] the total density of states of the present model does not depend on the position of the site considered in the crystal and we have $V(\vec{R}_p) = V(\vec{0})$. The change of sign in Eq. (63) is due to the fact that now

$$\frac{d\epsilon^{\Gamma_i,\lambda}}{d\kappa} = \frac{d}{d\kappa}\left(\tfrac{1}{2}\kappa^2\right) \tag{95}$$

(which holds for any Γ_i and λ) is positive for all $\kappa > 0$.

The difference between the present and the Clogston's approach is in the diagonalization of the energy operator which is absent in the Clogston's model. This diagonalization makes the density of states at site $\vec{0}$ contributed not by a single wave function but several wave functions. The diagonalization explains to us the decrease of the nearly-free electron $D(E)$ beginning near E which is at the critical point in the Brillouin zone; see Table II and Fig. 1. Correspondingly, we obtain several phase shifts $\delta^{\Gamma_1,\lambda}$ for the perturbation confined to $V(\vec{0})$ [Eq. (94)]. But these individual phase shifts can be added together and their sum is equal to the Clogston's phase shift.

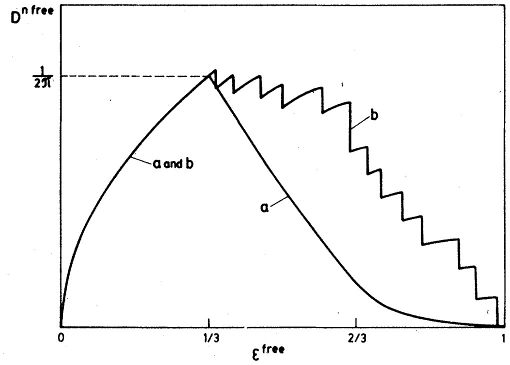

FIG. 1. Almost-free electron density of states, $D^{n\,\text{free}}$, in the sc lattice vs energy ϵ^{free}. Curve a is obtained from the itinerant, or Bloch's, crystal wave functions (Ref. 24), curve b from the standing crystal wave functions of the present scheme. In the present scheme

$$D^{n\,\text{free}}(\epsilon^{\text{free}}) \cong \frac{1}{2\pi^2}(2\epsilon^{\text{free}})^{1/2}\frac{1}{\lambda_{\max}}\sum_{\lambda=1}^{\lambda=\lambda_{\max}}\tilde{\Delta}^\lambda(\kappa) \ ,$$

where $\lambda_{\max}$ is the number of subbands taken into account in the model (Refs. 18–21 and 23); $\tilde{\Delta}^\lambda(\kappa)=1$ for $\kappa < \kappa_{\min}^\lambda$, otherwise $\tilde{\Delta}^\lambda(\kappa)=0$. The parameter $\kappa_{\min}^\lambda$ is the position of the first minimum of the energy curve $\epsilon^{\Gamma_1,\lambda}(\kappa)$ calculated for the tightly bound *s* electrons in the sc lattice (Ref. 25). This minimum position points to the boundary of the first Brillouin zone (Ref. 20), though only for certain directions taken from the center of the zone this position is exactly coincident with the boundary of the zone [T. Bulski, P. Modrak, and S. Olszewski, Acta Phys. Polon. (in press)]. For other directions (other λ) the $\kappa_{\min}^\lambda$ have to be replaced by certain κ_q^λ where $\kappa_q^\lambda < \kappa_{\min}^\lambda$. Then curve a and curve b will be closer together within the interval $\frac{1}{3} < \epsilon^{\text{free}} < 1$ than it is shown on the figure; within the interval $0 < \epsilon^{\text{free}} \lesssim \frac{1}{3}$ (or $(0 < \kappa \lesssim \pi)$ curve a and curve b coincide. The energy of the almost-free electrons is referred to the quantum parameter κ via the relation

$$\epsilon^{\text{free}} = \frac{1}{2}\kappa^2 \ ;$$

cf. Eq. (95). The bandwidth of the Bloch's almost-free electron states has been taken as the unit of energy.

VI. SCATTERING CROSS SECTION DUE TO AN IMPURITY

The perturbed coefficient function U can be set up as a combination of a part that represents an incident particle moving in the positive direction along Z and a part that represents a radially outgoing particle[26]

$$U(R,\theta,\phi) \propto e^{i\kappa Z} + R^{-1}f(\theta,\phi)e^{i\kappa R} \ . \tag{96}$$

The parameter $\kappa=|\vec{k}|$ is the magnitude of the propagation vector. The scattering amplitude $f(\theta,\phi)$ is obtained when $U(R,\theta,\phi)$ of Eq. (96) calculated at large R is identified with the general solution of the eigenproblem having the same perturbation potential. Unlike free electrons, the scattering in a crystal does not have the axial symmetry, hence f depends also on the angle ϕ. A component of the general solution of the energy eigenequation depends on certain κ and belongs to the μth row of the irreducible representation Γ_i:

$$\begin{aligned}\tilde{U}_{(\kappa)}^{(\Gamma_i,\mu)}(R,\theta,\phi)&=\sum_{\lambda} b_{\lambda}^{\Gamma_i,\mu}(\kappa)U^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})\\ &\xrightarrow[R\to\infty]{}\sum_{\lambda} b_{\lambda}^{\Gamma_i,\mu}(\kappa)N^{\Gamma_i,\mu,\lambda}(\kappa)\left[\sum_{l}\sum_{t}(-1)^{q}c_{l,t}^{\Gamma_i,\mu,\lambda}(\kappa)(H)_{l,t}^{\Gamma_i,\mu}\right]\frac{\sin[\kappa R+\delta^{\Gamma_i,\mu,\lambda}(\kappa)]}{\kappa R}\ .\end{aligned}\tag{97}$$

The sums run over l and t which label the harmonics of a given Γ_i; the meaning of q is explained before [Eqs. (65) and (66)]. The $b_{\lambda}^{\Gamma_i,\mu}(\kappa)$ are constants which should not be confused with those entering Eq. (42). At the next step we express $e^{i\kappa Z}$ in terms of $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$ which form an orthonormal set

$$\int A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})A^{\Gamma_j,\mu',\lambda'}(\kappa,\vec{R})\,d\Omega=\delta_{\lambda\lambda'}\delta_{\Gamma_i\Gamma_j}\delta_{\mu\mu'}\ .\tag{98}$$

The $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$, which are solutions of the energy eigenequation for the unperturbed crystal, form a complete set for the expansion of any function which is finite throughout the potential box. To have the expansion of $e^{i\kappa Z}$ it is enough to combine the functions having the same value of the parameter κ:

$$e^{i\kappa Z}=e^{i\kappa R\cos\theta}=\sum_{l=0}^{\infty}(2l+1)i^{l}j_{l}(\kappa R)P_{l}^{0}(\cos\theta)=\sum_{\Gamma_i}\sum_{\mu}\sum_{\lambda}d_{\lambda}^{\Gamma_i,\mu}(\kappa)A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})\ ,\tag{99}$$

where

$$\begin{aligned}d_{\lambda}^{\Gamma_i,\mu}(\kappa)&=\int e^{i\kappa Z}A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})\,d\Omega\\ &\cong N^{\Gamma_i,\mu,\lambda}(\kappa)\sum_{l=0}^{\infty}(2l+1)i^{l}\sum_{l'\in\Gamma_i}\sum_{t}\delta_{ll'}\int_{R_a}^{R_d}\frac{\sin^2(\kappa R-\frac{1}{2}\Delta\pi)}{\kappa^2R^2}R^2\,dR\,c_{l',t}^{\Gamma_i,\mu,\lambda}(\kappa)(-1)^{2q}\\ &\qquad\times\int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta\,d\theta\,(H)_{l',t}^{\Gamma_i,\mu}P_l^0(\cos\theta)\\ &=\sum_{l\in\Gamma_i}^{\infty}\sum_{t}(2l+1)i^{l}\frac{R_d}{2\kappa^2}N^{\Gamma_i,\mu,\lambda}(\kappa)c^{\Gamma_i,\mu,\lambda}(\kappa)\int_0^{2\pi}\int_0^{\pi}d\phi\sin\theta\,d\theta\,P_l^0(\cos\theta)(H)_{l,t}^{\Gamma_i,\mu}\ .\end{aligned}\tag{100}$$

$d_{ll'}$ is the Kronecker's symbol. Since the main contribution to $d_{\lambda}^{\Gamma_i,\mu}(\kappa)$ comes from large distances, the asymptotic form of $j_l(\kappa R)$ has been taken into account; the last step is due to the fact that $R_d>>R_a$ and the average of $\sin^2$ or $\cos^2$ is $\frac{1}{2}$.

Similarly to $e^{i\kappa Z}$ we assume that f can be decomposed into parts belonging to different Γ_i and μ:

$$f(\theta,\phi)=\sum_{\Gamma_i}\sum_{\mu}f^{\Gamma_i,\mu}(\theta,\phi)\ .\tag{101}$$

Then at large R we have the equation

$$\begin{aligned}\sum_{\lambda}d_{\lambda}^{\Gamma_i,\mu}(\kappa)A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})+\frac{f^{\Gamma_i,\mu}(\theta,\phi)}{R}e^{i\kappa R}\\ =\sum_{\lambda}b_{\lambda}^{\Gamma_i,\mu}(\kappa)[\cos\delta^{\Gamma_i,\mu,\lambda}(\kappa)A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})-\sin\delta^{\Gamma_i,\mu,\lambda}(\kappa)B^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})]\ .\end{aligned}\tag{102}$$

Denoting the angular part of $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$ at large R by

$$F^{\Gamma_i,\mu,\lambda}(\kappa,\theta,\phi)=N^{\Gamma_i,\mu,\lambda}(\kappa)\sum_{l}\sum_{t}c_{l,t}^{\Gamma_i,\mu,\lambda}(\kappa)(-1)^{q}(H)_{l,t}^{\Gamma_i,\mu}\tag{103}$$

and applying the asymptotic formulas for both $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$ and $B^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$ we obtain for Eq. (102)

$$\sum_\lambda d_\lambda^{\Gamma_i,\mu}(\kappa)F^{\Gamma_i,\mu,\lambda}(\kappa,\theta,\phi)\frac{\sin(\kappa R)}{\kappa R}+\frac{f^{\Gamma_i,\mu}(\theta,\phi)}{R}e^{i\kappa R}=\sum_\lambda b_\lambda^{\Gamma_i,\mu}(\kappa)F^{\Gamma_i,\mu,\lambda}(\kappa,\theta,\phi)\frac{\sin[\kappa R+\delta^{\Gamma_i,\mu,\lambda}(\kappa)]}{\kappa R}\ . \qquad (104)$$

Taking into account that

$$\sin\kappa R=\frac{e^{i\kappa R}-e^{-i\kappa R}}{2i};\ \ \sin(\kappa R+\delta)=\frac{e^{i(\kappa R+\delta)}-e^{-i(\kappa R+\delta)}}{2i} \qquad (105)$$

we can put equal the coefficients of $e^{i\kappa R}$ and $e^{-i\kappa R}$ on the two sides of Eq. (104). We obtain

$$2i\kappa f^{\Gamma_i,\mu}(\theta,\phi)+\sum_\lambda d_\lambda^{\Gamma_i,\mu}(\kappa)F^{\Gamma_i,\mu,\lambda}(\kappa,\theta,\phi)=\sum_\lambda b_\lambda^{\Gamma_i,\mu}(\kappa)F^{\Gamma_i,\mu,\lambda}(\kappa,\theta,\phi)\exp(i\delta^{\Gamma_i,\mu,\lambda}) \qquad (106)$$

and

$$\sum_\lambda d_\lambda^{\Gamma_i,\mu}(\kappa)F^{\Gamma_i,\mu,\lambda}(\kappa,\theta,\phi)=\sum_\lambda b_\lambda^{\Gamma_i,\mu}(\kappa)\exp(-i\delta^{\Gamma_i,\mu,\lambda})F^{\Gamma_i,\mu,\lambda}(\kappa,\theta,\phi)\ . \qquad (107)$$

These equations are true for all values θ and ϕ; moreover any two functions $F^{\Gamma_i,\mu,\lambda}$ which differ at least in one of the indices Γ_i, μ, and λ are orthogonal. Therefore from Eq. (107)

$$b_\lambda^{\Gamma_i,\mu}(\kappa)=d_\lambda^{\Gamma_i,\mu}(\kappa)\exp[i\delta^{\Gamma_i,\mu,\lambda}(\kappa)] \qquad (108)$$

and

$$f^{\Gamma_i,\mu}(\theta,\phi)=\frac{1}{2i\kappa}\sum_\lambda d_\lambda^{\Gamma_i,\mu}(\kappa)F^{\Gamma_i,\mu,\lambda}(\kappa,\theta,\phi)\{\exp[2i\delta^{\Gamma_i,\mu,\lambda}(\kappa)]-1\}\ . \qquad (109)$$

For $\delta^{\Gamma_i,\mu,\lambda}\rightarrow 0$ the scattering amplitude vanishes. It may happen that we have vanishing $f^{\Gamma_i,\mu}$ for certain Γ_i and μ and the nonvanishing for the other Γ_i and μ.

The differential cross section

$$\sigma(\theta,\phi)=|f(\theta,\phi)|^2 \qquad (110)$$

is also dependent on κ. Since we assume the elastic scattering, no velocity factors appear in passing from $f(\theta,\phi)$ to $\sigma(\theta,\phi)$. The total elastic cross section σ^t is the integral of the expression (110) over the spherical surface. Because $F^{\Gamma_i,\mu,\lambda}$ are orthogonal, and can be normalized, the cross products $F^{\Gamma_i,\mu,\lambda}F^{\Gamma_j,\mu',\lambda'}$ entering the integral of (110) vanish and we obtain

$$\sigma^t=\int\int\sigma(\theta,\phi)\sin\theta\,d\theta\,d\phi=(8\pi R_d)^{-1}\sum_{\Gamma_i}\sum_\mu\sum_\lambda[d_\lambda^{\Gamma_i,\mu}(\kappa)]^2\sin^2[\delta^{\Gamma_i,\mu,\lambda}(\kappa)]\ . \qquad (111)$$

The dependence on R_d is canceled if we take into account that $d_\lambda^{\Gamma_i,\mu}\propto R_d^{1/2}$; cf. Eqs. (100) and (27) which holds for $\Gamma_i=\Gamma_1$ taken as an example.

VII. OPTICAL THEOREM

The validity of the calculation of σ^t can be checked with the aid of the optical theorem. This theorem is valid also when f depends on the angle ϕ[26]:

$$\sigma^t=\frac{4\pi}{\kappa}\operatorname{Im}f(\theta,\phi)|_{\theta=0}\ . \qquad (112)$$

The σ^t and f are the sums of contributions coming from the individual Γ_i and μ; the theorem must hold for any of these contributions. Therefore it should be

$$\begin{aligned}\frac{4\pi}{\kappa}\operatorname{Im}f^{\Gamma_i,\mu}(0,\phi)&=\frac{4\pi}{\kappa}\sum_\lambda\sin^2\delta^{\Gamma_i,\mu,\lambda}(\kappa)d_\lambda^{\Gamma_i,\mu}(\kappa)F^{\Gamma_i,\mu,\lambda}(\kappa,0,\phi)\\&=\sigma^{t(\Gamma_i,\mu)}=(8\pi R_d)^{-1}\sum_\lambda[d_\lambda^{\Gamma_i,\mu}(\kappa)]^2\sin^2\delta^{\Gamma_i,\mu,\lambda}(\kappa)\end{aligned} \qquad (113)$$

which implies for any λ

$$\frac{1}{R_d} d_\lambda^{\Gamma_{i'},\mu}(\kappa) = F^{\Gamma_{i'},\mu,\lambda}(\kappa, 0, \phi) \tag{114}$$

with the accuracy to a constant multiplier. First we note that the dependence on R_d on the both sides is identical because the right-hand side is proportional to $N^{\Gamma_{i'},\mu,\lambda}(\kappa) \propto R_d^{-1/2}$ and the same dependence on the left is given by Eq. (100). Second, the Legendre polynomials satisfy the relation

$$P_l^m \propto (1-\cos^2\theta)^{m/2} \quad , \tag{115}$$

so $P_l^m(\cos 0) = P_l^m(1) = 0$ unless $m = 0$. If the last case applies these $(H)_{l,t}^{\Gamma_{i'},\mu}$ which do not contain $P_l^0(\cos\theta)$ vanish and these cubic harmonics which contain $P_l^0(\cos\theta)$ are reduced to a multiple of this function. Hence, for $\theta = 0$, any $F^{\Gamma_{i'},\mu,\lambda}$ and therefore any $f^{\Gamma_{i'},\mu}$ ceases to be dependent on ϕ. Furthermore, because $P_l^0(1) = 1$ for all l, any $F^{\Gamma_{i'},\mu,\lambda}$ becomes equal to the combination of the coefficients with which $P_l^0(\cos\theta)$ enter any $(H)_{l,t}^{\Gamma_{i'},\mu}$. Owing to the property of the orthogonality of $P_l^m(\cos\theta)$ the same result is obtained when $F^{\Gamma_{i'},\mu,\lambda}$ is multiplied by $P_l^0(\cos\theta)$ and integrated over the spherical surface. This is the essence of the expression (100) for $d_\lambda^{\Gamma_{i'},\mu}(\kappa)$ providing we note that

$$\int_0^\pi [P_l^0(\cos\theta)]^2 \sin\theta \, d\theta = 2(2l+1)^{-1} \tag{116}$$

and the factor $(-1)^q$ in $F^{\Gamma_{i'},\mu,\lambda}$ is rendered by the term i^l.

VIII. ELECTRON STATES BASED ON ATOMIC ORBITALS WHOSE SYMMETRY IS DIFFERENT THAN SPHERICAL

If the atomic orbitals ϕ have spherical symmetry (type s), the construction of the wave functions belonging to different rows of the irreducible representations is easy: we calculate the coefficient function $A^{\Gamma_{i'},\mu,\lambda}(\kappa, \vec{R})$ on each site $\vec{R} = \vec{R}_i$, then multiply it by $\phi(\vec{r} - \vec{R}_i)$ centered on this site, and add the products together. These wave functions are listed in Table III. For $\phi(\vec{r} - \vec{R}_i)$ having symmetry different than s the calculation of the wave functions is more complicated. In the Bloch LCAO theory we construct the Bloch sum for each atomic state ϕ separately. Then these sums are linearly combined into the full wave functions with the aid of the diagonalization procedure.[27] In general no splitting of the full band of states into subbands occurs since the nondiagonal matrix elements of the Hamiltonian calculated between Bloch sums based on different ϕ's do not vanish. But the change of symmetry of ϕ may change the symmetry of the differential operator for energy calculated with the aid of the wave functions based on that ϕ. Let us assume for example

$$\psi_{\vec{n}} = \sum_{\vec{R}_i} T(\vec{n}, \vec{R}_i) \phi_{p_z}(\vec{r} - \vec{R}_i) \quad , \tag{117}$$

where ϕ_{p_z} are orbitals which belong to zth row of irreducible representation Γ_{15}. The parameters which characterize the electron state are abbreviated to symbol $\vec{n}$. For the Bloch states index $\vec{n}$ is replaced by $\vec{k}$. The wave function $\psi_{\vec{n}}$ has to satisfy

$$\hat{H}\psi_{\vec{n}} = E_{\vec{n}}\psi_{\vec{n}} \quad , \tag{118}$$

where $\hat{H}$ is the crystal Hamiltonian, and $E_{\vec{n}}$ is energy. We multiply Eq. (118) on the left by $\phi_{p_z}^*(\vec{r} - \vec{R}_j)$ and integrate. We obtain

$$\int \phi_{p_z}^*(\vec{r} - \vec{R}_j)\hat{H}\psi_{\vec{n}} \, d\tau = (E_0^{(p_z)} + \gamma^{(p_z)}) T(\vec{n}, \vec{R}_j) + \sum_{\vec{R}_{vj}} \beta(\vec{R}_j, \vec{R}_{vj}) T(\vec{n}, \vec{R}_{vj}) \tag{119}$$

on one side and

$$\int \phi_{p_z}^*(\vec{r} - \vec{R}_j) E_{\vec{n}} \psi_{\vec{n}} \, d\tau = E_{\vec{n}} T(\vec{n}, \vec{R}_j) \tag{120}$$

on the other side, providing that ϕ_{p_z} centered on different lattice sites form an orthonormal set. $\vec{R}_{vj}$ label the sites which are in the neighborhood of $\vec{R}_j$. The term $E_0^{(p_z)} + \gamma^{(p_z)}$ is the value of the interaction integral $\beta(\vec{R}_j, \vec{R}_{vj})$ when $\vec{R}_{vj} = \vec{R}_j$. Any $T(\vec{n}, \vec{R}_{vj})$ can be expanded in the Taylor series about $\vec{R}_j$:

$$T(\vec{n}, \vec{R}_{vj}) = \sum_{m=0}^{\infty} \frac{1}{m!} [(\vec{R}_{vj} - \vec{R}_j) \cdot \nabla]^m \times T(\vec{n}, \vec{R}_j) \quad . \tag{121}$$

Let us assume a simple cubic lattice with the lattice parameter $a = 1$ and the atomic interaction reduced to nearest neighbors; then any distance $|\vec{R}_{vj} - \vec{R}_j| = 1$. Taking into account the symmetry of the lattice and that of the interaction integrals

$$\begin{aligned}\beta(\vec{R}_j, \vec{R}_{vj}^{(z)}) &= \int \phi_{p_z}^*(\vec{r} - \vec{R}_j)\hat{H}\phi_{p_z}(\vec{r} - \vec{R}_{vj}^{(z)}) \, d\tau \neq \beta(\vec{R}_j, \vec{R}_{vj}^{(x)}) = \int \phi_{p_z}^*(\vec{r} - \vec{R}_j)\hat{H}\phi_{p_z}(\vec{r} - \vec{R}_{vj}^{(x)}) \, d\tau \\ &= \beta(\vec{R}_j, \vec{R}_{vj}^{(y)}) = \int \phi_{p_z}^*(\vec{r} - \vec{R}_j)\hat{H}\phi_{p_z}(\vec{r} - \vec{R}_{vj}^{(y)}) \, d\tau \quad ;\end{aligned} \tag{122}$$

TABLE III. The wave functions of a cubic crystal based on the atomic states s and classified according to irreducible representations Γ_i of the crystal point group; the index λ has been omitted. The superscripts give the symbol of the irreducible representation and the characteristic polynomial of the lowest order. The approximate numerial data for $A^{\Gamma_1,1}(\kappa,\vec{R}_i)$; $A^{\Gamma_{12},2z^2-x^2-y^2}(\kappa,\vec{R}_i)$ [valid also for $A^{\Gamma_{12},x^2-y^2}(\kappa,\vec{R}_i)$]; $A^{\Gamma_{15},z}(\kappa,\vec{R}_i)$ [valid also for $A^{\Gamma_{15},x}(\kappa,\vec{R}_i)$ and $A^{\Gamma_{15},y}(\kappa,\vec{R}_i)$]; $A^{\Gamma_{25},z(x^2-y^2)}(\kappa,\vec{R}_i)$ [valid also for $A^{\Gamma_{25},x(y^2-z^2)}(\kappa,\vec{R}_i)$ and $A^{\Gamma_{25},y(z^2-x^2)}(\kappa,\vec{R}_i)$]; $A^{\Gamma_{25'},xy}(\kappa,\vec{R}_i)$ [valid also for $A^{\Gamma_{25'},yz}(\kappa,\vec{R}_i)$ and $A^{\Gamma_{25'},zx}(\kappa,\vec{R}_i)$] are published in Refs. 18, 19, and 21 for different lattices. $x=X/R$, $y=Y/R$, and $z=Z/R$.

$$\sum_{\vec{R}_i} A^{\Gamma_1,1}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_2,x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{12},2z^2-x^2-y^2}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{12},x^2-y^2}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{15},x}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{15},y}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{15},z}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{25},x(y^2-z^2)}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{25},y(z^2-x^2)}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{25},z(x^2-y^2)}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{1'},xyz[x^4(y^2-z^2)+y^4(z^2-x^2)+z^4(x^2-y^2)]}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{2'},xyz}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{12'},(2z^2-x^2-y^2)xyz}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{12'},(x^2-y^2)xyz}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{15'},xy(x^2-y^2)}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{15'},yz(y^2-z^2)}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{15'},zx(z^2-x^2)}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{25'},xy}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{25'},yz}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ ;$$

$$\sum_{\vec{R}_i} A^{\Gamma_{25'},zx}(\kappa,\vec{R}_i)\phi_s(\vec{r}-\vec{R}_i)\ .$$

superscripts x, y, and z denote that vectors $\vec{R}_{\upsilon j}-\vec{R}_j$ are taken parallel to X, Y, and Z axis, respectively. From Eq. (119)–(121) we obtain the equation for $T(\vec{n},\vec{R})$ which holds at any $\vec{R}=\vec{R}_j$:

$$(E-E_0^{(p_z)}-\gamma^{(p_z)})T(\vec{n},\vec{R})=\left\{q^{(z)}\beta^{(z)}\cos\left(i\frac{\partial}{\partial Z}\right)+q^{(x,y)}\beta^{(x,y)}\left[\cos\left(i\frac{\partial}{\partial X}\right)+\cos\left(i\frac{\partial}{\partial Y}\right)\right]\right\}T(\vec{n},\vec{R}) \ . \tag{123}$$

The $\beta^{(z)}$ is the abbreviated symbol of the integral in the first row in Eq. (122), $\beta^{(x,y)}$ denotes the integral in the second and the third row in Eq. (122). The $q^{(z)}=2$ and $q^{(x,y)}=4$ are numbers of the nearest neighbors in direction Z and directions X and Y together, respectively. It can be readily checked that $T(\vec{n},\vec{R})$, when it is put equal to the Bloch's expression given in Eq. (6), satisfies Eq. (123). The eigenvalue is the well known cosinelike expression dependent on k_x, k_y, and k_z.[27] To solve the eigenequation for $T(\vec{n},\vec{R})$ in the case when the wave functions are classified according to the cubic group-symmetry species we take as the trial functions the eigenfunctions $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$ of the eigenproblem having a full cubic symmetry. These functions form a complete set:

$$T(\vec{n},\vec{R})=\sum_{\Gamma_i}\sum_{\mu}\sum_{\lambda}C(\Gamma_i,\mu,\lambda)A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R}) \ . \tag{124}$$

The sum over κ can be omitted because

$$\int A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})\hat{W}^T A^{\Gamma_i',\mu',\lambda'}(\kappa',\vec{R})\,d\Omega\propto\delta_{\kappa\kappa'} \ ; \tag{125}$$

$\hat{W}^T$ is the differential operator given in Eq. (123); the integration in Eq. (125) is over the volume of a large sphere. The proof of Eq. (125) is as follows. We have

$$\int A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})\frac{\partial^{2\nu}}{\partial X^{2\nu}}A^{\Gamma_i',\mu',\lambda'}(\kappa',\vec{R})\,d\Omega\cong(-1)^{\nu}(\kappa')^{2\nu}\int_0^{R_d}R^2\,dR\int_0^{\pi}\sin\theta\,d\theta\int_0^{2\pi}d\phi\,A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})A^{\Gamma_i',\mu',\lambda'}(\kappa',\vec{R})$$
$$\times\cos^{2\nu}\phi\sin^{2\nu}\phi \tag{126}$$

and similar integrals can be obtained for the operators $\partial^{2\nu}/\partial Y^{2\nu}$ and $\partial^{2\nu}/\partial Z^{2\nu}$. Because of the asymptotic form of $j_l(\kappa R)$ and $j_{l'}(\kappa'R)$ which enter $A^{\Gamma_i,\mu,\lambda}$ and $A^{\Gamma_i',\mu',\lambda'}$ any integral (126) over R is reduced to the combination of the integrals represented by the first, or the last, integral entering Eq. (49) on condition that $\kappa\hat{\lambda}_E^{(\mu)}=\kappa$ and $\kappa\hat{\lambda}_E^{(\nu)}=\kappa'$. Also the $A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})$ having equal κ but different λ do not combine because they are the eigenfunctions of $\hat{W}$ having different energies.[20] The operator $\hat{W}^T$ commutes with the operator $\hat{W}$, therefore the nondiagonal elements of $\hat{W}^T$ between these eigenfunctions vanish and the sum over λ can be omitted.

Let us confine our problem to a situation when the impurity potential is extended only on one lattice site say $\vec{0}$; more extended potentials can be considered in a similar way. Our first task is to calculate the density of states of the matrix at $\vec{0}$. This is the density of states of the whole matrix crystal because the matrix potential at $\vec{0}$ repeats at any site which is far from the crystal boundary. The only nonvanishing coefficient function in $\vec{0}$ is $A^{\Gamma_1,\lambda}(\kappa,\vec{R})$. For states p_z the coefficient function $A^{\Gamma_1,\lambda}(\kappa,\vec{R})$ combines together with the coefficient function $A^{\Gamma_{12},2z^2-x^2-y^2,\lambda}(\kappa,\vec{R})$ into the wave function of symmetry Γ_{15}:

$$\psi^{\Gamma_{15},z,\lambda}=\sum_{\vec{R}_i}[A^{\Gamma_1,\lambda}(\kappa,\vec{R}_i)+c^{\lambda}(\kappa)A^{\Gamma_{12},2z^2-x^2-y^2,\lambda}(\kappa,\vec{R}_i)]$$
$$\times\phi_{p_z}(\vec{r}-\vec{R}_i) \ . \tag{127}$$

It is easy to show that no other coefficient functions than $A^{\Gamma_{12},2z^2-x^2-y^2,\lambda}(\kappa,\vec{R})$ can combine with $A^{\Gamma_1,\lambda}(\kappa,\vec{R})$. For, the differential operator in Eq. (123) can be represented as

$$\hat{W}^T=a\hat{W}^{\Gamma_1}+b\hat{W}^{\Gamma_{12},2z^2-x^2-y^2} \ , \tag{128}$$

where a and b are constants. If one of the bra or one of kets in the matrix element

$$\langle A^{\Gamma_i,\mu,\lambda}(\kappa,\vec{R})|\hat{W}^T|A^{\Gamma_j,\mu',\lambda}(\kappa,\vec{R})\rangle \tag{129}$$

is $A^{\Gamma_1,\lambda}$ the other has to be $A^{\Gamma_1,\lambda}$ or $A^{\Gamma_{12},2z^2-x^2-y^2,\lambda}$, otherwise Eq. (129) vanishes. Strictly speaking, the product $A^{\Gamma_{12},2z^2-x^2-y^2,\lambda}(\kappa,\vec{R})\phi_{p_z}(\vec{r}-\vec{R})$ is not of pure symmetry Γ_{15} but still contains a part which belongs to a different symmetry species dictated by the direct product

$$\Gamma_{12}\times\Gamma_{15}=\Gamma_{15}+\Gamma_{25} \ . \tag{130}$$

It is however not necessary to cutoff from $\sum_{\vec{R}_i}A^{\Gamma_{12},2z^2-x^2-y^2,\lambda}(\kappa,\vec{R}_i)\phi_{p_z}(\vec{r}-\vec{R}_i)$ the part which belongs to Γ_{25} because this is done automatically in the course of the diagonalization process. A similar situation we have for the wave function based on $\phi_{d_{xy}}$ states,

$$\psi^{\Gamma_{25'},xy,\lambda}=\sum_{\vec{R}_i}[A^{\Gamma_1,\lambda}(\kappa,\vec{R}_i)+\tilde{c}^{\lambda}(\kappa)$$
$$\times A^{\Gamma_{12},2z^2-x^2-y^2,\lambda}(\kappa,\vec{R}_i)]\phi_{d_{xy}}(\vec{r}-\vec{R}_i) \tag{131}$$

which belongs to the representation $\Gamma_{25'}$ because of the symmetry of $\phi_{d_{xy}}$. Similar wave functions can be constructed for other ϕ's.

Solving the 2 × 2 secular problem

$$\begin{vmatrix} \langle A^{\Gamma_1,\lambda} | \hat{W}^T | A^{\Gamma_1,\lambda}\rangle - E & \langle A^{\Gamma_1,\lambda} | \hat{W}^T | A^{\Gamma_{12},2z^2-x^2-y^2,\lambda}\rangle \\ \langle A^{\Gamma_{12},2z^2-x^2-y^2,\lambda} | \hat{W}^T | A^{\Gamma_1,\lambda}\rangle & \langle A^{\Gamma_{12},2z^2-x^2-y^2,\lambda} | \hat{W}^T | A^{\Gamma_{12},2z^2-x^2-y^2,\lambda}\rangle - E \end{vmatrix} = 0 \qquad (132)$$

we obtain two combinations of $A^{\Gamma_1,\lambda}$ and $A^{\Gamma_{12},2z^2-x^2-y^2,\lambda}$ and two energies for any λ and any κ. The new coefficient functions can be normalized and then the density of states calculated in the way described before. Preliminary calculations are done in Ref. 28. The solutions depend on the parameters which enter the operator $\hat{W}^T$ which, in their turn, depend on the form of ϕ's and the structure and the strength of the atomic interactions in the lattice. Furthermore, the $\psi^{\Gamma_i,\mu,\lambda}$ which belong to the same Γ_i and μ but are based on different ϕ's can be combined into more expanded ψ_c similarly to the well-known treatment used in the Bloch theory.[27] For example for ϕ_{p_z} and symmetry Γ_{15} the wave function (127) can be combined with the wave function

$$\psi^{\Gamma_{15},z,\lambda} = \sum_{\vec{R}_i} A^{\Gamma_{15},z,\lambda}(\kappa,\vec{R}_i)\,\phi_s(\vec{r}-\vec{R}_i) \ , \qquad (133)$$

which is based on ϕ_s and has the same symmetry Γ_{15}, into the new wave function $\psi_c^{\Gamma_{15},z,\lambda}$. Any energy

$$E_c = \int (\psi_c^{\Gamma_i,\mu,\lambda^*})\hat{H}\psi_c^{\Gamma_i,\mu,\lambda}\,d\tau \qquad (134)$$

can be expressed as a function of κ, $\beta^{(z)}$, $\beta^{(x,y)}$, and similar integrals whose number and magnitude depends on the range of the atomic interaction, the arrangement of the atoms in the lattice and the kind of ϕ considered in the combination. Replacing any κ by

$$\kappa' = \kappa - \delta_c^{\Gamma_i,\mu,\lambda}(\kappa)/R_d \qquad (135)$$

we obtain

$$\Delta E_c = E_c^{\Gamma_i,\lambda}(\kappa') - E_c^{\Gamma_i,\lambda}(\kappa) = \int \psi_c^{\Gamma_i,\mu,\lambda^*}\, V^p(\vec{r}-\vec{0})\, \psi_c^{\Gamma_i,\mu,\lambda}\, d\tau \qquad (136)$$

which is the equation for the phase shift $\delta_c^{\Gamma_i,\mu,\lambda}$; V^p is the perturbation potential.

The detailed calculations on the density of states and the corresponding phase shifts $\delta_c^{\Gamma_i,\mu,\lambda}$ are planned.

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APPENDIX: PROOF THAT THE COEFFICIENT FUNCTIONS BELONGING TO DIFFERENT IRREDUCIBLE REPRESENTATIONS OF THE CRYSTAL POINT GROUP ARE DEGENERATE

Let $\hat{W}^\alpha$ be the total-symmetry energy operator of the point group; for the cubic point group $\alpha = \Gamma_1$. For cubic crystals having the $\phi(\vec{r}-\vec{R}_i)$ of type s we have

$$\hat{W}^{\Gamma_1} = \epsilon^B\left[-i\frac{\partial}{\partial X}, -i\frac{\partial}{\partial Y}, -i\frac{\partial}{\partial Z}; \frac{\beta'}{\beta}, \frac{\beta''}{\beta}, \ldots; q', q'', \ldots\right] , \qquad (A1)$$

where

$$\epsilon^B\left[k_x, k_y, k_z; \frac{\beta'}{\beta}, \frac{\beta''}{\beta}, \ldots; q', q'', \ldots\right] = \frac{E - E_0^{(s)} - \gamma^{(s)}}{q\beta} \qquad (A2)$$

is the reduced Bloch energy of the crystal; E is the energy of the electron state, q is the number of the nearest neighbors of a given atom in the crystal lattice; q', q'', . . . are the numbers of the second-nearest, third-nearest, etc. neighbors, β is the interaction integral between an atom and one of its nearest neighbors, β', β'', . . . are the interaction intergrals between a given atom and one of its second-nearest, third-nearest, etc. neighbors. The term $E_0^{(s)} + \gamma^{(s)}$ is the matrix element of the Hamiltonian calculated on a given atom.[18,21]

We have the following set of eigenfunctions A of the operator $\hat{W}^\alpha$:

$$\hat{W}^\alpha A^\alpha = \epsilon^\alpha A^\alpha \ ; \qquad (A3)$$

$$\hat{W}^\alpha A^\beta = \epsilon^\beta A^\beta \ ; \qquad (A4)$$

$$\hat{W}^\alpha A^\gamma = \epsilon^\gamma A^\gamma; \ \ldots \ ; \qquad (A5)$$

β, γ, etc., denote the irreducible representations other than α. We can also have a set of differential operators of a symmetry different than α:

$$\hat{W}^\beta, \hat{W}^\gamma, \ldots \ . \qquad (A6)$$

Because the operators are differential, the commutation relations hold:

$$\hat{W}^{\alpha}\hat{W}^{\beta}=\hat{W}^{\beta}\hat{W}^{\alpha} , \tag{A7}$$

$$\hat{W}^{\alpha}\hat{W}^{\gamma}=\hat{W}^{\gamma}\hat{W}^{\alpha} , \tag{A8}$$

$$\hat{W}^{\beta}\hat{W}^{\gamma}=\hat{W}^{\gamma}\hat{W}^{\beta} . \tag{A9}$$

Operators $\hat{W}^{\alpha}, \hat{W}^{\beta}, \hat{W}^{\gamma}, \ldots$ are Hermitian, as it can be shown along the lines given in Ref. 29. For the sake of simplicity we assume that $\alpha, \beta, \gamma, \ldots$ are one-dimensional representations. Their direct products satisfy the following relations

$$a \times b = b \times a = c , \tag{A10}$$

where a , b, and c, . . . are any element of the set of representations $\alpha, \beta, \gamma, \ldots$. In particular

$$\alpha \times a = a \times \alpha = a; \quad \alpha \times b = b \times \alpha = b; \quad \ldots \tag{A11}$$

and

$$a \times a = b \times b = \cdots = \alpha . \tag{A12}$$

Hence

$$\hat{W}^{a}\hat{W}^{b}=\hat{\hat{W}}^{c} , \tag{A13}$$

etc.; in particular

$$\hat{W}^{\alpha}\hat{W}^{\alpha}=\hat{\hat{W}}^{\alpha} . \tag{A14}$$

Moreover

$$\hat{W}^{a}A^{b}=\epsilon^{ab}A^{c} ; \tag{A15}$$

$$\hat{W}^{a}A^{\alpha}=\epsilon^{a\alpha}A^{a} ; \tag{A16}$$

$$\hat{W}^{a}A^{a}=\epsilon^{aa}A^{\alpha} , \tag{A17}$$

where a and b are still any elements of the set $\alpha, \beta, \gamma, \ldots$; ϵ^{ab}, $\epsilon^{a\alpha}$, and ϵ^{aa} are numbers.

Function A^{c} in Eq. (A15) is the eigenfunction of the $\hat{W}^{\alpha}$ operator. To prove it let us note:

$$\hat{W}^{\alpha}\hat{W}^{a}A^{b}=\hat{W}^{a}\hat{W}^{\alpha}A^{b}=\hat{W}^{a}\epsilon^{b}A^{b}=\epsilon^{b}\hat{W}^{a}A^{b} , \tag{A18}$$

hence $\hat{W}^{a}A^{b}$ is the eigenfunction of $\hat{W}^{\alpha}$. The same holds for $\hat{W}^{a}A^{\alpha}$ and $\hat{W}^{a}A^{a}$. If we consider a Hilbert space whose main axes are eigenfunctions of operator $\hat{W}^{\alpha}$, the operators $\hat{W}^{\beta}$, $\hat{W}^{\gamma}$, $\hat{W}^{\delta}$, . . . where $\beta, \gamma, \delta, \ldots \neq \alpha$, transform the eigenvectors of the operator $\hat{W}^{\alpha}$ into other eigenvectors, whereas the operator $\hat{W}^{\alpha}$ leaves the vector unchanged to within a constant.

Let us take the pair of equations

$$\hat{W}^{\alpha}A^{\alpha}=\epsilon^{\alpha\alpha}A^{\alpha} ; \tag{A19}$$

$$\hat{W}^{\alpha}A^{\beta}=\epsilon^{\alpha\beta}A^{\beta} ; \tag{A20}$$

$\epsilon^{\alpha\alpha}=\epsilon^{\alpha}$ and $\epsilon^{\alpha\beta}=\epsilon^{\beta}$ are eigenvalues and A^{α} and A^{β} are eigenfunctions. We have additionally

$$\hat{W}^{\beta}A^{\alpha}=\epsilon^{\beta\alpha}A^{\beta} , \tag{A21}$$

where $\epsilon^{\beta\alpha}$ is *not* the eigenvalue. We act on Eq. (A19) with $\hat{W}^{\beta}$ and on Eq. (A21) with $\hat{W}^{\alpha}$. We have

$$\begin{aligned}\hat{W}^{\beta}\hat{W}^{\alpha}A^{\alpha}&=\epsilon^{\alpha\alpha}\hat{W}^{\beta}A^{\alpha}\\&=\epsilon^{\alpha\alpha}\epsilon^{\beta\alpha}A^{\beta} ,\end{aligned} \tag{A22}$$

$$\begin{aligned}\hat{W}^{\alpha}\hat{W}^{\beta}A^{\alpha}&=\epsilon^{\beta\alpha}\hat{W}^{\alpha}A^{\beta}\\&=\epsilon^{\beta\alpha}\epsilon^{\alpha\beta}A^{\beta} .\end{aligned} \tag{A23}$$

In Eq. (A23) we have made use of Eq. (A20). Since

$$\hat{W}^{\beta}\hat{W}^{\alpha}=\hat{W}^{\alpha}\hat{W}^{\beta} \tag{A24}$$

and $\epsilon^{\beta\alpha}$ is a number, we have

$$\epsilon^{\alpha\alpha}=\epsilon^{\alpha\beta} . \tag{A25}$$

Since β is chosen arbitrarily, Eq. (A25) holds for any one-dimensional irreducible representation.

The result can be readily extended to multidimensional irreducible representations, if we note that $\hat{W}^{\beta}A^{\alpha}$ is an eigenfunction of $\hat{W}^{\alpha}$ also when $\hat{W}^{\beta}$ belongs to a certain row of a multidimensional irreducible representation. For let us act on $\hat{W}^{\beta}A^{\alpha}$ with the operator $\hat{W}^{\alpha}$. We obtain

$$\begin{aligned}\hat{W}^{\alpha}(\hat{W}^{\beta}A^{\alpha})=\hat{W}^{\beta}(\hat{W}^{\alpha}A^{\alpha})&=\hat{W}^{\beta}\epsilon^{\alpha\alpha}A^{\alpha}\\&=\epsilon^{\alpha\alpha}\hat{W}^{\beta}A^{\alpha} .\end{aligned} \tag{A26}$$

The action of the operator $\hat{W}^{\beta}$ on the fully symmetric function A^{α} should give the function of symmetry β. This function is the eigenfunction of $\hat{W}^{\alpha}$ according to Eq. (A26). Hence Eq. (A21), and accordingly Eq. (A25), are satisfied also in the case of a multidimensional irreducible representation.

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