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Momentum density for Compton scattering from random alloys*

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We derive an explicit expression for the average momentum density $\langle \rho(\vec{p}) \rangle$ measured by a Compton-scattering experiment on a disordered binary alloy. Our treatment is based on the use of muffin-tin atomic potentials within the framework of the average t-matrix approximation. In the case of a perfect crystal the momentum density is also derived directly from the usual Korringa-Kohn-Rostoker wave functions, and the formula so obtained is shown to be identical to the crystalline limit of $\langle \rho(\vec{p}) \rangle$.

INTRODUCTION

In view of recent advances in the theoretical understanding of disordered alloys, realistic calculations of quasiparticle energy eigenvalues and densities of states in transition- and noble-metal alloys are now practical. In a series of articles,[1–4] Bansil and collaborators have considered the detailed application of the average t-matrix approximation (ATA) to an alloy Hamiltonian based on muffin-tin atomic potentials. This scheme has the advantage that the numerical techniques familiar from the Korringa, Kohn, and Rostoker (KKR) method[5,6] of band theory in ordered crystals can be easily extended to the alloy problem.[7] Extensive calculations on $\alpha-\mathrm{Cu}_x\mathrm{Zn}_{1-x}$,[1] $\mathrm{Cu}_x\mathrm{Ni}_{1-x}$,[3,4] and to a lesser extent on nonstoichiometric $\mathrm{Cu}_x\mathrm{H}_{1-x}$ systems[8] show that a wide variety of electronic properties can be understood consistently in the framework of such an alloy theory. Therefore, a study of the consequences of the muffin-tin ATA formalism for more detailed properties of disordered alloys is warranted. The present paper is an attempt to develop the formalism necessary for calculating momentum densities relevant to Compton-scattering measurements on disordered alloys. Application of this theory to the $\mathrm{Ag}_x\mathrm{Pd}_{1-x}$ system and also its generalization to include the positron wave function will be discussed in subsequent publications.

Momentum-density measurements by positron annihilation[9] and Compton-scattering[10] techniques constitute an important tool for studying the electronic states of solids. In contrast with de Haas–van Alphen effect related methods, such measurements do not require long electronic mean free paths and, consequently, they have the unique advantage that they can be easily extended to disordered solids. In particular, breaks in the momentum distributions have been used to determine the Fermi-surface geometry in nondilute alloys and high-temperature structural phase transitions.[9,10]

We note that the positron-annihilation and Compton-scattering techniques have important differences in both the underlying physical mechanisms and the state-of-the-art developments. Because positron-annihilation measurements are sensitive to the momentum distribution of the conduction electrons, and high resolutions are currently available, this method is particularly attractive as a Fermi-surface caliper. Nevertheless, its utility in testing electronic wave functions is complicated due to the folding of the positron wave function into the observed profiles and also due to positron-electron many-body correlation effects. By contrast, the interpretation of Compton-scattering experiments is not complicated by the positron wave function. However, high resolutions (which are still much lower than those presently available in positron annihilation) are possible only by the use of x-ray sources, limiting the applicability of Compton scattering to low-Z materials.

Conventional methods of energy-band theory have been used to obtain the momentum-density distributions in a number of ordered metals and semiconductors,[11] and the results are in general agreement with experiment. Central to these theoretical computations is the calculation of (Bloch) wave functions in the crystal. In a disordered alloy, however, due to the absence of translational invariance, the electronic wave functions are very difficult to calculate in practice, except in a few cases (such as dilute alloys) where perturbation theory may be applicable.[12] Fortunately, physically observable properties cannot depend on the detailed arrangement of the atoms in the alloy and may, therefore, be obtained by an average of the configuration-dependent properties. In Sec. II, we show that the average momentum density $\langle \rho(\vec{p}) \rangle$ for momentum transfer $\vec{p}$ (the angular brackets $\langle\ \rangle$ denote the ensemble average over all atomic configurations) is related to the imaginary part of the momentum-dependent average Green's function $\langle G(\vec{p},E)\rangle$. Even though the evaluation of $\langle G(\vec{p},E)\rangle$ is similar to that of the average spectral density $\langle \tilde{A}(\vec{k},E)\rangle$ in the alloy,[13] one significant difference in the formal expressions for $\langle G(\vec{p},E)\rangle$ and $\langle \tilde{A}(\vec{k},E)\rangle$ is noteworthy. It will be seen that

$\langle \tilde{A}(\vec{k}, E)\rangle$ in the perfect crystal and also in the disordered alloy can be expressed in terms of just two units of input: (a) the KKR structure functions $B(\vec{k}, E)$ and (b) the energy-shell matrix elements $t_l^A(\kappa,\kappa)$ and $t_l^B(\kappa,\kappa)$ (where $\kappa\equiv\sqrt{E}$ and l is an angular momentum index) of the t-matrices of the constituent A and B atom potentials.[2,7] By contrast, the computation of $\langle G(\vec{p}, E)\rangle$, even for a perfect crystal, requires the knowledge of off-the-energy-shell matrix elements $t_l^{A(B)}(k,\kappa)$. Nevertheless, as discussed in Sec. II, the numerical evaluation of $t_l^{A(B)}(k,\kappa)$ is fairly straightforward, and can be carried out by using formulas developed by Beeby.[14]

The momentum density in a perfect crystal is discussed in detail. Section III derives the relevant formula starting from the conventional KKR wave functions. We explicitly show that this expression is identical to the crystalline limit of the momentum density $\langle\rho(\vec{p})\rangle$ in the alloy. Several points of pedagogical interest are clarified in Secs. II and III. The detailed proofs of some of the results used in the text are presented in the Appendices.

II. FORMALISM

A. Evaluation of $\langle\rho(\vec{p})\rangle$

Assuming independent particles, the momentum density $\rho(\vec{p})$ for Compton scattering from a solid is given by

$$\rho(\vec{p})=\sum_\alpha n_\alpha\,|\psi_\alpha(\vec{p})|^2 \tag{2.1a}$$

$$=\sum_\alpha n_\alpha \int\int d\vec{r}\,d\vec{r}\,'\,e^{-i\vec{p}\cdot(\vec{r}-\vec{r}\,')}\,\psi_\alpha(\vec{r})\psi_\alpha^*(\vec{r}\,') . \tag{2.1b}$$

Here $\psi_\alpha(\vec{r})$ denotes the electronic wave function, $\psi_\alpha(\vec{p})$ the corresponding momentum transform, and n_α the occupation number for the energy eigenstate α. In writing Eqs. (2.1), multiple scattering corrections to the Compton profile have been neglected.

For the present purposes we wish to cast Eqs. (2.1) in terms of the Green's function

$$G(E^+)=(E+i0^+-H)^{-1} . \tag{2.2}$$

Equation (2.2) is an operator equation involving the Hamiltonian H of the system. The momentum transform $G(\vec{p},\vec{p};E^+)$ of the Green's function may be written in terms of the quantities $\psi_\alpha(\vec{p})$ and the eigenvalues E_α of H. Thus

$$G(\vec{p},\vec{p};E^+)\equiv G(\vec{p},E^+)=\sum_\alpha \frac{\psi_\alpha(\vec{p})\psi_\alpha^*(\vec{p})}{E-E_\alpha+i0^+} . \tag{2.3}$$

Using the identity

$$\mathrm{Im}(E-E_\alpha+i0^+)^{-1}=-\pi\delta(E-E_\alpha) , \tag{2.4}$$

and keeping the definition (2.1) of $\rho(\vec{p})$ in mind, it is immediately seen that

$$\rho(\vec{p})=-\frac{1}{\pi}\int_{-\infty}^{E_F} dE\ \mathrm{Im}G(\vec{p},E^+) , \tag{2.5}$$

where E_F denotes the Fermi energy.

Equations (2.1) and (2.5) are exact and, in principle, they are applicable to an ordered as well as a disordered solid. In a perfect crystal $\psi_\alpha(\vec{r})$ are the Bloch wave functions and Eqs. (2.1) are easy to apply. By contrast, in a disordered alloy, the computation of the energy eigenfunctions, and hence of $\rho(\vec{p})$, is a formidable task for a given (arbitrary) configuration of the atoms. As already noted, the quantity of physical interest is the configurationally averaged momentum density $\langle\rho(\vec{p})\rangle$. Using Eq. (2.5), this is seen to be

$$\langle\rho(\vec{p})\rangle=-\frac{1}{\pi}\int_{-\infty}^{E_F} dE\,\mathrm{Im}\langle G(\vec{p},E^+)\rangle . \tag{2.6}$$

We specialize now to a disordered alloy described by the Hamiltonian[15]

$$H=p^2+\sum_n v^{A(B)}(\vec{r}-\vec{R}_n) . \tag{2.7}$$

The potential at the site $\vec{R}_n$ is v^A (or v^B) depending on whether this site is occupied by an A (or B) atom. These potentials are assumed to be of muffin-tin type, i.e.,

$$v^{A(B)}(\vec{r})=\begin{cases} v^{A(B)}(|\vec{r}|) , & r\leq R_m , \\ 0 , & r>R_m . \end{cases} \tag{2.8}$$

The muffin-tin radius R_m is chosen such that none of the atomic spheres overlap. Experience with perfect crystals, and more recently with disordered alloys, shows that the form (2.8) describes the single-site potential in a close-packed solid quite well.[7] Finally, we assume the disorder to be random, i.e., the probability that an A (or B) atom occupies any site is proportional to its concentration, x (or $y\equiv 1-x$).

The techniques of multiple scattering theory will now be applied to obtain a closed expression for $\langle G(E^+)\rangle$.[1,7] The calculation is carried out most conveniently in terms of the scattering operator $T(E)$ defined by

$$G(E)=G_0(E)+G_0(E)T(E)G_0(E) , \tag{2.9}$$

where $G_0(E)\equiv(E-p^2)^{-1}$ is the free-electron propagator. The operator T can be expanded in a multiple scattering series in terms of the atomic scattering matrices, $t_n\equiv v_n(1-G_0v_n)^{-1}$, i.e.,

$$T=\sum_n t_n+\sum_n\sum_{m\neq n} t_nG_0t_m + \sum_n\sum_{m\neq n}\sum_{l\neq m} t_nG_0t_mG_0t_l+\cdots . \tag{2.10}$$

Averaging both sides of Eq. (2.10), $\langle T\rangle$ is given by the *exact* equation

$$\langle T\rangle = \sum_n \langle t_n\rangle + \sum_n \sum_{m\neq n} \langle t_n G_0 t_m\rangle + \sum_n \sum_{m\neq n} \sum_{l\neq m} \times\langle t_n G_0 t_m G_0 t_l\rangle + \cdots \ . \qquad (2.11)$$

The average t-matrix approximation (ATA) involves the replacement of the *average of the products* occurring in the successive terms of Eq. (2.11) by the corresponding *products of averages*. This approximation amounts to neglecting the corrections to the effective scattering from a given site arising from the fluctuations in this site's environment. Thus, within the ATA[16]

$$\langle T\rangle = \sum_n \langle t_n\rangle + \sum_n \sum_{m\neq n} \langle t_n\rangle G_0 \langle t_m\rangle + \sum_n \sum_{m\neq n} \sum_{l\neq m} \langle t_n\rangle G_0 \langle t_m\rangle G_0 \langle t_l\rangle + \cdots \ , \qquad (2.12)$$

where

$$\langle t_n\rangle = x\, t_n^A + (1-x)\, t_n^B \ . \qquad (2.13)$$

The approximations leading to Eq. (2.12) essentially replace the disordered alloy by an *ordered crystal* of effective scatterers $\langle t\rangle$. The translational invariance having thus been restored, the series (2.12) can be summed up exactly. To this end, we introduce the angular momentum decompositions of the t matrices and the Green's function. For the t matrices

$$t^{A(B)}(\vec{r},\vec{r}\,') = \sum_L Y_L(\hat{r})\, t_l^{A(B)}(r,r')\, Y_L(\hat{r}') \ . \qquad (2.14)$$

Here, $L\equiv(l,m)$ denotes the orbital and magnetic quantum numbers, and Y_L the corresponding real spherical harmonic. The momentum transform $t_l^{A(B)}(p,q)$ is defined by[17]

$$t_l^{A(B)}(p,q) = \int_0^\infty dr\, r^2 \int_0^\infty dr'\, r'^2 j_l(pr) \times t_l^{A(B)}(r,r')\, j_l(qr') \ . \qquad (2.15)$$

The energy-shell matrix elements $t_l^{A(B)}(\kappa,\kappa)$ (where $\kappa\equiv\sqrt{E}$) are related to the usual phase shifts $\delta_l^{A(B)}(\kappa)$ by the equation

$$t_l^{A(B)}(\kappa,\kappa) = -\kappa^{-1}\sin\delta_l^{A(B)}(\kappa)\, e^{i\delta_l^{A(B)}(\kappa)} \ . \qquad (2.16)$$

The off-the-energy-shell matrix elements $t_l^{A(B)}(p,\kappa)$ $(p\neq\kappa)$ are only slightly more complicated. The relevant formulas are discussed in Appendix A, where it is shown that, for $E>0$,

$$t_l^{A(B)}(p,\kappa) = t_l^{A(B)}(\kappa,p) = s_l^{A(B)}(p,E)\cot\delta_l^{A(B)}(\kappa)\, t_l^{A(B)}(\kappa,\kappa) \qquad (2.17a)$$

and

$$\operatorname{Im} t_l^{A(B)}(p,p) = -\kappa^{-1}\left[s_l^{A(B)}(p,E)\cos\delta_l^{A(B)}(\kappa)\right]^2 \ , \qquad (2.17b)$$

where

$$s_l^{A(B)}(p,E) = -\kappa\int_0^{R_m} dr\, r^2 j_l(pr) \times v^{A(B)}(r)\, R_l^{A(B)}(r;E) \qquad (2.18)$$

is given in terms of an integral involving the regular solution $R_l^{A(B)}(r;E)$ of the radial Schrödinger equation in the atomic potential $v^{A(B)}(r)$.

The free-electron lattice Green's function may similarly be decomposed as

$$\sum_{n\neq 0} e^{i\vec{p}\cdot\vec{R}_n} G_0(\vec{r}-\vec{r}\,'-\vec{R}_n) = \sum_{LL'} i^{l-l'}\, Y_L(\hat{r})\, j_l(\kappa r) \times B_{LL'}(\vec{k},E)\, j_{l'}(\kappa r')\, Y_{L'}(\hat{r}') \quad \text{for } r,r'<R_m \ . \qquad (2.19)$$

Here, $B(\vec{k},E)$ (suppressing the angular momentum indices) is the matrix of conventional KKR structure functions.[13] [Note that as long as $r,r'<R_m$, $B(\vec{k},E)$ is independent of r and r' and, furthermore, that $B(\vec{k},E)$ is periodic in $\vec{k}$.]

Using Eqs. (2.14)–(2.19), the momentum matrix element of the multiple scattering series on the right-hand side of Eq. (2.12) can be evaluated in a closed form. The result, after several lengthy but straightforward manipulations, is

$$\langle T(\vec{p},\vec{p};E)\rangle \equiv \langle T(\vec{p},E)\rangle = (4\pi)^2 N \sum_{LL'} Y_L(\hat{p})\Big(\langle t_l(p,p)\rangle\delta_{LL'} + \langle t_l(p,\kappa)\rangle\{B(\vec{k},E)[1-\langle t(\kappa,\kappa)\rangle B(\vec{k},E)]^{-1}\}_{LL'} \times\langle t_{l'}(\kappa,p)\rangle\Big)\, Y_{L'}(\hat{p}) \ , \qquad (2.20)$$

where N is the total number of lattice sites. In writing (2.20), we have introduced the diagonal matrix $\langle t(\kappa,\kappa)\rangle_{LL'}\equiv\delta_{LL'}\langle t_l(\kappa,\kappa)\rangle$.

Equation (2.20) makes clear the nature of an alloy's electronic spectrum. Since the poles of $\langle T(\vec{p},E)\rangle$ determine the quasiparticle energy levels, the secular equation is equivalent to the requirement that the determinant of the inverse matrix in (2.20) vanish, i.e.,

$$\|\langle t\rangle^{-1} - B(\vec{k},E)\| = 0 \ . \qquad (2.21)$$

Equation (2.21) reduces to the usual KKR equation[5,6] in a perfect crystal, and is, therefore, called the alloy KKR equation.[1] In a perfect crystal it yields a sequence of real solutions $E_i(\vec{k})$ for a given $\vec{k}$. By contrast, for the disordered alloy we obtain complex roots, $E_i(\vec{k}) \equiv E_i^{(1)}(\vec{k}) + iE_i^{(2)}(\vec{k})$. The imaginary part, $E_i^{(2)}(\vec{k})$, determines the half-width of the appropriate peak in the spectral density function and physically represents the damping of perfect Bloch states due to disorder in an alloy.[2-4]

The expression for $\langle \rho(\vec{p}) \rangle$ may now be obtained by the use of Eqs. (2.20), (2.9), and (2.6). The result after a few obvious rearrangements is

$$\langle \rho(\vec{p}) \rangle = -\frac{1}{\pi} \mathrm{Im} \int_{-\infty}^{E_F} dE \Bigg\{ \frac{1}{E + i0^+ - p^2} + (4\pi)^2 N \frac{1}{(E + i0^+ - p^2)^2} \sum_{LL'} Y_L(\vec{p}) \Bigg[\left(\langle t_l(p,p) \rangle - \frac{\langle t_l(p,\kappa) \rangle \langle t_l(\kappa,p) \rangle}{\langle t_l(\kappa,\kappa) \rangle} \right) \delta_{LL'}$$

$$+ \frac{\langle t_l(p,\kappa) \rangle}{\langle t_l(\kappa,\kappa) \rangle} [\langle t(\kappa,\kappa) \rangle^{-1} - B(\vec{k},E)]^{-1}_{LL'} \frac{\langle t_{l'}(\kappa,p) \rangle}{\langle t_{l'}(\kappa,\kappa) \rangle} \Bigg] Y_{L'}(\vec{p}) \Bigg\} . \qquad (2.22)$$

The Fermi energy E_F is to be obtained by calculating the integrated density of states following the method used by Bansil *et al.*[3] for CuNi alloys. In some cases (such as noble metal based alloys of polyvalent elements) approximate evaluations of E_F may be possible by simpler prescriptions.[1]

It is noteworthy that the free-electron singularities present in both the first and second terms in the square brackets in Eq. (2.22) cancel each other. (The details of this cancellation are discussed in Appendix B.) The contributions to $\langle \rho(\vec{p}) \rangle$, therefore, arise only from the complex energy solutions of the alloy KKR equation [cf. Eq. (2.21)]. In particular, the integrand of Eq. (2.22) varies smoothly at $E = p^2$.

We emphasize that the effort involved in computing $\langle \rho(\vec{p}) \rangle$ is comparable to a calculation of the spectral density function $\langle \tilde{A}(\vec{k},E) \rangle$ in the alloy. It has already been noted that the evaluation of $\langle \rho(\vec{p}) \rangle$ requires off-the-energy-shell matrix elements $t_l^{A(B)}(p,\kappa)$ [cf. Eq. (2.22)] with $p \neq \kappa$, even for a perfect crystal, whereas $\langle \tilde{A}(\vec{k},E) \rangle$ can be obtained in terms of only the energy-shell matrix elements $t_l^{A(B)}(\kappa,\kappa)$. This difference is basic to the two computations and may be understood most easily by specializing to the case of a perfect crystal. It is well known that, in this case, the momentum density corresponding to a Bloch state of wave vector $\vec{k}$ consists of δ-function peaks at momenta $\hbar(\vec{k}+\vec{K}_m)$, where $\vec{K}_m$ denotes an arbitrary vector of the reciprocal lattice. [The weight of the δ function at $\vec{p} = \hbar(\vec{k}+\vec{K}_m)$ is proportional to the square of the corresponding wave-function component.] By contrast, as discussed in Appendix C, the density of states[18] (per atom)

$$D(E) = \sum_{\vec{k}} A(\vec{k},E) , \qquad (2.23a)$$

or

$$D(E) \equiv {\sum_{\vec{k}}}' \tilde{A}(\vec{k},E) = N^{-1} {\sum_{\vec{k},i}}' \delta(E - E_i(\vec{k})) . \qquad (2.23b)$$

Note that the summation in (2.23a) extends to the entire reciprocal-lattice space. The (periodic) function $\tilde{A}(\vec{k},E)$ is thus obtained by adding up the contributions $A(\vec{k},E)$ from all the points $\vec{k}+\vec{K}_n$. [The primes in Eq. (2.23b) indicate that the summation is to be carried out only over the first Brillouin zone.] As is clear from the second equality in Eq. (2.23b), $\tilde{A}(\vec{k},E)$ does indeed include a unit contribution from each of the energy eigenvalues. Equations (2.23) show clearly how the details of the wave functions drop out in the computation of the density of states.

B. Crystalline limit

The perfect $A(B)$ crystal limit of $\langle \rho(\vec{p}) \rangle$ corresponds to $\langle t \rangle \to t^{A(B)}$, and is considered now as a check on formula (2.22). [In the following discussion, the superscripts $A(B)$ have been dropped for simplicity of notation.] In this limit, it is easy to show [by using Eqs. (2.16) and (2.17)] that the imaginary part of the term proportional to $\delta_{LL'}$ in curly brackets in (2.22) vanishes. By defining new coefficients

$$S_L(\vec{p},E) \equiv s_l(p,E) \cot\delta_l(\kappa) \, Y_L(\vec{p}) , \qquad (2.24)$$

Equation (2.22) then yields

$$\rho(\vec{p}) = -\frac{1}{\pi} \mathrm{Im} \int_{-\infty}^{E_F} dE \left[\frac{1}{E + i0^+ - p^2} + (4\pi)^2 N \frac{1}{(E + i0^+ - p^2)^2} \left(\sum_{LL'} S_L(\vec{p},E) M_{L'L}(\vec{k},E) S_{L'}(\vec{p},E) \right) \Big/ \| t^{-1} - B \| \right] , \qquad (2.25)$$

where the inverse of matrix $(t^{-1} - B)$ has been expressed in terms of its cofactors $M_{LL'}$.[19] As already noted, the integrand in (2.25) varies smoothly through $E = p^2$, and nonzero contributions arise only from the (real) energy eigenvalues $E_i(\vec{k})$ of the KKR determinant. Therefore

$$\rho(\vec{p}) = (4\pi)^2 N \sum_{E_i \leq E_F} \frac{1}{(E_i - p^2)^2} \left(\sum_{LL'} S_L(\vec{p},E_i) M_{L'L}(\vec{k},E_i) S_{L'}(\vec{p},E_i) \right) \Big/ \frac{d}{dE} \| t^{-1} - B \|_{E=E_i} . \qquad (2.26)$$

In deriving (2.26), we have used the identity

$$\operatorname{Im}\frac{1}{\|t^{-1}-B\|}=-\pi\sum_i\delta(\|t^{-1}-B\|_{E_i})$$
$$=-\pi\sum_i\delta(E-E_i)\Big/\frac{d}{dE}\|t^{-1}-B\|_{E=E_i}\,. \tag{2.27}$$

It is noteworthy that, in the perfect-crystal limit, by replacing the integral in Eq. (2.25) by a summation over occupied levels, we have *explicitly* removed free electron singularities from $\rho(\vec{p})$ [cf. Eq. (2.26)]. By contrast, in the alloy [cf. Eq. (2.22)], contributions to $\langle\rho(\vec{p})\rangle$ come from broad spectral peaks rather than real poles, and such a simplification is not possible.

III. KKR EXPRESSION FOR MOMENTUM DENSITY IN PERFECT CRYSTAL

We will now employ the KKR wave functions to obtain an explicit expression for the momentum density in a perfect crystal of muffin-tin potentials.[20] Even though this expression is given naturally in terms of the eigenfunction coefficients of the KKR matrix, we will show that it can be manipulated into the form (2.26) (which does not involve the wave-function coefficients explicitly).

The KKR wave function $\psi_{\vec{k}}^{(i)}(\vec{r})$, corresponding to the reduced wave vector $\vec{k}$ and energy $E_i(\vec{k})$ is given by the integral equation[21]

$$\psi_{\vec{k}}^{(i)}(\vec{r})=\int_\tau d\vec{r}'\,G_{\vec{k}}(\vec{r},\vec{r}';E_i)\,V(\vec{r}')\psi_{\vec{k}}^{(i)}(\vec{r}')\;, \tag{3.1}$$

which involves the crystal potential $V(\vec{r})$ and the lattice Green's function

$$G_{\vec{k}}(\vec{r},\vec{r}';E)=\tau^{-1}\sum_n\frac{e^{i(\vec{k}+\vec{K}_n)\cdot(\vec{r}-\vec{r}')}}{E-(\vec{k}+\vec{K}_n)^2}\;. \tag{3.2}$$

In Eqs. (3.1) and (3.2), τ denotes the volume of the unit cell. Since the crystal potential vanishes in the interstitial region [cf. Eq. (2.8)], nonzero contributions to the integral in (3.1) arise only when $\vec{r}'$ lies within the muffin-tin sphere at the origin. [In particular, $V(\vec{r}')\equiv\sum_n v(\vec{r}'-\vec{R}_n)$ may be replaced by $v(r')$ in (3.1).] It is clear, therefore, that if the wave function $\psi_{\vec{k}}^{(i)}(\vec{r})$ is known *within* this muffin tin sphere, its value over the entire crystal can be calculated by Eq. (3.1). In the KKR method $\psi_{\vec{k}}^{(i)}(\vec{r})$ is written as a superposition of the regular solutions $R_l(r;E_i)$ of the radial Schrödinger's equation. Thus

$$\psi_{\vec{k}}^{(i)}(\vec{r})=\sum_L i^l C_L^{(i)}(\vec{k})R_l(r;E_i)\,Y_L(\vec{r})\quad\text{for } r<R_m\;. \tag{3.3}$$

Equations (3.1) to (3.3) readily yield the momentum transform of the wave function

$$\psi_{\vec{k}}^{(i)}(\vec{p})=\frac{-4\pi N\kappa^{-1}}{E_i-p^2}\sum_L C_L^{(i)}(\vec{k})s_l(p,E_i)\,Y_L(\vec{p}) \tag{3.4}$$

in terms of the s_l functions defined in Eq. (2.18).

The wave function coefficients $C_L^{(i)}(\vec{k})$ in Eqs. (3.3) and (3.4) are not identical to the (more easily accessible) solutions $\overline{C}_L^{(i)}(\vec{k})$ of the (KKR) equations,

$$\sum_{L'}\left[t_l^{-1}(\sqrt{E_i},\sqrt{E_i})\,\delta_{LL'}-B_{LL'}(\vec{k},E_i)\right]\overline{C}_{L'}^{(i)}(\vec{k})=0\;. \tag{3.5}$$

The coefficients $C_L^{(i)}(\vec{k})$ can, however, be expressed in terms of the coefficients $\overline{C}_L^{(i)}(\vec{k})$ by the relation[21]

$$C_L^{(i)}(\vec{k})=\sqrt{E_i}\,R_m^2\cot\delta_l(\sqrt{E_i})\,\overline{C}_L^{(i)}(\vec{k})\;. \tag{3.6}$$

In order to properly normalize the wave function (3.3), we use the identity[22]

$$\int_\tau d\vec{r}\,|\psi_{\vec{k}}^{(i)}(\vec{r})|^2=\left.\frac{\partial\Lambda(E)}{\partial E}\right|_{E=E_i}\;, \tag{3.7}$$

where

$$\Lambda(E)\equiv\int_\tau d\vec{r}\,\psi_{\vec{k}}^*(\vec{r})V(\vec{r})\psi_{\vec{k}}(\vec{r})$$
$$-\int_\tau\int_{\tau'}d\vec{r}\,d\vec{r}'\,\psi_{\vec{k}}^*(\vec{r})V(\vec{r})\,G_{\vec{k}}(\vec{r},\vec{r}';E)\,V(\vec{r}')\psi_{\vec{k}}(\vec{r}') \tag{3.8}$$

is the variational form used by Kohn and Rostoker.[6] {In fact, the integral equation (3.1) for $\psi_{\vec{k}}(\vec{r})$ is equivalent to the requirement $[\delta\Lambda(E)/\delta\psi_{\vec{k}}]_{E=E_i}=0$.} It can now be shown that[22]

$$\left.\frac{\partial\Lambda(E)}{\partial E}\right|_{E=E_i}=R_m^4\sum_{LL'}\overline{C}_L^{(i)}(\vec{k})\left(\frac{d}{dE}(t_L^{-1}\delta_{LL'}-B_{LL'})\right)\overline{C}_{L'}^{(i)}(\vec{k})\;. \tag{3.9}$$

Using Eqs. (3.7) and (3.9), the normalization integral,

$$\int d\vec{r}\,|\psi_{\vec{k}}^{(i)}(\vec{r})|^2=N\int_\tau d\vec{r}\,|\psi_{\vec{k}}^{(i)}(\vec{r})|^2=NR_m^4\sum_{LL'}\overline{C}_L^{(i)}(\vec{k})\left(\frac{d}{dE}(t_L^{-1}\delta_{LL'}-B_{LL'})\right)\overline{C}_{L'}^{(i)}(\vec{k})\;. \tag{3.10}$$

The first equality in Eq. (3.10) results from the periodicity of the wave function $\psi_{\vec{k}}^{(i)}(\vec{r})$.

By using Eqs. (3.10) and (3.6) in Eq. (3.4), and substituting the resulting expression for $\psi_{\vec{k}}^{(i)}(\vec{p})$ into formula (2.1a), we obtain the momentum density,

$$\rho(\vec{p})=(4\pi)^2N\sum_{E_i\leq E_F}\frac{1}{(E_i-p^2)^2}\left(\sum_{LL'}\overline{C}_L^{(i)}(\vec{k})S_L(\vec{p},E_i)\overline{C}_{L'}^{(i)}(\vec{k})S_{L'}(\vec{p},E_i)\right)\Big/\sum_{LL'}\overline{C}_L^{(i)}(\vec{k})\left(\frac{d}{dE}(t_L^{-1}\delta_{LL'}-B_{LL'})\right)\overline{C}_{L'}^{(i)}(\vec{k})\;, \tag{3.11}$$

where the quantities $S_L(\vec{p},E)$ have been defined earlier in Eq. (2.25).[13]

The equivalence of (3.11) and (2.26) may be shown by using the matrix identity

$$\overline{C}_L^{(i)}(\vec{k})\,\overline{C}_{L'}^{(i)}(\vec{k}) = b^2 M_{LL'}(\vec{k},E_i)/M_{jj}(\vec{k},E_i) \ , \tag{3.12}$$

which relates the quantities $\overline{C}_L^{(i)}(\vec{k})$ to the cofactors of the KKR matrix. [j, here, denotes the index of the coefficient which is set equal to (an arbitrary number) b in solving the homogeneous set of KKR equations (3.5).] A detailed derivation of Eq. (3.12) is presented in Appendix D.

The substitution of (3.12) into (3.11) (followed by the cancellation of the factor $M_{jj}(\vec{k},E_i)/b^2$ from both the denominator and the numerator) yields

$$\rho(\vec{p}) = (4\pi)^2 N \sum_{E_i \leq E_F} \frac{1}{(E_i - p^2)^2} \left(\sum_{LL'} S_L(\vec{p},E_i) M_{L'L}(\vec{k},E_i) S_{L'}(\vec{p},E_i) \right) \Big/ \sum_{LL'} \left(\frac{d}{dE}(t^{-1}\delta_{LL'} - B_{LL'}) \right) M_{LL'}(\vec{k},E_i) \ . \tag{3.13}$$

The denominator in Eq. (3.13) is recognized as the derivative of the KKR determinant [cf. Eq. (2.26)], because[23]

$$\frac{d}{dE} \| t^{-1} - B \| = \sum_{LL'} \frac{\partial \| t^{-1} - B \|}{\partial (t_L^{-1}\delta_{LL'} - B_{LL'})} \frac{d}{dE}(t_L^{-1}\delta_{LL'} - B_{LL'}) = \sum_{LL'} \left(\frac{d}{dE}(t_L^{-1}\delta_{LL'} - B_{LL'}) \right) M_{LL'} \ . \tag{3.14}$$

The equivalence of the perfect crystal limit of $\langle \rho(\vec{p}) \rangle$ [cf. Eq. (2.26)] and the KKR formula (3.11) then follows.

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APPENDIX A: CALCULATION OF OFF-THE-ENERGY-SHELL MATRIX ELEMENTS OF t MATRIX

The cases $E>0$ and $E<0$ will be discussed separately.

1. $E>0$

The real (Re) and imaginary (Im) parts of the quantities $t_l(p,p)$, $t_l(p,\kappa)$, and $t_l(\kappa,\kappa)$ are related by the equations [see Eqs. (3.11)–(3.14) of Ref. 14]

$$\mathrm{Im}\,t_l(p,p) = s_l(p,E)\,\mathrm{Re}\,t_l(\kappa,p) \ , \tag{A1a}$$

$$\mathrm{Im}\,t_l(p,\kappa) = \mathrm{Im}\,t_l(\kappa,p) = s_l(p,E)\,\mathrm{Re}\,t_l(\kappa,\kappa) \ , \tag{A1b}$$

$$\mathrm{Re}\,t_l(p,\kappa) = \mathrm{Re}\,t_l(\kappa,p) = s_l(p,E) s_l^{-1}(\kappa,E)\,\mathrm{Re}\,t_l(\kappa,\kappa) \ , \tag{A1c}$$

where

$$s_l(p,E) = \int_0^\infty dr\, r^2 j_l(pr)\, s_l(r,E) \tag{A2}$$

is the Hankel transform of the function $s_l(r,E)$. As discussed in Ref. 14, $s_l(r,E)/v(r)$ satisfies the radial Schrödinger's equation, and therefore $s_l(r,E)/v(r) \propto R_l(r;E)$, the radial wave function. The proportionality constant can be determined by noting that[24]

$$s_l(\kappa,E) = \tan\delta_l(\kappa) \ . \tag{A3}$$

But[25]

$$\tan\delta_l(\kappa) = -\kappa \int_0^\infty dr\, r^2 j_l(\kappa r) v(r) R_l(r;E) \ . \tag{A4}$$

A comparison of Eqs. (A2) and (A4) shows that in order to satisfy (A3)

$$s_l(r,E) = -\kappa v(r) R_l(r;E) \ . \tag{A5}$$

It should be emphasized that the phase shifts are independent of the normalization of the wave functions and Eq. (A4) implicitly assumes that, for $r > R_m$,

$$R_l(r;E) = j_l(\kappa r) - \tan\delta_l(\kappa)\, n_l(\kappa r) \ . \tag{A6}$$

Equations (A1b) and (A1c), on using (A3) for $s_l(\kappa,E)$, yield

$$\begin{aligned} t_l(p,\kappa) &= t_l(\kappa,p) \\ &= s_l(p,E)[\cot\delta_l(\kappa) + i]\,\mathrm{Re}\,t_l(\kappa,\kappa) \\ &= s_l(p,E)\cot\delta_l(\kappa)\, t_l(\kappa,\kappa) \ , \end{aligned} \tag{A7}$$

where the second equality follows on using expression (2.16) for $t_l(\kappa,\kappa)$, and is identical to (2.17a). Similarly, Eqs. (A1a) and (A1c) give

$$\mathrm{Im}\,t_l(p,p) = s_l^2(p,E)\cot\delta_l(\kappa)\,\mathrm{Re}\,t_l(\kappa,\kappa) \ . \tag{A8}$$

Equation (A8) is once again trivially shown to be identical to (2.17b). [Note that $\mathrm{Re}\,t_l(p,p)$ is not required for evaluating expression (2.22) for $\langle \rho(\vec{p}) \rangle$.]

2. $E<0$

Since

$$t(\vec{r},\vec{r}) = v(r)\delta(\vec{r}-\vec{r}\,') + \int d\vec{r}_1\, v(r) G_0(\vec{r},\vec{r}_1) v(r_1) + \cdots \tag{A9}$$

and $G_0(\vec{r},\vec{r}\,')$ is real for $E<0$, $\mathrm{Im}\,t(\vec{r},\vec{r}\,')$ or, alternatively,[26]

$$\mathrm{Im}\, t_l(r, r') = 0 \ . \qquad \text{(A10)}$$

For negative energies, Ref. 14 employs the (real) function $i^l j_l(\kappa x)$ instead of $j_l(\kappa x)$ in Eq. (2.15), which defines the transforms $t_l(p, q)$. We will, however, use the same definition (2.15) for both $E > 0$ and $E < 0$. Equation (A10) immediately shows that

$$\mathrm{Im}\, t_l(p, p) = 0 \ , \quad p > 0 \ , \qquad \text{(A11a)}$$

and, furthermore, because $i^l j_l(\kappa x)$ (for imaginary κ) is real and Eq. (2.15) involves two factors of $j_l(\kappa x)$,

$$\mathrm{Im}\, t_l(\kappa, \kappa) = 0 \ . \qquad \text{(A11b)}$$

By contrast, $t_l(p, \kappa)$ involves one factor of $j_l(\kappa x)$ and will, therefore, be real (imaginary) for even (odd) l. The equations presented in Ref. 14 for $E < 0$ are then easily shown to be equivalent to

$$t_l(p, \kappa) = t_l(\kappa, p) = -\, s_l(p, E)/\kappa \ . \qquad \text{(A12a)}$$

In particular,

$$t_l(\kappa, \kappa) = -\, s_l(\kappa, E)/\kappa = -\,\kappa^{-1} \tan\delta_l(\kappa) \qquad \text{(A12b)}$$

as Eq. (A3) is still valid. Because $j_l(\kappa r)\, R_l(r; E)$ [in view of Eq. (A6)] is real, Eq. (A4) shows that $\tan\delta_l$ (and therefore δ_l) is purely imaginary.

APPENDIX B: CANCELLATION OF FREE-ELECTRON SINGULARITIES IN EQ. (2.22)

The integrand in Eq. (2.22) consists of two terms, each of which is singular at $E = p^2$. The part of the second term proportional to

$$(E - p^2)^{-2} \sum_{LL'} Y_L(\vec{\mathrm{p}})\, \mathrm{Im} \left(\langle t_l(p, p) \rangle - \frac{\langle t_l(p, \kappa)\rangle \langle t_l(\kappa, p)\rangle}{\langle t_l(\kappa, \kappa)\rangle} \right) Y_L(\vec{\mathrm{p}}) \qquad \text{(B1)}$$

is, in fact, of the indeterminate form (0/0) at $E = p^2$ (or $p = \kappa$). Nevertheless, by expanding $\langle t_l(p, p)\rangle$ and $\langle t_l(p, \kappa)\rangle$ in powers of $p - \kappa$ (around $p = \kappa$), it is straightforward to show that the quantity in large parentheses in (B1) is of order $(p - \kappa)^2$ and, therefore, that expression (B1) varies smoothly at $E = p^2$. {The required expansions are obtained most easily by expanding $s_l^{A(B)}(p)$ [or alternatively, $j_l(pr)$: cf. Eq. (2.18)], and using the result in Eqs. (2.17a) and (2.17b) for $t_l^{A(B)}(p, \kappa)$ and $\mathrm{Im}\, t_l^{A(B)}(p, p)$, respectively.}

It now remains to be shown that

$$\lim_{\eta \to 0} (4\pi)^2 N \eta^{-1} \sum_{LL'} Y_L(\vec{\mathrm{p}})\, Y_{L'}(\vec{\mathrm{p}}) \times [\langle t(\kappa, \kappa)\rangle^{-1} - B(\vec{\mathrm{p}}, E)]^{-1}_{LL'} = -1, \qquad \text{(B2)}$$

where $\eta \equiv E - p^2$. [In writing (B2) factors like $\langle t_l(p, \kappa)\rangle \langle t_l(\kappa, \kappa)\rangle^{-1}$ in (2.22) have been set equal to unity.] By considering the structure functions[13,27]

$$B_{LL'} = \frac{(4\pi)^2 N}{j_l(\kappa r) j_{l'}(\kappa r')} \sum_n \frac{j_l(|\vec{\mathrm{k}} + \vec{\mathrm{K}}_n| r)\, j_{l'}(|\vec{\mathrm{k}} + \vec{\mathrm{K}}_n| r')\, Y_L(\vec{\mathrm{k}} + \vec{\mathrm{K}}_n)\, Y_{L'}(\vec{\mathrm{k}} + \vec{\mathrm{K}}_n)}{E - (\vec{\mathrm{k}} + \vec{\mathrm{K}}_n)^2} + \left(i\kappa - \kappa \frac{n_l(\kappa r')}{j_l(\kappa r)} \right) \delta_{LL'} \ , \quad r < r' < R_m \ , \qquad \text{(B3)}$$

in the limit $E \to p^2$, it is immediately seen that

$$\lim_{\eta \to 0} (\langle t \rangle^{-1} - B) = \lim_{\eta \to 0} (X - A/\eta) \ , \qquad \text{(B4)}$$

where

$$A_{LL'} \equiv (4\pi)^2 N Y_L(\vec{\mathrm{p}})\, Y_{L'}(\vec{\mathrm{p}}) \ , \qquad \text{(B5)}$$

and the matrix X defined by (B4) varies smoothly at $E = p^2$. (The detailed form of X is not important for the present purposes.) Using Eqs. (B4) and (B5), the left-hand side of (B2) reduces to

$$\lim_{\eta \to 0} \sum_{LL'} A_{LL'} (\eta X - A)^{-1}_{L'L} = \lim_{\eta \to 0} \sum_{LL'} A_{LL'} \frac{C_{LL'}(\eta X - A)}{\| \eta X - A \|} \ , \qquad \text{(B6)}$$

where $C_{LL'}$ is the (L, L') cofactor of the matrix $(\eta X - A)$. We now invoke the relations[28]

$$\| \eta X - A \| = -\, \eta^{d-1} \sum_{LL'} A_{LL'}\, C_{LL'}(X) + O(\eta^d) \qquad \text{(B7a)}$$

and

$$\sum_{LL'} A_{LL'}\, C_{LL'}(\eta X - A) = \eta^{d-1} \sum_{LL'} A_{LL'}\, C_{LL'}(X) + O(\eta^d) \ , \qquad \text{(B7b)}$$

which are valid for a matrix of form (B5). In view of Eqs. (B7), expression (B6) is seen to be equal to -1. (d, here, denotes the dimension of the KKR matrix.)

APPENDIX C: DERIVATION OF EQ. (2.23)

The spectral decomposition of the density of states (per atom), $D(E)$, is given by

$$D(E) = \sum_{\vec{\mathrm{k}}} A(\vec{\mathrm{k}}, E) \qquad \text{(C1a)}$$

$$= \sum_{\vec{\mathrm{k}}}{}' \sum_n A(\vec{\mathrm{k}} + \vec{\mathrm{K}}_n, E) \qquad \text{(C1b)}$$

$$\equiv \sum_{\vec{k}}{}' \tilde{A}(\vec{k}, E) \; . \tag{C1c}$$

The spectral density $\tilde{A}(\vec{k}, E)$ defined by (C1c) is periodic in $\vec{k}$, and is a more pertinent object than (the usual spectral density) $A(\vec{k}, E)$ in crystalline problems. (Note that the summation of $\tilde{A}(\vec{k}, E)$ over only the first Brillouin zone [indicated by primes in Eqs. (C1b) and (C1c)] yields the total density of states.)

$\tilde{A}(\vec{k}, E)$ is related to the Fourier transform of the Green's function $G(E^{+})$ defined in Eq. (2.2):

$$\tilde{A}(\vec{k}, E) = -\frac{1}{\pi N} \operatorname{Im} \sum_{n} G(\vec{k} + \vec{K}_n, E^{+}) \tag{C2a}$$

$$= -\frac{1}{\pi N^2} \operatorname{Im} \sum_{m} \int d\vec{r}\, G(\vec{r}, \vec{r} + \vec{R}_m; E^{+})\, e^{i\vec{k}\cdot\vec{R}_m} \; , \tag{C2b}$$

where the second equality expresses $\tilde{A}(\vec{k}, E)$ in the direct lattice space.[29] (The crystal is assumed to have a unit volume.) The multiple scattering series expansion of G in (C2b) [obtained by using Eqs. (2.9) and (2.10)] then yields

$$\tilde{A}(\vec{k}, E) = -\frac{1}{\pi N^2} \operatorname{Im} \sum_{m} \int d\vec{r}\, e^{i\vec{k}\cdot\vec{R}_m} \langle \vec{r} | \Big(G_0 + \sum_{\alpha} G_0 t_\alpha G_0 + \sum_{\alpha} \sum_{\beta \neq \alpha} G_0 t_\alpha G_0 t_\beta G_0$$

$$+ \sum_{\alpha} \sum_{\beta \neq \alpha} \sum_{\gamma \neq \beta} G_0 t_\alpha G_0 t_\beta G_0 t_\gamma G_0 + \cdots \Big) \, | \vec{r} + \vec{R}_m \rangle \; . \tag{C3}$$

The procedure of simplifying the right-hand side of (C3) may be illustrated by considering in detail the second-order term

$$\sum_{m} \int d\vec{r} \int d\vec{r}_1 \cdots \int d\vec{r}_4\, e^{i\vec{k}\cdot\vec{R}_m} \sum_{\alpha} \sum_{\beta \neq \alpha} G_0(\vec{r}, \vec{r}_1)\, t(\vec{r}_1 - \vec{R}_\alpha, \vec{r}_2 - \vec{R}_\alpha)\, G_0(\vec{r}_2, \vec{r}_3)\, t(\vec{r}_3 - \vec{R}_\beta, \vec{r}_4 - R_\beta) G_0(\vec{r}_4, \vec{r} + \vec{R}_m) \; , \tag{C4a}$$

where the operator multiplications are explicitly displayed. Because the crystal is translationally invariant, contributions to (C3) and (C4a) are independent of the site index α. Therefore, we may set $\vec{R}_\alpha = \vec{0}$ and replace the sum over α by N. A regrouping of terms in (C4a) then gives[30]

$$N \sum_{\beta \neq 0} \int d\vec{r}_1 \cdots \int d\vec{r}_4\, t(\vec{r}_3, \vec{r}_4) G_0^2(\vec{r}_4, \vec{r}_1)\, t(\vec{r}_1, \vec{r}_2) G_0(\vec{r}_2, \vec{r}_3 + \vec{R}_\beta)\, e^{i\vec{k}\cdot\vec{R}_\beta}$$

$$+ N \sum_{\beta \neq 0} \sum_{m \neq \beta} \int d\vec{r}_1 \cdots \int d\vec{r}_4\, t(\vec{r}_1, \vec{r}_2) G_0(\vec{r}_2, \vec{r}_3 + \vec{R}_\beta)\, t(\vec{r}_3, \vec{r}_4) G_0^2(\vec{r}_4 + \vec{R}_\beta - \vec{R}_m, \vec{r}_1)\, e^{i\vec{k}\cdot\vec{R}_m} \; . \tag{C4b}$$

Using the matrix identities, $dG_0/dE = -G_0^2$, $dt/dE = -tG_0^2 t$, and the lattice free-electron Green's function [cf. Eq. (2.19)]

$$G_0'(\vec{r}, \vec{r}\,'; \vec{k}) \equiv \sum_{\beta \neq 0} G_0(\vec{r}, \vec{r}\,' + \vec{R}_\beta; \vec{k})\, e^{i\vec{k}\cdot\vec{R}_\beta} \; , \tag{C4c}$$

expression (C4b) reduces to

$$-N \int d\vec{r}_2 \int d\vec{r}_3\, \frac{dt(\vec{r}_3, \vec{r}_2)}{dE}\, G_0'(\vec{r}_2, \vec{r}_3; \vec{k}) - N \int d\vec{r}_1 \cdots \int d\vec{r}_4\, t(\vec{r}_1, \vec{r}_2) G_0'(\vec{r}_2, \vec{r}_3; \vec{k})\, t(\vec{r}_3, \vec{r}_4)\, \frac{dG_0'(\vec{r}_4, \vec{r}_1; \vec{k})}{dE} \; . \tag{C4d}$$

The formal manipulations used in transforming the second-order term in (C3) into the form (C4d) can be performed on any of the higher-order terms. For example, the third-order term reduces to

$$-N \int d\vec{r}_2 \cdots \int d\vec{r}_5\, t(\vec{r}_3, \vec{r}_4) G_0'(\vec{r}_4, \vec{r}_5; \vec{k}) \Big(\frac{d}{dE}\, t(\vec{r}_5, \vec{r}_2) \Big)\, G_0'(\vec{r}_2, \vec{r}_3; \vec{k})$$

$$-N \int d\vec{r}_1 \cdots \int d\vec{r}_6\, t(\vec{r}_1, \vec{r}_2) G_0'(\vec{r}_2, \vec{r}_3; \vec{k})\, t(\vec{r}_3, \vec{r}_4) G_0'(\vec{r}_4, \vec{r}_5; \vec{k})\, t(\vec{r}_5, \vec{r}_6)\, \frac{d}{dE}\, G_0'(\vec{r}_6, \vec{r}_1; \vec{k}) \; . \tag{C5}$$

Expressions similar to (C5) can also be obtained for the fourth- and higher-order terms in (C3). The first-order term, however, yields the expression

$$N \int d\vec{r}_1 \int d\vec{r}_2\, t(\vec{r}_1, \vec{r}_2) G_0^2(\vec{r}_2, \vec{r}_1) - N \int d\vec{r}_1 \int d\vec{r}_2\, t(\vec{r}_1, \vec{r}_2)\, \frac{d}{dE}\, G_0'(\vec{r}_2, \vec{r}_1; \vec{k}) \; , \tag{C6}$$

in which the first term has a slightly different form from (C4) or (C5). This term may, nevertheless, be simplified by using the identity[7]

$$\operatorname{Im}\int d\vec{r}_1\int d\vec{r}_2\, t(\vec{r}_1,\vec{r}_2)\,G_0^2(\vec{r}_2,\vec{r}_1) = -\operatorname{Im}\frac{d}{dE}\{\operatorname{Tr}\ln[t(\kappa,\kappa)]\}\ , \tag{C7}$$

where $[t(\kappa,\kappa)]$ denotes the matrix of energy-shell elements of the t matrix and the trace operation (Tr) is to be carried out in the angular momentum space.

Substituting (C4d), (C5), and (C6) into (C3) and noticing that the second term of (C4d) can be combined with the first term of (C5) to yield a complete derivative (d/dE) (tG_0) (this simplification, in fact, occurs whenever any two successive terms are added), we obtain

$$\begin{aligned}\tilde{A}(\vec{k},E) = -(\pi N)^{-1}\operatorname{Im}\bigg[\sum_n \frac{1}{E-(\vec{k}+\vec{K}_n)^2+i0^+} - \frac{d}{dE}\{\operatorname{Tr}\ln[t(\kappa,\kappa)]\} - \int d\vec{r}\int d\vec{r}\,'\int d\vec{r}\,''\Big(\delta(\vec{r}-\vec{r}\,'')\\ + \int d\vec{r}_1\, t(\vec{r},\vec{r}_1)G_0'(\vec{r}_1,\vec{r}\,'';\vec{k}) + \int d\vec{r}_1\cdots\int d\vec{r}_3\, t(\vec{r},\vec{r}_1)G_0'(\vec{r}_1,\vec{r}_2;\vec{k})\, t(\vec{r}_2,\vec{r}_3)G_0'(\vec{r}_3,\vec{r}\,'';\vec{k}) + \cdots\Big)\\ \times\frac{d}{dE}[t(\vec{r}\,'',\vec{r}\,')G_0'(\vec{r}\,',\vec{r};\vec{k})]\bigg]\ .\end{aligned} \tag{C8}$$

The $\vec{r}$-space integrals in (C8) can be carried out explicitly by using angular momentum expansions (2.14) and (2.19) for $t(\vec{r},\vec{r}\,')$ and $G_0'(\vec{r},\vec{r}\,';\vec{k})$, respectively. The result after some straightforward manipulations is

$$\begin{aligned}\tilde{A}(\vec{k},E) = -(\pi N)^{-1}\operatorname{Im}\Big(\sum_n \frac{1}{E+i0^+-(\vec{k}+\vec{K}_n)^2} - \frac{d}{dE}\{\operatorname{Tr}\ln[t(\kappa,\kappa)]\} - \operatorname{Tr}\{[1-t(\kappa,\kappa)B(\vec{k},E)]^{-1}\\ \times\frac{d}{dE}[t(\kappa,\kappa)B(\vec{k},E)]\}\Big)\end{aligned} \tag{C9a}$$

$$= -(\pi N)^{-1}\operatorname{Im}\Big(\sum_n \frac{1}{E+i0^+-(\vec{k}+\vec{K}_n)^2} + \frac{d}{dE}\ln\|t^{-1}(\kappa,\kappa)-B(\vec{k},E)\|\Big)\ . \tag{C9b}$$

In obtaining (C9b), we have used the general matrix identity $\operatorname{Tr}\ln[M] = \ln\|M\|$. Using Eqs. (2.27) for obtaining the imaginary part of the determinant in (C9b), we finally obtain

$$\tilde{A}(\vec{k},E) = N^{-1}\sum_i \delta(E-E_i(\vec{k}))\ , \tag{C10}$$

where in accordance with the discussion presented in Appendix B, the free electron roots have been explicitly removed. The substitution of (C10) into (C1c) immediately proves the validity of Eq. (2.23).

APPENDIX D: DERIVATION OF EQ. (3.12)

Equation (3.12) expresses a relation between the eigenvector coefficients $\bar{C}_L^{(i)}(\vec{k})$ [for the eigenvalue $E_i(\vec{k})$] and the cofactors $M_{LL'}(\vec{k},E_i)$ of the KKR matrix $[t^{-1}(\sqrt{E_i},\sqrt{E_i}) - B(\vec{k},E_i)]$. It will be recalled that a homogeneous system of N equations in N variables [such as Eqs. (3.5)] is solved by setting one of the variables equal to an arbitrary constant, deleting one of the equations, and solving the remaining inhomogeneous system of $(N-1)$ equations in $(N-1)$ variables. In the notation of Eqs. (3.5), (if we set $\bar{C}_j^{(i)}(\vec{k}) = b$, and delete the Lth equation) the result is[31]

$$\bar{C}_{L'}^{(i)}(\vec{k}) = b\, M_{LL'}(\vec{k},E_i)/M_{Lj}(\vec{k},E_i)\ . \tag{D1}$$

Similarly, for the coefficient $\bar{C}_L^{(i)}(\vec{k})$, (by deleting the jth equation this time) we obtain

$$\bar{C}_L^{(i)}(\vec{k}) = b\, M_{jL}(\vec{k},E_i)/M_{jj}(\vec{k},E_i)\ . \tag{D2}$$

Equations (D1) and (D2) immediately yield

$$\bar{C}_L^{(i)}(\vec{k})\bar{C}_{L'}^{(i)}(\vec{k}) = b^2\,\frac{M_{LL'}(\vec{k},E_i)}{M_{jj}(\vec{k},E_i)}\,\frac{M_{jL}(\vec{k},E_i)}{M_{Lj}(\vec{k},E_i)}\ . \tag{D3}$$

Since the KKR matrix is symmetric, the matrix M of cofactors is also symmetric. In particular, $M_{jL} = M_{Lj}$. Therefore, Eq. (D3) implies Eq. (3.12).

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[15] Atomic units, $\hbar = c = 2m = 1$, are used in this paper.

[16] In the following, $\langle T \rangle$ will refer to the ATA expression for the average scattering operator.

[17] Note that the integrations in (2.15) will, in fact, extend only to the muffin-tin radius R_m because $t(\vec{r}, \vec{r}\,') = 0$ if r or $r' > R_m$, for a potential of form (2.8).

[18] A configuration-*dependent* quantity is generally *not* enclosed in the angular brackets. In particular, this is true of the quantities referring to the perfect crystal case.

[19] The functional dependence of the matrices t^{-1} and B (on $\vec{k}$ and E) has been suppressed for notational convenience.

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[25] P. Roman, *Advanced Quantum Theory* (Addison-Wesley, Reading, Mass., 1965), Sec. 3.3.

[26] $\mathrm{Im}\, t(\vec{r}, \vec{r}\,')$ will, of course, be nonzero at the energies of the bound states of potential $v(r)$.

[27] $B_{LL'}$, defined through Eq. (2.19), is equal to $i^{l'-l} \kappa G_{LL'}$ [in the notation of Eqs. (A2.5) and (A3.5) of Ref. 6]. Note that in writing (B3), we have set $\tau^{-1} = N$, because the volume of the crystal is taken to be unity.

[28] Our treatment of the cancellation of the free-electron singularities is similar to that given by P. Soven, Phys. Rev. B 2, 4715 (1970).

[29] Since $N^{-1} \sum_{\vec{k}}' e^{i \vec{k} \cdot \vec{R}_m} = \delta_{m0}$, summing both sides of (C2b) over the Brillouin zone gives, $D(E) = -(\pi N)^{-1}\, \mathrm{Im} \int d\vec{r}\, G(\vec{r}, \vec{r};\, E^{+})$. Therefore, the factor of N^2 appearing in (C2b) is proper.

[30] The formal manipulations used to simplify (C4a), are similar to those employed by L. Schwartz, H. K. Peterson, and A. Bansil, Phys. Rev. B 12, 3113 (1975).

[31] H. Jeffries and B. S. Jeffries, *Methods of Mathematical Physics*, 3rd ed. (Cambridge U. P., Cambridge, England, 1962), p. 126.