

Interatomic electron transport by semiempirical and *ab initio* tight-binding approaches

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A unified approach to interatomic electron transport within Kubo linear-response theory is sketched that is applicable both in semiempirical (matrix-element-based) and *ab initio* (wave-function-based) tight-binding (TB) techniques. This approach is based on a systematic neglect of the electron motion inside the atomic (Wigner-Seitz) cells leading thus to velocity operators describing pure intersite hopping. This is achieved by using piecewise constant coordinates, i.e., coordinates that are constant inside the cells. The formalism is presented within the simple semiempirical TB method, the TB linear muffin-tin orbital (LMTO) method, and the screened Korringa-Kohn-Rostoker (KKR) method with emphasis on the formal analogy of the derived formulas. The results provide a justification of current assumptions used in semiempirical TB schemes, an assessment of properties of recent TB-LMTO approaches, and an alternative formulation of electron transport within the screened KKR method. The formalism is illustrated by a calculation of residual resistivity of substitutionally disordered fcc Ag-Pd alloys.

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I. INTRODUCTION

During the last few decades, the tight-binding (TB) picture proved to be indispensable in modern solid-state physics as it provides transparent theoretical concepts and leads to numerical problems featured by relatively small matrix dimensions, typically of the order of ten orbitals per lattice site.¹ The semiempirical scheme, originally based on a parametrization of matrix elements of a TB Hamiltonian,² was recently recast into *ab initio*-type schemes based on local orbitals corresponding to an effective one-electron Hamiltonian defined within the local-density approximation of the density-functional formalism.³ The optimized linear combination of atomic orbitals (LCAO) method⁴ and the TB linear muffin-tin orbital (LMTO) method⁵ are just two examples of such schemes which can be derived in terms of a variational principle. In addition, the Korringa-Kohn-Rostoker (KKR) method,⁶ which relies on multiple-scattering theory, has recently been reformulated as a TB (screened) KKR scheme⁷ representing thus an alternative to more traditional TB techniques. Despite the very different formulations of the above TB approaches, a number of clear links between them is well established, such as phase shifts, TB parameters, etc.⁸ For example, the KKR method is closely related to the LMTO method⁹ while the simplest TB-LMTO Hamiltonian bears a two-center form usually encountered in semiempirical TB schemes.⁵

For an obvious reason, the situation is much less satisfactory regarding transport properties: while wave-function-based techniques naturally start from a continuous change of the electron position in real space, matrix-element-based approaches can describe essentially only an intersite electron hopping from one local (and possibly localized) orbital to another. It is the aim of the present paper to sketch an analogy between the semiempirical and the *ab initio*-type de-

scriptions of interatomic electron transport. This analogy is derived by a systematic neglect of intra-atomic motion in wave-function-based methods. Our results justify some assumptions often used in semiempirical TB theories, shed some light on the accuracy of recent TB-LMTO results, and provide an alternative formulation of intersite electron transport within the screened KKR method. As an illustrating example, the developed formalism is applied to the residual resistivity of substitutionally disordered Ag-Pd bulk alloys.

In the following use will be made of Kubo's linear-response theory,¹⁰ which is a good starting point for properties such as the residual resistivity of disordered bulk metals and bulk alloys,¹¹⁻¹⁵ the conductivity of disordered layered systems,^{16,17} as well as the conductance of quasi-one-dimensional systems.^{18,19} In the simplest case (i.e., zero temperature, zero frequency, and neglect of electron-electron correlations and of any inelastic processes), transport properties such as the conductivity or the conductance reduce to expressions of the form

$$\mathcal{C}(E) \propto \text{Tr}\{\delta(E-H)J\delta(E-H)J\}, \quad (1)$$

where the energy variable E refers to the Fermi level of the system, H is the effective one-electron Hamiltonian, and J is a velocity (current) operator. The latter is defined by a quantum-mechanical relation ($e = \hbar = 1$)

$$J = -i[X, H], \quad (2)$$

where X is a coordinate (position) operator and $[A, B] = AB - BA$ denotes a commutator. In the following, $X(\mathbf{r})$ is supposed to describe not only Cartesian coordinates but also any other real function of the position vector \mathbf{r} . In particular, the operator X can also correspond to a projector onto a given subset of the real space in which case the function $X(\mathbf{r})$ acquires only two values: zero and unity. Consequently, the

operator J in Eq. (2) represents a generalized velocity depending on the definition of X .

In terms of a complex energy variable z and the one-electron Green function (resolvent)

$$G(z) = (z - H)^{-1}, \quad (3)$$

the spectral density operator in Eq. (1) can be written as

$$\delta(E - H) = -\frac{1}{\pi} \text{Im} G(E + i0), \quad (4)$$

where $\text{Im} A = (A - A^\dagger)/(2i)$ denotes the anti-Hermitian part of an operator A . The resulting response coefficient is given then by

$$C(E) = -\text{Tr}\{\text{Im} G(E + i0)[X, H]\text{Im} G(E + i0)[X, H]\}. \quad (5)$$

The use of Eq. (5) within the semiempirical TB, the TB-LMTO, and the TB-KKR approaches will be discussed in Secs. II–IV, respectively.

II. SEMIEMPIRICAL TIGHT-BINDING APPROACHES

In a semiempirical TB scheme a matrix representation of the operators in Eq. (5) is used. Most applications assume that the corresponding local orbitals $|\mathbf{R}L\rangle$ are orthonormal, $\langle \mathbf{R}L | \mathbf{R}'L' \rangle = \delta_{\mathbf{R}L, \mathbf{R}'L'}$, where \mathbf{R} denotes a site index and $L = (l, m)$ is the orbital momentum index (the spin index is ignored here as it is irrelevant for our purposes). In addition to that, two important assumptions are made: the Hamiltonian matrix $H = \{H_{\mathbf{R}L, \mathbf{R}'L'}\}$ is short range and the coordinate operator X can be represented by a diagonal matrix

$$X_{\mathbf{R}L, \mathbf{R}'L'} = X_{\mathbf{R}} \delta_{\mathbf{R}L, \mathbf{R}'L'} \quad (6)$$

specified by a set of constants $\{X_{\mathbf{R}}\}$. Consequently, the velocity matrix is short range with vanishing on-site elements

$$J_{\mathbf{R}L, \mathbf{R}'L'} = -i(X_{\mathbf{R}} - X_{\mathbf{R}'})H_{\mathbf{R}L, \mathbf{R}'L'} \quad (7)$$

describing explicitly intersite electron hopping.

Using the above assumptions, a number of techniques were introduced in order to handle Eq. (5), such as, e.g., the recursion method for topologically disordered systems,¹⁴ the coherent-potential approximation (CPA) for substitutionally disordered systems,^{11,12,16} a surface Green-function technique for layered systems with semi-infinite leads,^{19,20} etc. They are well documented in the literature and need not be described here.

As mentioned in Sec. I, the generalized coordinate operator X and the underlying constants $\{X_{\mathbf{R}}\}$ can be chosen in various ways. If $X_{\mathbf{R}}$ denotes a Cartesian coordinate (x, y, z) of the \mathbf{R} th lattice site, such a choice is suitable, e.g., for the residual resistivity of disordered bulk systems¹⁴ or for the electrical conductivity of layered systems with the current parallel to the layers.¹⁶ If X is a projector on a subspace, i.e., if $X_{\mathbf{R}}$ equals either 0 or 1, the velocity operator J gives the total current flowing out of the subspace and the formalism can be applied to describe tunneling between two electrodes, or layered systems with electric currents perpendicular to the

layers.^{19,20} In all cases, however, the diagonal shape of the matrix representation of the coordinate operator X , Eq. (6), remains merely an assumption, sometimes loosely justified by a small overlap of the local orbitals $|\mathbf{R}L\rangle$ on neighboring atoms.¹⁴

III. TIGHT-BINDING LMTO METHOD

The LMTO method is routinely used for first-principles electronic structure calculations with sophistications ranging from full-potential implementations to the atomic sphere approximation (ASA). However, transport properties of systems without three-dimensional translational symmetry were formulated and calculated only using the least accurate version, namely, the first-order TB-LMTO-ASA method. Below, we first repeat briefly the basic expressions and then present a less intuitive formulation in terms of a more accurate second-order Hamiltonian.

A. First-order accuracy

The first-order TB-LMTO-ASA Hamiltonian is of two-center form similar to the semiempirical TB Hamiltonian and can be written in two equivalent ways,⁵

$$\begin{aligned} H_{\mathbf{R}L, \mathbf{R}'L'}^{(1, \alpha)} &= C_{\mathbf{R}l}^{\alpha} \delta_{\mathbf{R}L, \mathbf{R}'L'} + (\Delta_{\mathbf{R}l}^{\alpha})^{1/2} S_{\mathbf{R}L, \mathbf{R}'L'}^{\alpha} (\Delta_{\mathbf{R}'l'}^{\alpha})^{1/2} \\ &= E_{\nu, \mathbf{R}l} \delta_{\mathbf{R}L, \mathbf{R}'L'} + h_{\mathbf{R}L, \mathbf{R}'L'}^{\alpha}. \end{aligned} \quad (8)$$

The superscript α in Eq. (8) denotes the LMTO representation, defined unambiguously by a set $\{\alpha_{\mathbf{R}l}\}$ of screening constants, and the quantities $C_{\mathbf{R}l}^{\alpha}$ and $\Delta_{\mathbf{R}l}^{\alpha}$ are the potential parameters related to the l th-channel scattering properties of the \mathbf{R} th atom near an energy $E_{\nu, \mathbf{R}l}$. The matrix $S^{\alpha} = \{S_{\mathbf{R}L, \mathbf{R}'L'}^{\alpha}\}$ is the matrix of screened structure constants in representation α while the matrix $h^{\alpha} = \{h_{\mathbf{R}L, \mathbf{R}'L'}^{\alpha}\}$ is related to S^{α} by a diagonal rescaling and shift, see Eq. (8). The matrix S^{α} is given explicitly by the following matrix equation:

$$S^{\alpha} = S^0 (1 - \alpha S^0)^{-1}, \quad (9)$$

where $S^0 = \{S_{\mathbf{R}L, \mathbf{R}'L'}^0\}$ is the matrix of canonical structure constants and $\alpha = \{\alpha_{\mathbf{R}l} \delta_{\mathbf{R}L, \mathbf{R}'L'}\}$ denotes a diagonal matrix of the screening constants. With a suitable choice of the latter, the spatial range of the screened structure constant matrix S^{α} can be reduced typically to the second-nearest neighbors for close-packed lattices.⁵ Consequently, the matrices $H^{(1, \alpha)}$ and h^{α} become short range with obvious advantages in numerical applications. However, the eigenvalues of the Hamiltonian (8) are correct only up to first order in the parameter $\varepsilon = E - E_{\nu}$. Moreover, the Hamiltonian as well as its spectrum depend explicitly on the representation, i.e., on the chosen set of screening constants $\{\alpha_{\mathbf{R}l}\}$.

Using the first-order Hamiltonian (8) and assuming again the diagonal character of the coordinate X , Eq. (6), the velocity operator J and the resolvent $G(z)$ can be written as

$$J = -i(\Delta^{\alpha})^{1/2}[X, S^{\alpha}](\Delta^{\alpha})^{1/2} \quad (10)$$

and

$$G(z) = (\Delta^\alpha)^{-1/2} [(z - C^\alpha)(\Delta^\alpha)^{-1} - S^\alpha]^{-1} (\Delta^\alpha)^{-1/2}. \quad (11)$$

Here we used an obvious matrix notation with the symbols C^α , Δ^α denoting diagonal matrices of the form $A = \{A_{\mathbf{R}l} \delta_{\mathbf{R}l, \mathbf{R}'l'}\}$ ($A = C^\alpha, \Delta^\alpha$). Now let us introduce the so-called auxiliary Green function $g^\alpha(z) = \{g_{\mathbf{R}l, \mathbf{R}'l'}^\alpha(z)\}$ in the α representation as

$$g^\alpha(z) = [P^\alpha(z) - S^\alpha]^{-1}, \quad (12)$$

where $P^\alpha(z) = \{P_{\mathbf{R}l}^\alpha(z) \delta_{\mathbf{R}l, \mathbf{R}'l'}\}$ is a diagonal matrix of screened potential functions in the α representation, given explicitly in first order as

$$P_{\mathbf{R}l}^\alpha(z) = (z - C_{\mathbf{R}l}^\alpha)(\Delta_{\mathbf{R}l}^\alpha)^{-1} \equiv P_{\mathbf{R}l}^{(1, \alpha)}(z). \quad (13)$$

The response coefficient $\mathcal{C}(E)$ in Eq. (5) can then be rewritten as

$$\mathcal{C}(E) = -\text{Tr}\{\text{Im} g^\alpha(E + i0)[X, S^\alpha] \text{Im} g^\alpha(E + i0)[X, S^\alpha]\}. \quad (14)$$

It is clear that this expression is a trivial modification of the original equation, see Eq. (5), used in the semiempirical approach: S^α and $g^\alpha(z)$ substitute the TB Hamiltonian H and its resolvent $G(z)$, respectively. However, keeping in mind parameter-free applications of the TB-LMTO method, a few concerns related to Eq. (14) emerge: (i) the validity of the diagonal character of the coordinate X , Eq. (6), and (ii) the accuracy of Eq. (14). These two items were addressed in a recent paper on electrical conductivity of liquid metals.¹⁵ Another important concern refers to the sensitivity of Eq. (14) with respect to the LMTO representation α : the most localized representation, advantageous for the numerical treatment, need not be the best one from a physical point of view.

B. Second-order accuracy

Quite clearly, a more profound treatment than that presented in Secs. II and III A must be based on orbitals. The basic blocks of the linear muffin-tin orbitals (LMTO's) (Refs. 5 and 9) are functions defined inside each atomic (Wigner-Seitz) sphere centered at a lattice site \mathbf{R} , namely,

$$\begin{aligned} \phi_{\mathbf{R}l}(\mathbf{r}) &= \phi_{\mathbf{R}l}(r) Y_L(\hat{\mathbf{r}}), \\ \dot{\phi}_{\mathbf{R}l}(\mathbf{r}) &= \dot{\phi}_{\mathbf{R}l}(r) Y_L(\hat{\mathbf{r}}), \end{aligned} \quad (15)$$

where the radial amplitudes $\phi_{\mathbf{R}l}(r)$ and $\dot{\phi}_{\mathbf{R}l}(r)$ are the regular solution of the radial Schrödinger equation inside the sphere at an energy $E_{\nu, \mathbf{R}l}$ and its first energy derivative, respectively. The functions $Y_L(\hat{\mathbf{r}})$ in Eq. (15) are real spherical harmonics and $\hat{\mathbf{r}} = \mathbf{r}/r$. The radial amplitudes in Eq. (15) satisfy standard normalization conditions and orthogonality relations,^{5,9} namely,

$$\int_0^{s_{\mathbf{R}}} \phi_{\mathbf{R}l}^2(r) r^2 dr = 1,$$

$$\int_0^{s_{\mathbf{R}}} \phi_{\mathbf{R}l}(r) \dot{\phi}_{\mathbf{R}l}(r) r^2 dr = 0, \quad (16)$$

where $s_{\mathbf{R}}$ denotes the radius of the \mathbf{R} th sphere. Using the abbreviation $\mathbf{r}_{\mathbf{R}} = \mathbf{r} - \mathbf{R}$ and the ASA, the LMTO's in the α representation are defined as

$$\begin{aligned} \chi_{\mathbf{R}l}^\alpha(\mathbf{r}) &= \sum_{\mathbf{R}'l'} \phi_{\mathbf{R}'l'}(\mathbf{r}_{\mathbf{R}'}) (1 + o^\alpha h^\alpha)_{\mathbf{R}'l', \mathbf{R}l} \\ &+ \sum_{\mathbf{R}'l'} \dot{\phi}_{\mathbf{R}'l'}(\mathbf{r}_{\mathbf{R}'}) h_{\mathbf{R}'l', \mathbf{R}l}^\alpha, \end{aligned} \quad (17)$$

where the interstitial part of the orbital is omitted and the functions $\phi_{\mathbf{R}l}(\mathbf{r}_{\mathbf{R}})$ and $\dot{\phi}_{\mathbf{R}l}(\mathbf{r}_{\mathbf{R}})$ are set to zero outside the \mathbf{R} th atomic sphere. In Eq. (17), the diagonal matrix $o^\alpha = \{o_{\mathbf{R}l}^\alpha \delta_{\mathbf{R}l, \mathbf{R}'l'}\}$ contains potential parameters neglected in the first-order approximation in Sec. III A.

Within the \mathbf{R} th Wigner-Seitz cell, the position vector can be decomposed as $\mathbf{r} = \mathbf{R} + \mathbf{r}_{\mathbf{R}}$, where the first term on the right-hand side specifies the center of the cell, i.e., it is constant throughout the cell, and the second one vanishes for $\mathbf{r} = \mathbf{R}$. Let us now consider the following analogous decomposition of the generalized coordinate $X(\mathbf{r})$ based on the concept of nonoverlapping cells:

$$X(\mathbf{r}) = \sum_{\mathbf{R}} X_{\mathbf{R}} \Theta_{\mathbf{R}}(\mathbf{r}) + \sum_{\mathbf{R}} \xi_{\mathbf{R}}(\mathbf{r}). \quad (18)$$

In Eq. (18), valid throughout the whole space, the $X_{\mathbf{R}}$ are some constants, and the functions $\Theta_{\mathbf{R}}(\mathbf{r})$ and $\xi_{\mathbf{R}}(\mathbf{r})$ are non-zero only in the \mathbf{R} th Wigner-Seitz cell: the former function is constant throughout the cell, $\Theta_{\mathbf{R}}(\mathbf{r}) = 1$, while the latter one vanishes at the cell center, $\xi_{\mathbf{R}}(\mathbf{R}) = 0$. It is clear that any function $X(\mathbf{r})$ can be decomposed according to Eq. (18) with $X_{\mathbf{R}} = X(\mathbf{R})$. The two terms on the right-hand side of Eq. (18) represent the “integer” and “fractional” parts of $X(\mathbf{r})$, respectively.

Within the ASA, the matrix elements of the functions $\Theta_{\mathbf{R}}(\mathbf{r})$ with respect to the LMTO's defined in Eq. (17) are given by

$$\begin{aligned} \langle \chi_{\mathbf{R}'l'}^\alpha | \Theta_{\mathbf{R}} | \chi_{\mathbf{R}''l''}^\alpha \rangle &= \sum_L (1 + h^\alpha o^\alpha)_{\mathbf{R}'l', \mathbf{R}l} \\ &\times (1 + o^\alpha h^\alpha)_{\mathbf{R}l, \mathbf{R}''l''}, \end{aligned} \quad (19)$$

where we used the normalization and orthogonality conditions for the spherical harmonics $Y_L(\hat{\mathbf{r}})$ as well as for the radial amplitudes, Eq. (16), but neglected the normalization integral of $\dot{\phi}_{\mathbf{R}l}(r)$. This is fully compatible with the present second-order accuracy of the LMTO-ASA method.⁵ From the corresponding overlap matrix

$$\langle \chi_{\mathbf{R}l}^\alpha | \chi_{\mathbf{R}'l'}^\alpha \rangle = \{(1 + h^\alpha o^\alpha)(1 + o^\alpha h^\alpha)\}_{\mathbf{R}l, \mathbf{R}'l'} \quad (20)$$

an orthonormal basis of LMTO's $\{\tilde{\chi}_{\mathbf{R}l}(\mathbf{r})\}$ can be defined by

$$\begin{aligned}\tilde{\chi}_{\mathbf{R}L}(\mathbf{r}) &= \sum_{\mathbf{R}'L'} \chi_{\mathbf{R}'L'}^\alpha(\mathbf{r}) \{ (1 + o^\alpha h^\alpha)^{-1} \}_{\mathbf{R}'L', \mathbf{R}L} \\ &= \phi_{\mathbf{R}L}(\mathbf{r}_{\mathbf{R}}) + \sum_{\mathbf{R}'L'} \phi_{\mathbf{R}'L'}(\mathbf{r}_{\mathbf{R}'}) \\ &\quad \times \{ h^\alpha (1 + o^\alpha h^\alpha)^{-1} \}_{\mathbf{R}'L', \mathbf{R}L}.\end{aligned}\quad (21)$$

In this orthonormal basis, the matrix elements of $\Theta_{\mathbf{R}}(\mathbf{r})$ are given by

$$\langle \tilde{\chi}_{\mathbf{R}'L'} | \Theta_{\mathbf{R}} | \tilde{\chi}_{\mathbf{R}''L''} \rangle = \delta_{\mathbf{R}'\mathbf{R}} \delta_{\mathbf{R}''\mathbf{R}} \delta_{L'L''}, \quad (22)$$

and therefore the matrix elements of $X(\mathbf{r})$ by

$$X_{\mathbf{R}'L', \mathbf{R}''L''} = X_{\mathbf{R}'} \delta_{\mathbf{R}'L', \mathbf{R}''L''} + \sum_{\mathbf{R}} \langle \tilde{\chi}_{\mathbf{R}'L'} | \xi_{\mathbf{R}} | \tilde{\chi}_{\mathbf{R}''L''} \rangle. \quad (23)$$

A comparison of Eq. (6) with Eq. (23) shows that the simple diagonal form of X is equivalent to neglecting the ‘‘fractional’’ part of the function $X(\mathbf{r})$. In other words, Eq. (6) can be justified for piecewise constant functions

$$X(\mathbf{r}) = \sum_{\mathbf{R}} X_{\mathbf{R}} \Theta_{\mathbf{R}}(\mathbf{r}) \quad (24)$$

using standard approximations of the second-order LMTO-ASA method.

Let us emphasize that we have proved the diagonal character of the matrix representation of X for piecewise constant functions, Eq. (24), but without any assumptions about the spatial localization of the orthonormal LMTO's, Eq. (21). Our proof of Eq. (6) differs from those found usually in the literature in which the electric dipole contributions to the matrix elements of the position operator are neglected.^{15,21} The magnitude of the dipole contributions is difficult to estimate quantitatively, in contrast to the approximations used in our proof of Eq. (6) in which the error cannot be greater than the neglected ‘‘fractional’’ part of $X(\mathbf{r})$.

Piecewise constant coordinates X , Eq. (24), need not be considered merely as approximations to the ‘‘true’’ coordinates, Eq. (18), but can be viewed as quantities appropriate for a pure interatomic (intersite) electron transport. The velocity operators, Eq. (2), describe then only the electron hopping between two different Wigner-Seitz cells and do not take into account the electron motion inside the individual cells. Such an approach is undoubtedly useful, e.g., for describing systems consisting (really or virtually) of two subsystems (tunneling between two electrodes).

The second-order LMTO-ASA Hamiltonian in the orthonormal basis (21) can be written as⁵

$$H^{(2)} = E_\nu + h^\alpha (1 + o^\alpha h^\alpha)^{-1} = E_\nu + h^\alpha - h^\alpha o^\alpha h^\alpha + \dots, \quad (25)$$

which yields eigenvalues correct up to second order in $\varepsilon = E - E_\nu$. A comparison with the first-order Hamiltonian, Eq. (8), reveals that it is the terms containing o^α that distinguish these two levels of accuracy. For our purposes, alternative forms of $H^{(2)}$ will be used, namely,

$$H^{(2)} = C + \Delta^{1/2} S \gamma \Delta^{1/2} \quad (26)$$

and

$$\begin{aligned}H^{(2)} &= C + \Delta^{1/2} S^\alpha [1 + (\alpha - \gamma) S^\alpha]^{-1} \Delta^{1/2} \\ &= C + \Delta^{1/2} [1 + S^\alpha (\alpha - \gamma)]^{-1} S^\alpha \Delta^{1/2},\end{aligned}\quad (27)$$

where C, Δ, γ are diagonal matrices of standard potential parameters $C_{\mathbf{R}l}$, $\Delta_{\mathbf{R}l}$, and $\gamma_{\mathbf{R}l}$ and α is the diagonal matrix of the screening constants $\alpha_{\mathbf{R}l}$ defining a particular LMTO representation. As follows from Eq. (26), the Hamiltonian matrix $H^{(2)}$ is representation invariant despite its explicit α dependence in Eqs. (25) and (27).

The velocity operator for a diagonal coordinate X follows now from Eqs. (2), (6), and (27) and is equal to

$$J = -i \Delta^{1/2} \{1 + S^\alpha (\alpha - \gamma)\}^{-1} [X, S^\alpha] \{1 + (\alpha - \gamma) S^\alpha\}^{-1} \Delta^{1/2}, \quad (28)$$

where we employed the fact that $[A, B] = 0$ for any pair of diagonal matrices A, B . Using Eq. (28), the response coefficient $\mathcal{C}(E)$, Eq. (5), can be recast into the form

$$\mathcal{C}(E) = -\text{Tr}\{\text{Im } M(E + i0) [X, S^\alpha] \text{Im } M(E + i0) [X, S^\alpha]\}, \quad (29)$$

where

$$\begin{aligned}M(z) &= [1 + (\alpha - \gamma) S^\alpha]^{-1} \Delta^{1/2} (z - H^{(2)})^{-1} \Delta^{1/2} \\ &\quad \times [1 + S^\alpha (\alpha - \gamma)]^{-1}.\end{aligned}\quad (30)$$

Using the explicit form of $H^{(2)}$, Eq. (27), this matrix can be rewritten as

$$\begin{aligned}M(z) &= [1 + (\alpha - \gamma) S^\alpha]^{-1} \{ (z - C) \Delta^{-1} \\ &\quad + S^\alpha [(\alpha - \gamma)(z - C) \Delta^{-1} - 1] \}^{-1} \\ &= \{ (z - C) [\Delta + (\gamma - \alpha)(z - C)]^{-1} - S^\alpha \}^{-1} \\ &\quad + [1 + (\alpha - \gamma) S^\alpha]^{-1} (\alpha - \gamma).\end{aligned}\quad (31)$$

By introducing the second-order screened potential functions⁵

$$\begin{aligned}P_{\mathbf{R}l}^\alpha(z) &= (z - C_{\mathbf{R}l}) [\Delta_{\mathbf{R}l} + (\gamma_{\mathbf{R}l} - \alpha_{\mathbf{R}l})(z - C_{\mathbf{R}l})]^{-1} \\ &\equiv P_{\mathbf{R}l}^{(2, \alpha)}(z),\end{aligned}\quad (32)$$

using the definition of the auxiliary Green function $g^\alpha(z)$, Eq. (12), and by taking into account that the last term in Eq. (31) is a Hermitean matrix, we finally get

$$\text{Im } M(z) = \text{Im } g^\alpha(z). \quad (33)$$

This relation can now be inserted into Eq. (29) such that the resulting $\mathcal{C}(E)$ is again of the form given by Eq. (14).

The present analysis based on the LMTO's proves that the previous expression for the response coefficient, Eq. (14), is correct up to second order in $\varepsilon = E - E_\nu$. Even more important, we have shown that the result is invariant with respect to the LMTO representation, despite the fact that the right-hand side of Eq. (14) contains α -dependent quantities. The last property implies that by using the most localized repre-

sensation α , one can treat numerically the full second-order Hamiltonian, Eqs. (25) and (27), again in terms of the short-range structure constants S^α . As a consequence, the recently developed first-order TB-LMTO formalism for conductances of layered systems with currents perpendicular to the atomic planes²² yields results accurate up to second order. Similarly, the existing approach to the electrical resistivity of topologically disordered metals,¹⁵ based on the recursion method and a truncated series in Eq. (25), can easily be improved (without additional numerical effort) by taking all energies $E_{\nu, \mathbf{R}l}$ equal to the Fermi energy, recalculating all potential parameters at this energy, and performing the recursion calculations with the short-range first-order Hamiltonian (8). This improvement was suggested in Ref. 15 and the above analysis shows that such a procedure is equivalent to using the complete second-order Hamiltonian (25). The last statement follows from Eq. (14) and from the fact that at a particular energy E (the Fermi level) $\text{Im} g^\alpha(E+i0)$ depends only on the potential functions $P_{\mathbf{R}l}^\alpha(z)$ and their first derivatives at $z=E$. Both parametrizations, Eqs. (13) and (32), reproduce the values and the first derivatives of the screened potential functions at the energies $E_{\nu, \mathbf{R}l}$ exactly.

IV. SCREENED KKR METHOD

The proved properties of the TB-LMTO approach based on the piecewise constant coordinates X indicate a possibility to obtain an analogous formulation of the intersite transport in the TB-KKR method. In order to achieve this, one has to start from Eq. (5) and replace the local velocity operator due to the kinetic energy by a nonlocal operator describing the intersite hopping. Finally, the general operator formulas have to be transformed into the matrix ones.

A. Formal theory

In the KKR theory, both the conventional⁶ and the screened,^{7,23} the system Hamiltonian H is defined with respect to the Hamiltonian $H^{(r)}$ of a reference system as

$$H = H^{(r)} + U, \quad (34)$$

where U denotes the corresponding perturbation. The kinetic-energy term is contained in $H^{(r)}$ while the perturbation U is a local potential, $\langle \mathbf{r} | U | \mathbf{r}' \rangle = U(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')$. Let us assume that the coordinate operator X in Eq. (2) represents as well a local function, $\langle \mathbf{r} | X | \mathbf{r}' \rangle = X(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}')$, then

$$\begin{aligned} [X, U] &= 0, \\ [X, H] &= [X, H^{(r)}], \end{aligned} \quad (35)$$

which means that the velocity operator is entirely due to the reference Hamiltonian. The response coefficient in Eq. (5) can then be written as

$$\mathcal{C}(E) = -\text{Tr}\{\text{Im} G(E+i0)[X, H^{(r)}]\text{Im} G(E+i0)[X, H^{(r)}]\}. \quad (36)$$

In practical calculations with the screened KKR method,⁷ the reference Hamiltonian $H^{(r)}$ is chosen in such a way that

its spectrum is located above the Fermi energy of the studied solid. Consequently, the corresponding Green function

$$G^{(r)}(z) = (z - H^{(r)})^{-1} \quad (37)$$

is uniquely defined also for real energies of interest including the Fermi energy. Starting thus from the definition (37) for $z=E$, one can easily prove a relation

$$[X, H^{(r)}] = (E - H^{(r)})[X, G^{(r)}(E)](E - H^{(r)}), \quad (38)$$

which can be used in Eq. (36) to obtain

$$\begin{aligned} \mathcal{C}(E) &= -\text{Tr}\{(E - H^{(r)})\text{Im} G(E+i0)(E - H^{(r)})[X, G^{(r)}(E)] \\ &\quad \times (E - H^{(r)})\text{Im} G(E+i0)(E - H^{(r)})[X, G^{(r)}(E)]\}. \end{aligned} \quad (39)$$

The physical meaning of Eqs. (35) and (38) is clear: the local velocity operator (2) is expressed in terms of a nonlocal operator $G^{(r)}(E)$. The latter plays then a role of a TB Hamiltonian of the semiempirical approach.

The last expression for the response coefficient, Eq. (39), can be written in equivalent forms. A well-known property of the delta function, namely, $x \delta(x) = 0$,²⁴ leads to the following identity for the spectral density (4):

$$(E - H)\text{Im} G(E+i0) = 0. \quad (40)$$

By inserting the decomposition (34), one gets immediately

$$(E - H^{(r)})\text{Im} G(E+i0) = U \text{Im} G(E+i0). \quad (41)$$

This identity and its conjugate counterpart can be now used in Eq. (39) which yields

$$\begin{aligned} \mathcal{C}(E) &= -\text{Tr}\{U \text{Im} G(E+i0)U[X, G^{(r)}(E)] \\ &\quad \times U \text{Im} G(E+i0)U[X, G^{(r)}(E)]\}. \end{aligned} \quad (42)$$

This relation shows that the spatial integrations involved in the evaluation of the trace extend only over the region of the nonzero local perturbation U . One can further introduce the T matrix corresponding to the perturbation U , namely,

$$T(z) = U + UG(z)U, \quad (43)$$

which leads to a more compact form of $\mathcal{C}(E)$:

$$\begin{aligned} \mathcal{C}(E) &= -\text{Tr}\{\text{Im} T(E+i0)[X, G^{(r)}(E)]\text{Im} T(E+i0) \\ &\quad \times [X, G^{(r)}(E)]\}. \end{aligned} \quad (44)$$

The last two expressions, Eqs. (42) and (44), will be used in the next section.

B. Muffin-tin model

Let us now reduce the general operator form of the equations in Sec. IV A into a matrix form. As in Sec. III B we will consider the coordinate X as a piecewise constant function, Eq. (24), which in an operator form can be written as

$$\langle \mathbf{r} + \mathbf{R} | X | \mathbf{r}' + \mathbf{R}' \rangle = X_{\mathbf{R}} \delta_{\mathbf{R}\mathbf{R}'} \delta(\mathbf{r} - \mathbf{r}'). \quad (45)$$

Here we introduced the usual notation^{7,23} in which a vector inside the Wigner-Seitz cell centered at the \mathbf{R} th lattice site is denoted as $\mathbf{r}+\mathbf{R}$. The Hamiltonians H and $H^{(r)}$ of the system and the reference system will be chosen in the simplest muffin-tin form, i.e.,

$$H=H^0+\sum_{\mathbf{R}}V_{\mathbf{R}}, \quad H^{(r)}=H^0+\sum_{\mathbf{R}}V_{\mathbf{R}}^{(r)}, \quad (46)$$

where $H^0=-\Delta$ is the kinetic-energy part (in Rydberg atomic units) while the individual site contributions are local spherically symmetric potentials $V_{\mathbf{R}}(r)$ and $V_{\mathbf{R}}^{(r)}(r)$, the latter being nonzero only inside the nonoverlapping muffin-tin spheres centered at \mathbf{R} . Consequently, the perturbation U is a sum of spherically symmetric muffin-tin contributions $U_{\mathbf{R}}(r)=V_{\mathbf{R}}(r)-V_{\mathbf{R}}^{(r)}(r)$.

As follows from Eq. (42), one has to specify the Green functions $G(z)$ and $G^{(r)}(z)$ only for vectors in the range of the nonzero perturbation U , i.e., inside the muffin-tin spheres. In this case, the Green function of the system can be written as^{7,23}

$$\begin{aligned} \langle \mathbf{r}+\mathbf{R}|G(z)|\mathbf{r}'+\mathbf{R}'\rangle &= \delta_{\mathbf{R}\mathbf{R}'}\sqrt{z}\sum_L \mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r}^<,z)\mathcal{S}_{\mathbf{R}\mathbf{L}}(\mathbf{r}^>,z) \\ &+ \sum_{LL'} \mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r},z)\mathcal{G}_{\mathbf{R}\mathbf{L},\mathbf{R}'\mathbf{L}'}(z) \\ &\times \mathcal{R}_{\mathbf{R}'\mathbf{L}'}(\mathbf{r}',z), \end{aligned} \quad (47)$$

where $\mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r},z)$ and $\mathcal{S}_{\mathbf{R}\mathbf{L}}(\mathbf{r},z)$ denote, respectively, the regular and singular scattering solutions of the Schrödinger equation corresponding to the spherically symmetric potential $V_{\mathbf{R}}(r)$, the symbol $\mathbf{r}^<$ ($\mathbf{r}^>$) refers to that of the vectors \mathbf{r},\mathbf{r}' with the smaller (greater) modulus, and the quantities $\mathcal{G}_{\mathbf{R}\mathbf{L},\mathbf{R}'\mathbf{L}'}(z)$ are elements of the Green-function matrix $\mathcal{G}(z)$ containing all multiple-scattering effects. With restriction to the most frequent case in which the Fermi energy is located above the muffin-tin zero, the value of \sqrt{z} in Eq. (47) for $\text{Re } z>0, \text{Im } z\geq 0$ is unambiguously specified by $\text{Re}\sqrt{z}>0, \text{Im}\sqrt{z}\geq 0$. The functions $\mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r},z)$ and $\mathcal{S}_{\mathbf{R}\mathbf{L}}(\mathbf{r},z)$ are written in terms of their radial amplitudes and the real spherical harmonics as

$$\begin{aligned} \mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r},z) &= \mathcal{R}_{\mathbf{R}\mathbf{L}}(r,z)Y_L(\hat{\mathbf{r}}), \\ \mathcal{S}_{\mathbf{R}\mathbf{L}}(\mathbf{r},z) &= \mathcal{S}_{\mathbf{R}\mathbf{L}}(r,z)Y_L(\hat{\mathbf{r}}). \end{aligned} \quad (48)$$

The normalization of the radial amplitudes for the present purposes is given by the following conditions of smooth matching at the muffin-tin radius ($r=a_{\mathbf{R}}$):

$$\begin{aligned} \mathcal{R}_{\mathbf{R}\mathbf{L}}(r,z) &\rightarrow \cos[\delta_{\mathbf{R}\mathbf{L}}(z)]j_l(r\sqrt{z}) - \sin[\delta_{\mathbf{R}\mathbf{L}}(z)]n_l(r\sqrt{z}), \\ \mathcal{S}_{\mathbf{R}\mathbf{L}}(r,z) &\rightarrow \sin[\delta_{\mathbf{R}\mathbf{L}}(z)]j_l(r\sqrt{z}) + \cos[\delta_{\mathbf{R}\mathbf{L}}(z)]n_l(r\sqrt{z}), \end{aligned} \quad (49)$$

where $j_l(x)$ and $n_l(x)$ denote the spherical Bessel and Neumann functions, respectively, while the quantities $\delta_{\mathbf{R}\mathbf{L}}(z)$ are the phase shifts corresponding to the spherically symmetric potential $V_{\mathbf{R}}(r)$ and the orbital quantum number l . It should

be noted that the adopted normalization of the radial amplitudes differs from more traditional ones⁷ but it is quite advantageous for taking the anti-Hermitian part of $G(z)$ in Eq. (42) since the functions $\mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r},z)$ and $\mathcal{S}_{\mathbf{R}\mathbf{L}}(\mathbf{r},z)$ are analytic functions of z near the real energy axis and they are real for real energies.²³

The Green-function matrix $\mathcal{G}(z)=\{\mathcal{G}_{\mathbf{R}\mathbf{L},\mathbf{R}'\mathbf{L}'}(z)\}$ in Eq. (47) is given by^{7,23}

$$\mathcal{G}(z) = \sqrt{z}\cot[\delta(z)] + \frac{\sqrt{z}}{\sin[\delta(z)]}\tau(z)\frac{\sqrt{z}}{\sin[\delta(z)]}, \quad (50)$$

where $\delta(z)$ denotes a diagonal matrix of the phase shifts, $\delta(z)=\{\delta_{\mathbf{R}\mathbf{L}}(z)\delta_{\mathbf{R}\mathbf{L},\mathbf{R}'\mathbf{L}'}\}$, and where the matrix $\tau(z)=\{\tau_{\mathbf{R}\mathbf{L},\mathbf{R}'\mathbf{L}'}(z)\}$ refers to the scattering path operators. The latter is given by

$$\tau(z) = [t^{-1}(z) - \mathcal{G}^0(z)]^{-1}, \quad (51)$$

where $t(z)=\{t_{\mathbf{R}\mathbf{L}}(z)\delta_{\mathbf{R}\mathbf{L},\mathbf{R}'\mathbf{L}'}\}$ is a diagonal matrix of the single-site t matrices

$$t_{\mathbf{R}\mathbf{L}}(z) = -\frac{\sin[\delta_{\mathbf{R}\mathbf{L}}(z)]\exp[i\delta_{\mathbf{R}\mathbf{L}}(z)]}{\sqrt{z}} \quad (52)$$

and the symbol $\mathcal{G}^0(z)=\{\mathcal{G}_{\mathbf{R}\mathbf{L},\mathbf{R}'\mathbf{L}'}^0(z)\}$ refers to the standard matrix of the bare KKR structure constants. The linear relation between $\mathcal{G}(z)$ and $\tau(z)$, Eq. (50), differs from analogous relations of other authors⁷ due to different normalizations of the radial amplitudes, cf. the text after Eq. (49). The Green function $G^{(r)}(z)$ of the reference system as well as the related quantities [denoted systematically by the superscript (r) below] satisfy the same relations as Eqs. (47)–(52) which are omitted here for brevity.

For the individual operators appearing in Eq. (42) and for vectors inside the muffin-tin spheres, we get from Eq. (47)

$$\begin{aligned} \langle \mathbf{r}+\mathbf{R}|U \text{Im } G(E+i0)U|\mathbf{r}'+\mathbf{R}'\rangle &= \sum_{LL'} U_{\mathbf{R}\mathbf{L}}(r)\mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r},E)\text{Im } \mathcal{G}_{\mathbf{R}\mathbf{L},\mathbf{R}'\mathbf{L}'}(E+i0) \\ &\times \mathcal{R}_{\mathbf{R}'\mathbf{L}'}(\mathbf{r}',E)U_{\mathbf{R}'\mathbf{L}'}(r'), \end{aligned} \quad (53)$$

and

$$\begin{aligned} \langle \mathbf{r}+\mathbf{R}|[X, G^{(r)}(E)]|\mathbf{r}'+\mathbf{R}'\rangle &= \sum_{LL'} \mathcal{R}_{\mathbf{R}\mathbf{L}}^{(r)}(\mathbf{r},E)[X, \mathcal{G}^{(r)}(E)]_{\mathbf{R}\mathbf{L},\mathbf{R}'\mathbf{L}'} \\ &\times \mathcal{R}_{\mathbf{R}'\mathbf{L}'}^{(r)}(\mathbf{r}',E), \end{aligned} \quad (54)$$

where the symbol X on the right-hand side of Eq. (54) denotes a diagonal matrix $X=\{X_{\mathbf{R}}\delta_{\mathbf{R}\mathbf{L},\mathbf{R}'\mathbf{L}'}\}$, cf. Eq. (6). Using Eqs. (53) and (54) in the expression for $\mathcal{C}(E)$, Eq. (42), we obtain a formula with matrix quantities instead of operators:

$$\begin{aligned} \mathcal{C}(E) &= -\text{Tr}\{\tilde{W}(E)\text{Im } \mathcal{G}(E+i0)W(E)[X, \mathcal{G}^{(r)}(E)] \\ &\times \tilde{W}(E)\text{Im } \mathcal{G}(E+i0)W(E)[X, \mathcal{G}^{(r)}(E)]\}. \end{aligned} \quad (55)$$

Here we introduced a site-diagonal matrix $W(E) = \{W_{\mathbf{R},LL'}(E)\delta_{\mathbf{R}\mathbf{R}'}\}$ together with its transpose $\tilde{W}(E)$, the elements of which are given by single-sphere integrals

$$W_{\mathbf{R},LL'}(E) = \int_{(\mathbf{R})} \mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r}, E) U_{\mathbf{R}}(r) \mathcal{R}_{\mathbf{R}\mathbf{L}'}^{(r)}(\mathbf{r}, E) d^3\mathbf{r}. \quad (56)$$

These integrals can be simplified using the fact that the scattering solutions $\mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r}, E)$ and $\mathcal{R}_{\mathbf{R}\mathbf{L}'}^{(r)}(\mathbf{r}, E)$ refer to the potentials $V_{\mathbf{R}}(r)$ and $V_{\mathbf{R}'}^{(r)}(r)$, respectively, and that $U_{\mathbf{R}}(r) = V_{\mathbf{R}}(r) - V_{\mathbf{R}'}^{(r)}(r)$. We get

$$\begin{aligned} W_{\mathbf{R},LL'}(E) &= \int_{(\mathbf{R})} [\mathcal{R}_{\mathbf{R}\mathbf{L}'}^{(r)}(\mathbf{r}, E) \Delta \mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r}, E) \\ &\quad - \mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r}, E) \Delta \mathcal{R}_{\mathbf{R}\mathbf{L}'}^{(r)}(\mathbf{r}, E)] d^3\mathbf{r} \\ &= \int_{\partial(\mathbf{R})} \left[\mathcal{R}_{\mathbf{R}\mathbf{L}'}^{(r)}(\mathbf{r}, E) \frac{\partial}{\partial n} \mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r}, E) \right. \\ &\quad \left. - \mathcal{R}_{\mathbf{R}\mathbf{L}}(\mathbf{r}, E) \frac{\partial}{\partial n} \mathcal{R}_{\mathbf{R}\mathbf{L}'}^{(r)}(\mathbf{r}, E) \right] dF \\ &= \delta_{LL'} r^2 \left[\mathcal{R}_{\mathbf{R}\mathbf{L}'}^{(r)}(r, E) \frac{\partial}{\partial r} \mathcal{R}_{\mathbf{R}\mathbf{L}}(r, E) \right. \\ &\quad \left. - \mathcal{R}_{\mathbf{R}\mathbf{L}}(r, E) \frac{\partial}{\partial r} \mathcal{R}_{\mathbf{R}\mathbf{L}'}^{(r)}(r, E) \right] \Bigg|_{r=r_{\mathbf{R}}}, \quad (57) \end{aligned}$$

where we used the Green theorem to transform the volume integral into a surface one and took into account the orthogonality conditions for the spherical harmonics. The last expression represents a Wronskian of two radial amplitudes evaluated at the muffin-tin radius. It can be calculated using the matching conditions (49) and the well-known Wronskian relation for the spherical Bessel and Neumann functions. The result is

$$W_{\mathbf{R},LL'}(E) = \delta_{LL'} \frac{1}{\sqrt{E}} \sin[\delta_{\mathbf{R}\mathbf{L}'}^{(r)}(E) - \delta_{\mathbf{R}\mathbf{L}}(E)], \quad (58)$$

which has to be inserted into the matrix formula (55).

In order to obtain a complete analogy to the results of Secs. II and III, let us express explicitly the Green-function matrix of the system, $\mathcal{G}(z)$, in terms of that of the reference system, $\mathcal{G}^{(r)}(z)$. This can be accomplished in two steps. First, we exclude the bare structure constant matrix $\mathcal{G}^0(z)$ from Eq. (51) and from the same equation for the reference system. We get a Dyson equation for the scattering path operator matrices:

$$\tau(z) = \tau^{(r)}(z) \{1 + [t^{-1}(z) - t^{(r)-1}(z)] \tau^{(r)}(z)\}^{-1}. \quad (59)$$

Second, we replace the matrices $\tau(z)$ and $\tau^{(r)}(z)$ by the corresponding Green-function matrices $\mathcal{G}(z)$ and $\mathcal{G}^{(r)}(z)$ according to Eq. (50). After longer but straightforward algebraic manipulations, we get the result again in the form of Eqs. (50) and (51), namely,

$$\mathcal{G}(z) = \sqrt{z} \cot[\varphi(z)] + \frac{\sqrt{z}}{\sin[\varphi(z)]} \mathcal{T}(z) \frac{\sqrt{z}}{\sin[\varphi(z)]}, \quad (60)$$

where we introduced a diagonal matrix $\varphi(z) = \{\varphi_{\mathbf{R}\mathbf{L}}(z)\delta_{\mathbf{R}\mathbf{L},\mathbf{R}'\mathbf{L}'}\}$ with elements

$$\varphi_{\mathbf{R}\mathbf{L}}(z) = \delta_{\mathbf{R}\mathbf{L}}(z) - \delta_{\mathbf{R}\mathbf{L}}^{(r)}(z) \quad (61)$$

and a nondiagonal matrix $\mathcal{T}(z) = \{\mathcal{T}_{\mathbf{R}\mathbf{L},\mathbf{R}'\mathbf{L}'}(z)\}$ defined as

$$\mathcal{T}(z) = \{-\sqrt{z} \cot[\varphi(z)] - \mathcal{G}^{(r)}(z)\}^{-1}. \quad (62)$$

The interpretation of Eqs. (60)-(62) is obvious: the Green-function matrix of the system is obtained by a diagonal rescaling and shift of the scattering path operator matrix $\mathcal{T}(z)$ defined with respect to the reference system. The slight formal difference between Eq. (62) and Eq. (51) is again due to different normalizations of the corresponding radial amplitudes.

Let us now substitute the relations (58), (60), and (61) into the matrix expression for $\mathcal{C}(E)$, Eq. (55). Using the fact that the phase shifts are real quantities for real energies, we can write the final TB-KKR formula for the response coefficient:

$$\begin{aligned} \mathcal{C}(E) &= -\text{Tr}\{\text{Im} \mathcal{T}(E+i0)[X, \mathcal{G}^{(r)}(E)] \text{Im} \mathcal{T}(E+i0) \\ &\quad \times [X, \mathcal{G}^{(r)}(E)]\}. \quad (63) \end{aligned}$$

This relation is a matrix counterpart of the previous operator formula in Eq. (44).

The analogy between the TB-KKR and the TB-LMTO results is now evident, cf. Eqs. (62) and (63) and Eqs. (12) and (14). The cotangents of the phase shifts $\varphi_{\mathbf{R}\mathbf{L}}(z)$ with respect to the reference system, Eq. (61), correspond to the screened potential functions $P_{\mathbf{R}\mathbf{L}}^\alpha(z)$, Eqs. (13) and (32), the Green-function matrix of the reference system $\mathcal{G}^{(r)}(E)$, being a short-range Hermitean matrix, corresponds to the screened structure constant matrix S^α , and the scattering path operator matrix $\mathcal{T}(z)$ with respect to the reference system, Eq. (62), corresponds to the auxiliary Green-function matrix $g^\alpha(z)$, Eq. (12). This correspondence was established in a number of papers from the point of view of one-electron quantities;^{9,25,26} here we rederived it on the basis of the Kubo response coefficient for the interatomic electron transport.

V. EXAMPLE: RESISTIVITY OF BULK RANDOM ALLOYS

Let us illustrate the developed formalism by an application to the static residual resistivity of a substitutionally disordered bulk alloy. Using the notation and results of Sec. III, the diagonal elements of the conductivity tensor according to the Kubo-Greenwood formula^{10,27} can be written (in mksa units) as

$$\begin{aligned} \sigma^{\mu\mu} &= -\frac{e^2}{\pi\hbar V_0 N} \text{Tr}\{\text{Im} g^\alpha(E+i0)[X^\mu, S^\alpha] \\ &\quad \times \text{Im} g^\alpha(E+i0)[X^\mu, S^\alpha]\}, \quad (64) \end{aligned}$$

where $\mu = x, y, z$ is the Euclidean index, V_0 is the volume of the primitive cell, N is the number of cells in a large but finite solid with three-dimensional periodic boundary conditions, the trace operation includes the spin index σ ($\sigma = \uparrow, \downarrow$), and $\langle \dots \rangle$ denotes the configurational averaging. Within the CPA and neglecting vertex corrections,^{11,13} Eq. (64) can be rewritten as

$$\sigma^{\mu\mu} = -\frac{e^2}{\pi\hbar V_0 N} \text{Tr}\{\text{Im}\bar{g}^\alpha(E+i0)[X^\mu, S^\alpha] \times \text{Im}\bar{g}^\alpha(E+i0)[X^\mu, S^\alpha]\}, \quad (65)$$

where

$$\bar{g}^\alpha(z) = \langle g^\alpha(z) \rangle = [\mathcal{P}^\alpha(z) - S^\alpha]^{-1} \quad (66)$$

is the configurationally averaged auxiliary Green function (12) defined in terms of a site-diagonal matrix of the coherent-potential functions $\mathcal{P}^\alpha(z) = \{\mathcal{P}_{\mathbf{R},L\sigma, \mathbf{L}'\sigma'}^\alpha(z) \delta_{\mathbf{R}\mathbf{R}'}\}$ satisfying the CPA self-consistency conditions.^{26,28} The numerical evaluation of Eq. (65) is then based on lattice Fourier transforms of the corresponding matrix quantities

$$\sigma^{\mu\mu} = -\frac{e^2}{\pi\hbar V_0} \frac{1}{N} \sum_{\mathbf{k}} \text{tr}\{\text{Im}\bar{g}^\alpha(\mathbf{k}, E+i0)[X^\mu, S^\alpha](\mathbf{k}) \times \text{Im}\bar{g}^\alpha(\mathbf{k}, E+i0)[X^\mu, S^\alpha](\mathbf{k})\}, \quad (67)$$

where the summation is performed over N \mathbf{k} points sampling the first Brillouin zone and the trace is evaluated in general over a composed matrix index $\mathbf{B}L\sigma$, where \mathbf{B} denotes the basis vectors (nonprimitive translations) of the configurationally averaged system. The \mathbf{k} -dependent matrices in Eq. (67) are given explicitly by

$$\bar{g}_{\mathbf{B}L\sigma, \mathbf{B}'L'\sigma'}^\alpha(\mathbf{k}, z) = \{[\mathcal{P}^\alpha(z) - S^\alpha(\mathbf{k})]^{-1}\}_{\mathbf{B}L\sigma, \mathbf{B}'L'\sigma'}, \quad (68)$$

$$S_{\mathbf{B}L\sigma, \mathbf{B}'L'\sigma'}^\alpha(\mathbf{k}) = \delta_{\sigma\sigma'} \sum_{\mathbf{T}} S_{\mathbf{B}L, (\mathbf{B}'+\mathbf{T})L'}^\alpha \exp(i\mathbf{k}\cdot\mathbf{T}), \quad (69)$$

$$\begin{aligned} [X^\mu, S^\alpha]_{\mathbf{B}L\sigma, \mathbf{B}'L'\sigma'}(\mathbf{k}) \\ = \delta_{\sigma\sigma'} \sum_{\mathbf{T}} (X_{\mathbf{B}}^\mu - X_{\mathbf{B}'+\mathbf{T}}^\mu) S_{\mathbf{B}L, (\mathbf{B}'+\mathbf{T})L'}^\alpha \exp(i\mathbf{k}\cdot\mathbf{T}), \end{aligned} \quad (70)$$

where \mathbf{T} denote the translation vectors (primitive translations) while $X_{\mathbf{B}}^\mu$ and $X_{\mathbf{B}'+\mathbf{T}}^\mu$ are the μ th components of the vectors \mathbf{B} and $\mathbf{B}'+\mathbf{T}$, respectively.

The calculations were carried out for random fcc $\text{Ag}_x\text{Pd}_{1-x}$ alloys in the whole concentration range. The self-consistent one-electron potentials in the local-density approximation with the exchange-correlation potential of Ref. 29 were obtained using the all-electron scalar-relativistic TB-LMTO-CPA method in the ASA with an angular momentum cutoff $l_{max}=2$ (*spd* basis) and $l_{max}=3$ (*spdf* basis). Further details of the numerical implementation can be found

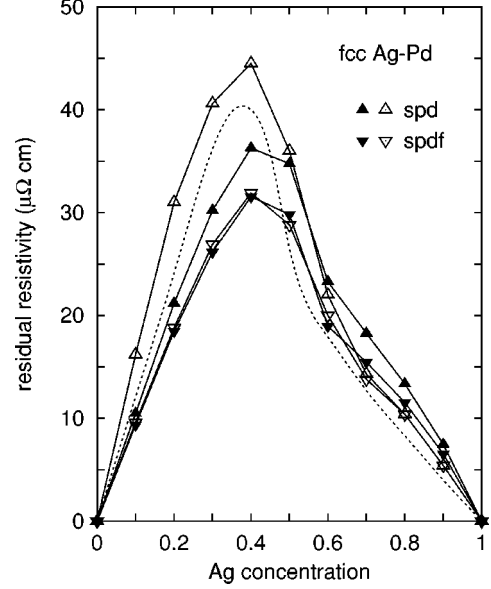


FIG. 1. The residual resistivity of disordered fcc Ag-Pd alloys calculated by the present TB-LMTO approach (full symbols) and the standard KKR method in Ref. 32 (open symbols). Results for angular momentum cutoff $l_{max}=2$ (*spd* basis, triangles up) and $l_{max}=3$ (*spdf* basis, triangles down) are given. The dotted curve denotes experimental results of Ref. 31.

elsewhere.²⁶ The values of the coherent-potential functions at the Fermi energy were obtained first by solving the CPA self-consistency condition in the upper complex energy half-plane and then by a numerical analytic continuation to the real axis.³⁰ The Brillouin-zone average in Eq. (67) was evaluated by using $N=10^7$ \mathbf{k} points whereby its convergence with respect to N was checked carefully. The results for the resistivity $\rho = 1/\sigma^{\mu\mu}$ are presented in Fig. 1 together with experimental values³¹ and with results of the standard KKR method.³² The latter—based on usual concepts and continuous coordinates¹³—were obtained in the muffin-tin model and the scalar-relativistic approximation and with inclusion of the vertex corrections. A comparison of all data sets shows a good overall agreement in magnitude of the resistivity as well as in its concentration dependence which exhibits a typical asymmetric shape. This means that the net effect due to a different description of the electron motion inherent to the two approaches—interatomic (TB-LMTO) and intra-atomic (KKR)—is quite small. Moreover, both approaches show similar sensitivity with respect to the angular momentum cutoff l_{max} : inclusion of *f* states decreases the resistivity typically by 10%. A part of the deviations between the TB-LMTO and KKR resistivities can be surely ascribed to different technical details of the calculations. Equally important might be the role of the vertex corrections, omitted in the TB-LMTO conductivity formula, Eq. (67), but included in the KKR results plotted in Fig. 1. It should be noted that the vertex corrections to the resistivity of the Ag-Pd alloys are rather small, changing from about 30% for Ag-rich alloys to less than 5% for Pd-rich systems.^{32,33} A systematic TB-LMTO study of this and related items, analogous to Ref. 34 for the KKR case, has to be left to future investigations.

VI. DISCUSSION

It is now obvious that the semiempirical TB approach to the response coefficient (5) with diagonal coordinate operators (6) has its TB-LMTO and TB-KKR counterparts given by Eqs. (14) and (63). The latter are based on coordinates $X(\mathbf{r})$ that are constant within a given Wigner-Seitz cell, Eqs. (24) and (45), leading thus to velocity operators which describe the pure intersite hopping. The role of the coordinate operator X in Kubo formalism is twofold:¹⁰ it is related both to the current operator and to the applied external field that brings the system out of equilibrium. Consequently, the present formulation neglects the variation of applied electrostatic potentials inside individual atomic cells. While this is certainly an approximation, the validity of which is to be checked in each particular case, it should be noted that the detailed microscopic behavior of the effective electrostatic field inside the cells due to an applied voltage is in general unknown.

The effective velocity operators in the present TB-LMTO and TB-KKR formalisms are represented by short-range matrices with vanishing on-site blocks in clear contrast to the site-diagonal matrices representing the local velocity operators in usual KKR approaches.^{15,17,32} Another pronounced difference appears in the context of substitutionally disordered systems where an evaluation of the response coefficient requires configuration averaging. Within self-consistent mean-field theories such as the CPA, this leads inevitably to the problem of vertex corrections. While the original formulation¹¹ assumes nonrandom (configuration-independent) velocity operators as encountered in semiempirical TB schemes, the standard KKR theory of electron transport becomes more complicated due to the random (configuration-dependent) site-diagonal velocity matrices.¹³ Since the structure constant matrix S^α of the TB-LMTO approach as well as the reference system of the screened KKR method are usually taken independent of the configuration, the effective velocity operators in Eqs. (14) and (63) are nonrandom and the configuration averaging reduces completely to the original version¹¹ which might be of advantage in calculating the vertex corrections.

VII. CONCLUSIONS

We have shown that a systematic use of piecewise constant coordinates for transport properties leads to a complete analogy between TB schemes based only on Hamiltonian matrix elements and those based on orbitals (wave functions). This link allows a direct translation of existing techniques between the semiempirical and first-principles methods. This can simplify, e.g., the evaluation of the vertex corrections in the coherent-potential approximation combined with *ab initio* methods. We have presented a detailed derivation within the TB-LMTO method that clarified some properties (accuracy, representation invariance) of recent calculations and gave arguments in favor of some assumptions made in semiempirical schemes (diagonality of matrix representation of the position operator). An analogous formalism worked out within the screened KKR method can serve as an alternative to the existing KKR formulations, both for bulk¹³ and layered systems.^{17,35}

The full assessment of the applicability of the suggested scheme to various physical situations remains to be done. Nevertheless, the results shown here for substitutionally disordered alloys as well as existing results of other authors, e.g., for the residual resistivity¹⁵ and the Hall conductivity³⁶ of topologically disordered metals or for the conductance of layered systems with perfect and imperfect interfaces,^{22,37} obtained by the parameter-free TB-LMTO method, indicate that the most important ingredients of the interatomic electron transport are within the range of the present approach.

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