Relativistic single-site Green function for general potentials

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The fully relativistic single-site Green function is derived for generally shaped and magnetically polarized cell potentials. It is shown that the right- and left-hand-side (i.e., ket and bra) solutions of the Dirac equations are the necessary ingredients and their generalized Wronskian relation provides important identities, which play a decisive role in the construction of the Green function.

I. INTRODUCTION

Over the past two decades a considerable amount of effort has been paid to extend the Korringa-Kohn-Rostoker (KKR) -type Green function formalism[1,2] that was originally constructed in connection with potentials of the muffin-tin (nonoverlapping spherically symmetric) form to be applied to generally shaped cell potentials.[3–9] A generalization of the formalism is necessary in the study of systems where the muffin-tin construct provides only a rough approximation to realistic potentials, e.g., covalently bonded materials, atoms located near a surface, interface, or impurity.[10] The development along this line, however, has been made only in the nonrelativistic frame where the electrons are governed by the Schrödinger equation. Regarding a recent tendency to invent new materials such as high-T_c superconductors that contain often high-atomic-number elements,[11] it seems rather urgent to develop a relativistic version. Since the Schrödinger equation itself is an approximation to describe the motion of electrons, the theory shall give an ultimate description of the electronic structure of matter within the single-particle approximation.[12,13] Among the various steps that are necessary to complete the theory, I present here a method to obtain the relativistic single-site Green function. The other steps can be rather easily carried out in the analog to the nonrelativistic case.

In the cases of the muffin-tin or the magnetically polarized muffin-tin potentials, the expressions for the relativistic Green function have been already given by various authors.[14–17] The latter case is sometimes referred to as the nonspherically symmetric potential, since the Dirac Hamiltonian has only a cylindrical symmetry along the direction of the magnetic moment incorporating it with the spin-orbit interaction. It will be seen, however, that the nomenclature "nonspherical" may not be suitable since the assumed potential belongs to the case where its matrix representation in a spin-angular-momentum space can be set into a special form. Furthermore, the expressions hitherto presented for both of two above-mentioned potential models are often incorrect or correct only for the energy on its real axis. Although the Green function for the energy off the real axis might be unimportant in the band-structure calculations, it is desirable to obtain its expression on the complex physical energy sheet where the Green function is analytic. The advantage of knowing the Green function for the complex energy is not only that we can calculate the density of states efficiently through contour integration,[18] but also that we can introduce the lifetime to describe the quasiparticles at least phenomenologically,[19] e.g., the photocurrent has been formulated in terms of the Green function in the most sophisticated photoemission theory.[20]

Bearing this situation in mind, we proceed to derive the Green function for general potentials. In Sec. II we prepare the bra (left-hand side) and ket (right-hand side) solutions for the homogeneous Dirac equation, both of which are necessary to construct the Green function, and obtain the identities that stand on their radial solutions. These identities play a decisive role in Sec. III where we obtain the Green function. To avoid any mathematical ambiguity, we show the equations in every step of the derivation, in particular, the difference between the right- and left-hand-side solutions, which is often overlooked even in the case of the scalar differential equations, such as the Schrödinger equation.

II. THE DIRAC EQUATION, SOLUTIONS, AND WRONSKIAN RELATION

The Dirac Hamiltonian is written in the form

$$\hat{H}=-ic\boldsymbol{\alpha}\cdot\nabla+c^2\beta+V(\mathbf{r}) , \tag{1}$$

where c is the light velocity in atomic units.[21] The matrices $\boldsymbol{\alpha}$ and β are given in Dirac's notation as

$$\boldsymbol{\alpha}=\begin{bmatrix}0 & \boldsymbol{\sigma}\\ \boldsymbol{\sigma} & 0\end{bmatrix} , \quad \beta=\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix} , \tag{2}$$

where $\boldsymbol{\sigma}=(\sigma_x,\sigma_y,\sigma_z)$ are the Pauli spin operators. The potential matrix $V(\mathbf{r})$ is generally decomposed into the form

$$V(\mathbf{r})=\begin{bmatrix}v_+(\mathbf{r}) & u(\mathbf{r})\\ u(\mathbf{r}) & v_-(\mathbf{r})\end{bmatrix} , \tag{3}$$

and its elements may be complex (the optical potential). In the most general case, they can be described by the *effective* scalar and vector potentials $v(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$ as[13,14]

$$v_+(\mathbf{r})=v_-(\mathbf{r})=v(\mathbf{r}) , \quad u(\mathbf{r})=\boldsymbol{\sigma}\cdot\mathbf{A}(\mathbf{r}) . \tag{4}$$

But in view of application to ferromagnets, an approximation can be employed where the *internal* magnetostatic field, $\mathbf{B}(\mathbf{r})=\nabla\times\mathbf{A}(\mathbf{r})$ couples only to the spin of electrons, and we find[15,16,22–24]

$$v_{\pm}(\mathbf{r})=v(\mathbf{r})\pm\boldsymbol{\sigma}\cdot\mathbf{B}(\mathbf{r}) , \quad u(\mathbf{r})=0 . \tag{5}$$

Let $|Z^R\rangle$ and $\langle Z^L|$ be right- and left-hand-side bispinor solutions of the Dirac equation

$$(E-\hat{H})|Z^R\rangle=0 , \tag{6a}$$

$$\langle Z^L|(E-\hat{H})=0 , \tag{6b}$$

where E is the *complex* energy including the rest mass energy c^2. The left-hand-side solution $\langle Z^L|$ can be understood as the Hermitian conjugate of the right-hand-side solution for the adjoint equation

$$(E^*-\hat{H}^\dagger)|Z^L\rangle=0 , \tag{6b'}$$

where $\hat{H}^\dagger$ may not be equal to $\hat{H}$ owing to the complex potentials. The solutions can be conveniently described by expansions in terms of the spin-angular functions[14]

$$\langle\hat{\mathbf{r}}|\chi_\kappa^\mu\rangle=\sum_{s=\pm1/2}C(l,\tfrac{1}{2},j;\mu-s,s)Y_l^{\mu-s}(\hat{\mathbf{r}})\chi^s , \tag{7}$$

where $Y_l^m(\hat{\mathbf{r}})$ are the usual spherical harmonics, χ^s are the Pauli two-component spinors, and $C(l,\frac{1}{2},j;\mu-s,s)$ the Clebsch-Gordan coefficients, and hereafter we write the coordinate as $\mathbf{r}=(r,\hat{\mathbf{r}})$ dividing into the radial and angular parts. The quantum numbers κ incorporate the orbital and total-angular-momentum numbers l and j, as $\kappa=-l-1$ for $j=l+\frac{1}{2}$ and $\kappa=l$ for $j=l-\frac{1}{2}$, the magnetic quantum numbers are $\mu=-j,-j+1,\ldots,j-1,j$. Expressing the solutions as

$$|Z^R\rangle=\sum_{\kappa,\mu}\begin{bmatrix}\psi_{\kappa\mu}^R(r) & |\chi_\kappa^\mu\rangle\\ i\phi_{\kappa\mu}^R(r) & |\chi_{-\kappa}^\mu\rangle\end{bmatrix} \tag{8a}$$

and

$$\langle Z^L|=\sum_{\kappa,\mu}(\psi_{\kappa\mu}^L(r)\langle\chi_\kappa^\mu| , -i\phi_{\kappa\mu}^L(r)\langle\chi_{-\kappa}^\mu|) , \tag{8b}$$

we obtain coupled radial differential equations for the right-hand-side solutions

$$\begin{bmatrix}E-c^2 & -ic[d/dr+(-\kappa+1)/r]\\ -ic[d/dr+(\kappa+1)/r] & E+c^2\end{bmatrix}\begin{bmatrix}\psi_{\kappa\mu}^R(r)\\ i\phi_{\kappa\mu}^R(r)\end{bmatrix}=\sum_{\kappa',\mu'}\begin{bmatrix}u_{\kappa\mu\kappa'\mu'}^{+}(r) & u_{\kappa\mu\kappa'\mu'}(r)\\ \bar{u}_{\kappa\mu\kappa'\mu'} & v_{\kappa\mu\kappa'\mu'}^{-}(r)\end{bmatrix}\begin{bmatrix}\psi_{\kappa'\mu'}^R(r)\\ i\phi_{\kappa'\mu'}^R(r)\end{bmatrix} \tag{9a}$$

and for the left-hand-side solutions

$$[\psi_{\kappa\mu}^L(r),-i\phi_{\kappa\mu}^L(r)]\begin{bmatrix}E-c^2 & -ic[d/dr+(-\kappa+1)/r]\\ -ic[d/dr+(\kappa+1)/r] & E+c^2\end{bmatrix}$$
$$=\sum_{\kappa',\mu'}[\psi_{\kappa'\mu'}^L(r),-i\phi_{\kappa'\mu'}^L(r)]\begin{bmatrix}v_{\kappa'\mu'\kappa\mu}^{+}(r) & u_{\kappa'\mu'\kappa\mu}(r)\\ \bar{u}_{\kappa'\mu'\kappa\mu}(r) & v_{\kappa'\mu'\kappa\mu}^{-}(r)\end{bmatrix} , \tag{9b}$$

where the potentials, in the angular-momentum representation, are defined by

$$v_{\kappa\mu\kappa'\mu'}^{+}(r)=\langle\chi_\kappa^\mu|v_+(\mathbf{r})|\chi_{\kappa'}^{\mu'}\rangle , \tag{10a}$$

$$v_{\kappa\mu\kappa'\mu'}^{-}(r)=\langle\chi_{-\kappa}^\mu|v_-(\mathbf{r})|\chi_{-\kappa'}^{\mu'}\rangle , \tag{10b}$$

$$u_{\kappa\mu\kappa'\mu'}(r)=\langle\chi_\kappa^\mu|u(\mathbf{r})|\chi_{-\kappa'}^{\mu'}\rangle , \tag{10c}$$

$$\bar{u}_{\kappa\mu\kappa'\mu'}(r)=\langle\chi_{-\kappa}^\mu|u(\mathbf{r})|\chi_{\kappa'}^{\mu'}\rangle . \tag{10d}$$

In the following discussion we do not describe the direction of the magnetic field $\mathbf{B}$ (or the vector potential $\mathbf{A}$) explicitly unless it is necessary, since its information is already included in the above potential matrices. Recalling Eq. (6b'), we immediately recognize that the differentiation in Eq. (9b) should be understood as

$$f(r)\left[-ic\left[\frac{d}{dr}+\frac{1}{r}\right]\right]=ic\left[\frac{d}{dr}+\frac{1}{r}\right]f(r)$$

for an arbitrary function $f(r)$. Equations (9a) and (9b) are, therefore, identical if the potential matrices defined by Eqs. (10) satisfy the following special conditions:

$$v_{\kappa\mu\kappa'\mu'}^{\pm}=v_{\kappa'\mu'\kappa\mu}^{\pm}, \quad u_{\kappa\mu\kappa'\mu'}=-\bar{u}_{\kappa'\mu'\kappa\mu} . \tag{11}$$

Note that these conditions are satisfied in the cases of the muffin-tin potentials and of the magnetically polarized muffin-tin potentials choosing the z axis parallel to the magnetic field $\mathbf{B}$ in Eq. (5). Contrary to the case of the Schrödinger equation where the potential matrix can be always chosen in a symmetric form [the corresponding condition to Eq. (11)] employing the *real* spherical harmonics,[25] it is, however, generally impossible to find such a set of angular functions in our case.

Fortunately there is a relation between the right- and left-hand-side solutions that is particularly useful if the potential is not magnetically polarized. Introducing the time-reversal operator K as[26]

$$K=-i\begin{bmatrix}\sigma_y & 0\\ 0 & \sigma_y\end{bmatrix}K_0 , \tag{12}$$

where K_0 is the complex-conjugation operator, we find

$$\hat{H}^\dagger(\mathbf{B})=K\hat{H}(-\mathbf{B})K^{-1} . \tag{13}$$

We obtain, therefore, the left-hand-side solutions for the magnetic field $\mathbf{B}$ (or the vector potential $\mathbf{A}$) from the right-hand-side solutions for $-\mathbf{B}$ (or $-\mathbf{A}$) through the relation

$$\langle Z^L(\mathbf{B})| = [K|Z^R(-\mathbf{B})\rangle]^\dagger \ . \tag{14}$$

Knowing the time-reversal operation on the spin-angular functions as[27]

$$-i\sigma_y K_0|\chi_\kappa^\mu\rangle = (-1)^{\mu+1/2} S_\kappa |\chi_\kappa^{-\mu}\rangle \ , \tag{15}$$

the relation is translated into the radial solutions

$$\begin{bmatrix} \psi_{\kappa\mu}^L(r;\mathbf{B}) \\ \phi_{\kappa\mu}^L(r;\mathbf{B}) \end{bmatrix} = (-1)^{\mu-1/2} S_\kappa \begin{bmatrix} \psi_{\kappa-\mu}^R(r;-\mathbf{B}) \\ \phi_{\kappa-\mu}^R(r;-\mathbf{B}) \end{bmatrix} , \tag{16}$$

where $S_\kappa = \kappa/|\kappa|$. We now recognize that the left-hand-side radial solutions can be always obtained from the right-hand-side solutions in the nonmagnetic case ($\mathbf{B}=\mathbf{0}$), even if the potential matrices in Eqs. (10) do not satisfy the conditions of Eq. (11), i.e., the right- and left-hand-side radial solutions are not identical. This relation is also useful for the magnetic case in view of programming a computer code, since all necessary solutions can be calculated by the right-hand-side-type differential equation solver.

Subtracting Eq. (9b) from Eq. (9a) after multiplying Eq. (9a) by $(\psi_{\kappa\mu}^L(r), -i\phi_{\kappa\mu}^L(r))$ from the left-hand side and Eq. (9b) by $(\psi_{\kappa\mu}^R(r), i\phi_{\kappa\mu}^R(r))^T$ from the right-hand side and taking the summation over κ and μ, we obtain a generalized Wronskian relation between the right- and left-hand-side solutions

$$[\langle Z^L|, |Z^R\rangle] \equiv \sum_{\kappa,\mu} cr^2 [\psi_{\kappa\mu}^L(r)\phi_{\kappa\mu}^R(r) - \phi_{\kappa\mu}^L(r)\psi_{\kappa\mu}^R(r)] = \text{const.} \tag{17}$$

Since this Wronskian value does not depend on r, we can perform its calculation at an arbitrary position, for example, where the potential is zero or where it takes a simple asymptotic form.

So far we have learned a general property that solutions of the Dirac equation should possess. Let us now consider the boundry conditions by which the solutions can be characterized. Since the Hamiltonian has no spherical symmetry due to a general form of the potential, the angular momentum is not constant through the scattering any more; that is, for the incident wave with a certain angular momentum specified by (κ,μ), the scattering wave contains various angular momenta (κ',μ'). It is, however, obvious that these kind of scattering states are still well characterized by the angular momentum of the incident waves, i.e., (κ,μ).[23,24] More precisely, for any incidence condition, the scattering state (so-called regular solutions) can be uniquely described by the linear combination of these solutions owing to the linearity of the Dirac equation. Now suppose a set of solutions. Each has only an outgoing wave characterized by one kind of angular momentum (κ,μ) outside of the cell. These solutions are irregular, since they cannot be expressed by any linear combination of the scattering-state (regular) solutions. In the same manner as the regular solutions, these irregular solutions can be characterized by their own outgoing waves. We write the regular (J) and irregular (H) solutions as

$$|J_{\kappa\mu}^R\rangle = \sum_{\kappa',\mu'} \begin{bmatrix} \psi_{\kappa'\mu'\kappa\mu}^{R(1)}(r)|\chi_{\kappa'}^{\mu'}\rangle \\ i\phi_{\kappa'\mu'\kappa\mu}^{R(1)}(r)|\chi_{-\kappa'}^{\mu'}\rangle \end{bmatrix} , \tag{18a}$$

$$|H_{\kappa\mu}^R\rangle = \sum_{\kappa',\mu'} \begin{bmatrix} \psi_{\kappa'\mu'\kappa\mu}^{R(2)}(r)|\chi_{\kappa'}^{\mu'}\rangle \\ i\phi_{\kappa'\mu'\kappa\mu}^{R(2)}(r)|\chi_{-\kappa'}^{\mu'}\rangle \end{bmatrix} , \tag{18b}$$

for the right-hand-side solutions and

$$\langle J_{\kappa\mu}^L| = \sum_{\kappa',\mu'} (\psi_{\kappa'\mu'\kappa\mu}^{L(1)}(r)\langle\chi_{\kappa'}^{\mu'}| \ , \ -i\phi_{\kappa'\mu'\kappa\mu}^{L(1)}(r)\langle\chi_{-\kappa'}^{\mu'}|) \ , \tag{18c}$$

$$\langle H_{\kappa\mu}^L| = \sum_{\kappa',\mu'} (\psi_{\kappa'\mu'\kappa\mu}^{L(2)}(r)\langle\chi_{\kappa'}^{\mu'}| \ , \ -i\phi_{\kappa'\mu'\kappa\mu}^{L(2)}(r)\langle\chi_{-\kappa'}^{\mu'}|) \ , \tag{18d}$$

for the left-hand-side solutions. Their asymptotic forms are given outside the cell by

$$\begin{bmatrix} \psi_{\kappa'\mu'\kappa\mu}^{R,L(1)}(r) \\ \psi_{\kappa'\mu'\kappa\mu}^{R,L(1)}(r) \end{bmatrix} \to \begin{bmatrix} j_{l'}(kr)\delta_{\kappa'\mu'\kappa\mu} + h_{l'}^{(1)}(kr) t_{\kappa'\mu'\kappa\mu}^{R,L} \\ ckS_{\kappa'}/(E+c^2)[j_{\bar{l}'}(kr)\delta_{\kappa'\mu'\kappa\mu} + h_{\bar{l}'}^{(1)}(kr) t_{\kappa'\mu'\kappa\mu}^{R,L}] \end{bmatrix} \tag{19a}$$

and

$$\begin{bmatrix} \psi_{\kappa'\mu'\kappa\mu}^{R,L(2)}(r) \\ \psi_{\kappa'\mu'\kappa\mu}^{R,L(2)}(r) \end{bmatrix} \to \begin{bmatrix} h_{l'}^{(1)}(kr)\delta_{\kappa'\mu'\kappa\mu} \\ ckS_{\kappa'}/(E+c^2) h_{\bar{l}'}^{(1)}(kr)\delta_{\kappa'\mu'\kappa\mu} \end{bmatrix} , \tag{19b}$$

where $\bar{l} = l - S_\kappa$, $k = \sqrt{E^2 - c^4}/c$, and the spherical Bessel $j_l(z)$ and the first kind of spherical Hankel $h_l^{(1)}(z)$ functions are defined in the usual manner.[28] Kronecker's $\delta_{\kappa'\mu'\kappa\mu}$ stands for $\delta_{\kappa'\kappa}\delta_{\mu'\mu}$.

Since the Wronskian relation Eq. (17) holds for any pair of right- and left-hand-side solutions, using the asymptotic forms given by Eqs. (19a) and (19b) we obtain

$$[\langle J_{\kappa\mu}^L|, |H_{\kappa'\mu'}^R\rangle] = \sum_{\kappa'',\mu''} cr^2 [\psi_{\kappa''\mu''\kappa\mu}^{L(1)}(r)\phi_{\kappa''\mu''\kappa'\mu'}^{R(2)}(r) - \phi_{\kappa''\mu''\kappa\mu}^{L(1)}(r)\psi_{\kappa''\mu''\kappa'\mu'}^{R(2)}(r)] = W\delta_{\kappa\mu\kappa'\mu'} \tag{20a}$$

and also for another couple

$$[\langle H^L_{\kappa\mu}|, |J^R_{\kappa'\mu'}\rangle] = -W\delta_{\kappa\mu\kappa'\mu'} , \tag{20b}$$

where the Wronskian W is common for any diagonal and is given by

$$W = -\frac{1}{ik}\frac{c^2}{E+c^2} . \tag{21}$$

In the derivation of Eqs. (20a), (20b), and (21), we have used the formulas[28]

$$\begin{aligned} j_l(z)n_{l-1}(z) - n_l(z)j_{l-1}(z) &= \frac{1}{z^2} \quad (l>0) , \\ j_l(z)n_{l+1}(z) - n_l(z)j_{l+1}(z) &= -\frac{1}{z^2} \quad (l\geq 0) , \end{aligned} \tag{22}$$

where $n_l(z)$ are the spherical Neumann functions and stand in the relation $h_l^{(1)} = j_l + in_l$. We have two other identities between the regular (irregular) solutions themselves

$$[\langle J^L_{\kappa\mu}|, |J^R_{\kappa'\mu'}\rangle] = 0 , \tag{23a}$$

$$[\langle H^L_{\kappa\mu}|, |H^R_{\kappa'\mu'}\rangle] = 0 . \tag{23b}$$

While Eq. (23b) is rather clear, Eq. (23a) is also recognized in the following. Suppose the asymptotic form of the potential at the nucleus, where the spherically symmetric nuclear Coulomb potential is dominant,[29] i.e., the potential matrices defined by Eqs. (10) are entirely diagonal (equivalent to the case of the nonmagnetic muffin-tin potentials). Then we can choose a set of right- and left-hand-side regular solutions of which radial solutions are, at the nucleus, identical and diagonal with respect to the angular momentum (κ,μ). The Wronskian relation is zero for any pair of these solutions and also for any pair of right- and left-hand-side solutions that are expressed by their linear combinations. Since regular solutions of a linear differential equation system can be expressed by the linear combination of another set of regular solutions that satisfy the other boundary conditions, we can obtain Eq. (23a). Calculating Eq. (23a) with use of the asymptotic form of Eq. (19a), we find the relation between the right- and left-hand-side t matrices as

$$t^L_{\kappa'\mu'\kappa\mu} = t^R_{\kappa\mu\kappa'\mu'} . \tag{24}$$

Since t^L is related to t^R through successive operations, time reversal, and Hermitian conjugation, the relation is understood as the reciprocity theorem for the single-site scattering

$$t^R_{\kappa'\mu'\kappa\mu}(\mathbf{B}) = (-1)^{\mu'-\mu} S_{\kappa'} S_\kappa t^R_{\kappa-\mu\kappa'-\mu'}(-\mathbf{B}) . \tag{25}$$

While Eq. (24) holds for the t matrices of the same magnetization direction, the reciprocity theorem gives the relation between opposite magnetizations. This simply means that the theorem holds if the whole system is taken into account. In a similar way, Eqs. (14) and (16) can be rewritten more concretely including the boundary conditions as

$$\langle J^L_{\kappa\mu}(\mathbf{B})| = (-1)^{\mu-1/2} S_\kappa [K|J^R_{\kappa-\mu}(-\mathbf{B})\rangle]^\dagger , \tag{26a}$$

$$\langle H^L_{\kappa\mu}(\mathbf{B})| = (-1)^{\mu-1/2} S_\kappa [K|H^R_{\kappa-\mu}(-\mathbf{B})\rangle]^\dagger , \tag{26b}$$

and for the radial solutions

$$\begin{bmatrix} \psi^{L(1,2)}_{\kappa'\mu'\kappa\mu}(r;\mathbf{B}) \\ \phi^{L(1,2)}_{\kappa'\mu'\kappa\mu}(r;\mathbf{B}) \end{bmatrix} = (-1)^{\mu'-\mu} S_{\kappa'} S_\kappa \begin{bmatrix} \psi^{R(1,2)}_{\kappa'-\mu'\kappa-\mu}(r;-\mathbf{B}) \\ \phi^{R(1,2)}_{\kappa'-\mu'\kappa-\mu}(r;-\mathbf{B}) \end{bmatrix} . \tag{27}$$

Any solutions of the linear differential equation can be described by a linear combination of regular and irregular solutions. This general statement is expressed in our case as

$$|Z^R\rangle = \sum_{\kappa,\mu} (C^{R(1)}_{\kappa\mu}|J^R_{\kappa\mu}\rangle + C^{R(2)}_{\kappa\mu}|H^R_{\kappa\mu}\rangle) , \tag{28a}$$

and

$$\langle Z^L| = \sum_{\kappa,\mu} (C^{L(1)}_{\kappa\mu}\langle J^L_{\kappa\mu}| + C^{L(2)}_{\kappa\mu}\langle H^L_{\kappa\mu}|) , \tag{28b}$$

for any right- and left-hand-side solutions $|Z^R\rangle$ and $\langle Z^L|$. The coefficients can be determined through the Wronskian relations given by Eqs. (20a), (20b), (23a), and (23b) as

$$C^{R(1)}_{\kappa\mu} = -\frac{1}{W}[\langle H^L_{\kappa\mu}|, |Z^R\rangle] , \tag{29a}$$

$$C^{R(2)}_{\kappa\mu} = \frac{1}{W}[\langle J^L_{\kappa\mu}|, |Z^R\rangle] , \tag{29b}$$

$$C^{L(1)}_{\kappa\mu} = \frac{1}{W}[\langle Z^L|, |H^R_{\kappa\mu}\rangle] , \tag{29c}$$

$$C^{L(2)}_{\kappa\mu} = -\frac{1}{W}[\langle Z^L|, |J^R_{\kappa\mu}\rangle] . \tag{29d}$$

The Wronskian relation Eq. (17) can be also described in terms of these coefficients as

$$[\langle Z^L|, |Z^R\rangle] = W\sum_{\kappa,\mu}[C^{L(1)}_{\kappa\mu}C^{R(2)}_{\kappa\mu} - C^{L(2)}_{\kappa\mu}C^{R(1)}_{\kappa\mu}] . \tag{30}$$

Since $|Z^R\rangle$ and $\langle Z^L|$ are arbitrary solutions, we can obtain various identities for the radial solutions comparing Eq. (17) with Eq. (30). Recalling Eqs. (8a) and (8b) if we set

$$\begin{bmatrix} \psi^R_{\kappa''\mu''} \\ \phi^R_{\kappa''\mu''} \\ \psi^L_{\kappa''\mu''} \\ \phi^L_{\kappa''\mu''} \end{bmatrix} = \begin{bmatrix} 0 \\ \delta_{\kappa''\mu''\kappa'\mu'} \\ \delta_{\kappa''\mu''\kappa\mu} \\ 0 \end{bmatrix}, \begin{bmatrix} \delta_{\kappa''\mu''\kappa'\mu'} \\ 0 \\ 0 \\ \delta_{\kappa''\mu''\kappa\mu} \end{bmatrix}$$

at a certain position r, we obtain the identities

$$\sum_{\kappa'',\mu''} cr^2[\psi^{L(1)}_{\kappa'\mu'\kappa''\mu''}(r)\phi^{R(2)}_{\kappa\mu\kappa''\mu''}(r) - \psi^{L(2)}_{\kappa'\mu'\kappa''\mu''}(r)\phi^{R(1)}_{\kappa\mu\kappa''\mu''}(r)] = W\delta_{\kappa'\mu'\kappa\mu} , \tag{31a}$$

$$\sum_{\kappa'',\mu''} cr^2[\phi^{L(1)}_{\kappa'\mu'\kappa''\mu''}(r)\psi^{R(2)}_{\kappa\mu\kappa''\mu''}(r) - \phi^{L(2)}_{\kappa'\mu'\kappa''\mu''}(r)\psi^{R(1)}_{\kappa\mu\kappa''\mu''}(r)] = -W\delta_{\kappa'\mu'\kappa\mu} ; \tag{31b}$$

and also for

$$\begin{bmatrix} \psi^R_{\kappa''\mu''} \\ \phi^R_{\kappa''\mu''} \\ \psi^L_{\kappa''\mu''} \\ \phi^L_{\kappa''\mu''} \end{bmatrix} = \begin{bmatrix} 0 \\ \delta_{\kappa''\mu''\kappa'\mu'} \\ 0 \\ \delta_{\kappa''\mu''\kappa\mu} \end{bmatrix} \begin{bmatrix} \delta_{\kappa''\mu''\kappa'\mu'} \\ 0 \\ \delta_{\kappa''\mu''\kappa\mu} \\ 0 \end{bmatrix},$$

we have

$$\sum_{\kappa'',\mu''} cr^2[\psi^{L(1)}_{\kappa'\mu'\kappa''\mu''}(r)\psi^{R(2)}_{\kappa\mu\kappa''\mu''}(r)-\psi^{L(2)}_{\kappa'\mu'\kappa''\mu''}(r)\psi^{R(1)}_{\kappa\mu\kappa''\mu''}(r)]=0 , \tag{32a}$$

$$\sum_{\kappa'',\mu''} cr^2[\phi^{L(1)}_{\kappa'\mu'\kappa''\mu''}(r)\phi^{R(2)}_{\kappa\mu\kappa''\mu''}(r)-\phi^{L(1)}_{\kappa'\mu'\kappa''\mu''}(r)\phi^{R(1)}_{\kappa\mu\kappa''\mu''}(r)]=0 . \tag{32b}$$

If the right- and left-hand-side radial solutions are identical [for the potentials satisfying the conditions of Eq. (11)], then Eqs. (31a) and (31b) are equivalent, but none of the identities becomes trivial. Only if all radial solutions are diagonal (e.g., in the case of the spherically symmetric nonmagnetic potential), the identities Eqs. (31a) and (31b) are equivalent to the Wronskian relation.[17] Comparing with the Wronskian relations Eqs. (20a), (20b), (23a), and (23b) in which the summation is taken over the former subscript, these identities might be called the second kind of Wronskian relation. The relation between the first and second kind of Wronskian relations may be understood as an analog to that of the matrix products between unitary matrices and their inverse, which also yield unity for the interchanged multiplication order.

III. GREEN FUNCTION

We define the retarded (outgoing wave) Green function as

$$G(\mathbf{r},\mathbf{r}';E)=\begin{cases} \frac{1}{W}\sum_{\kappa,\mu}\langle \mathbf{r}|J^R_{\kappa\mu}\rangle\langle H^L_{\kappa\mu}|\mathbf{r}'\rangle & \text{for } r<r' \\ \frac{1}{W}\sum_{\kappa,\mu}\langle \mathbf{r}|H^R_{\kappa\mu}\rangle\langle J^L_{\kappa\mu}|\mathbf{r}'\rangle & \text{for } r>r' , \end{cases} \tag{33}$$

and it will be seen that $G(\mathbf{r},\mathbf{r}';E)$ satisfies the following inhomogeneous equations:

$$(E-\hat{H})G(\mathbf{r},\mathbf{r}';E)=\delta(\mathbf{r}-\mathbf{r}') \tag{34a}$$

and

$$G(\mathbf{r},\mathbf{r}';E)(E-\hat{H})=\delta(\mathbf{r}-\mathbf{r}') . \tag{34b}$$

In Eq. (34b) the Hamiltonian operates on the Green function through the coordinator $\mathbf{r}'$. For the sake of convenience, we write the Green function in a 2×2 matrix form[14]

$$G(\mathbf{r},\mathbf{r}';E)=\begin{bmatrix} G_{11}(\mathbf{r},\mathbf{r}') & G_{12}(\mathbf{r},\mathbf{r}') \\ G_{21}(\mathbf{r},\mathbf{r}') & G_{22}(\mathbf{r},\mathbf{r}') \end{bmatrix} , \tag{35}$$

and decompose its elements into the radial and angular parts by means of the angular-momentum expansion as

$$G_{11}(\mathbf{r},\mathbf{r}')=\sum_{\substack{\kappa,\mu\\ \kappa',\mu'}}\langle\hat{\mathbf{r}}|\chi^\mu_\kappa\rangle G^{11}_{\kappa\mu\kappa'\mu'}(r,r')\langle\chi^{\mu'}_{\kappa'}|\hat{\mathbf{r}}'\rangle , \tag{36a}$$

$$G_{12}(\mathbf{r},\mathbf{r}')=\sum_{\substack{\kappa,\mu,\\ \kappa',\mu'}}\langle\hat{\mathbf{r}}|\chi^\mu_\kappa\rangle G^{12}_{\kappa\mu\kappa'\mu'}(r,r')\langle\chi^{\mu'}_{-\kappa'}|\hat{\mathbf{r}}'\rangle , \tag{36b}$$

$$G_{21}(\mathbf{r},\mathbf{r}')=\sum_{\substack{\kappa,\mu,\\ \kappa',\mu'}}\langle\hat{\mathbf{r}}|\chi^\mu_{-\kappa}\rangle G^{21}_{\kappa\mu\kappa'\mu'}(r,r')\langle\chi^{\mu'}_{\kappa'}|\hat{\mathbf{r}}'\rangle , \tag{36c}$$

$$G_{22}(\mathbf{r},\mathbf{r}')=\sum_{\substack{\kappa,\mu,\\ \kappa',\mu'}}\langle\hat{\mathbf{r}}|\chi^\mu_{-\kappa}\rangle G^{22}_{\kappa\mu\kappa'\mu'}(r,r')\langle\chi^{\mu'}_{-\kappa'}|\hat{\mathbf{r}}'\rangle . \tag{36d}$$

It is clear from its definition that $G(\mathbf{r},\mathbf{r}';E)$ satisfies Eqs. (34a) and (34b) when $\mathbf{r}\neq\mathbf{r}'$. On the other hand, the radial Green functions have a discontinuity at $r=r'$, of which values are obtained from Eqs. (31a), (31b), (32a), and (32b) as

$$G^{12}_{\kappa\mu\kappa'\mu'}(r,r')|^{r=r'+0}_{r=r'-0}=G^{21}_{\kappa\mu\kappa'\mu'}(r,r')|^{r=r'+0}_{r=r'-0} =i\frac{1}{cr^2}\delta_{\kappa\mu\kappa'\mu'} , \tag{37a}$$

$$G^{11}_{\kappa\mu\kappa'\mu'}(r,r')|^{r=r'+0}_{r=r'-0}=G^{22}_{\kappa\mu\kappa'\mu'}(r,r')|^{r=r'+0}_{r=r'-0} =0 . \tag{37b}$$

This discontinuity is to be differentiated in the operation of the Hamiltonian [refer to Eqs. (9a) and (9b)] and produces the δ function. Knowing the expression of the δ function

$$\delta(\mathbf{r}-\mathbf{r}')=\frac{1}{r^2}\delta(r-r')\sum_{\kappa,\mu}\langle\hat{\mathbf{r}}|\chi^\mu_\kappa\rangle\langle\chi^\mu_\kappa|\hat{\mathbf{r}}'\rangle , \tag{38}$$

we obtain Eqs. (34a) and (34b) and have, therefore, proven that the Green function for general potentials is given by Eq. (33).

Taking the Hermitian conjugation after operating the time-reversal operator K from the left-hand side and its inverse from the right-hand side on Eqs. (34), we obtain the reciprocity of the Green function

$$G(\mathbf{r},\mathbf{r}';E,-\mathbf{B})=[KG(\mathbf{r}',\mathbf{r};E,\mathbf{B})K^{-1}]^\dagger . \tag{39}$$

This can be also proven directly from the definition of the Green functions Eq. (33) and the analogous relations to Eqs. (26), paying attention on the operation of K such as

$$(K|Z^L\rangle)^\dagger=\langle Z^L|K^{-1} .$$

In the case of the Schrödinger equation where the time reversal and Hermitian conjugation operations are formally identical,[30] the reciprocity is given simply by the interchange between $\mathbf{r}$ and $\mathbf{r}'$. Equation (39) can be written more precisely in terms of the radial Green functions as

$$G^{11}_{\kappa\mu\kappa'\mu'}(r,r';-\mathbf{B})=(-1)^{\mu-\mu'}S_\kappa S_{\kappa'}G^{11}_{\kappa'-\mu'\kappa-\mu}(r',r;\mathbf{B}) , \tag{40a}$$

$$G^{12}_{\kappa\mu\kappa'\mu'}(r,r';-\mathbf{B})=-(-1)^{\mu-\mu'}S_\kappa S_{\kappa'}G^{21}_{\kappa'-\mu'\kappa-\mu}(r',r;\mathbf{B}) , \tag{40b}$$

$$G^{21}_{\kappa\mu\kappa'\mu'}(r,r';-\mathbf{B})=-(-1)^{\mu-\mu'}S_\kappa S_{\kappa'}G^{12}_{\kappa'-\mu'\kappa-\mu}(r';r;\mathbf{B}) , \tag{40c}$$

$$G^{22}_{\kappa\mu\kappa'\mu'}(r,r';-\mathbf{B})=(-1)^{\mu-\mu'}S_\kappa S_{\kappa'}G^{22}_{\kappa'-\mu'\kappa-\mu}(r',r;\mathbf{B}) . \tag{40d}$$

For the nonmagnetic and spherically symmetric (muffin-tin) potentials, the radial Green functions are diagonal with respect to (κ,μ) and independent of μ, and Eqs. (40) are reduced to a very simple form, i.e., $G^{11}_\kappa(r,r')=G^{11}_\kappa(r',r)$, $G^{22}_\kappa(r,r')=G^{22}_\kappa(r',r)$, and $G^{12}_\kappa(r,r')=-G^{21}_\kappa(r',r)$. These simple relations are also true for the free-electron $[V(\mathbf{r})=0;t^R=t^L=0]$ radial Green functions which can be explicitly given by

$$G^{11}_\kappa(r,r')=-ik\frac{E+c^2}{c^2}\times\begin{cases} j_l(kr)h_l^{(1)}(kr') & \text{for } r<r' \\ h_l^{(1)}(kr)j_l(kr') & \text{for } r>r' \end{cases} , \tag{41a}$$

$$G^{12}_\kappa(r,r')=-\frac{k^2}{c}S_\kappa\times\begin{cases} j_l(kr)h_{\bar{l}}^{(1)}(kr') & \text{for } r<r' \\ h_l^{(1)}(kr)j_{\bar{l}}(kr') & \text{for } r>r' \end{cases} , \tag{41b}$$

$$G^{21}_\kappa(r,r')=\frac{k^2}{c}S_\kappa\times\begin{cases} j_{\bar{l}}(kr)h_l^{(1)}(kr') & \text{for } r<r' \\ h_{\bar{l}}^{(1)}(kr)j_l(kr') & \text{for } r>r' \end{cases} , \tag{41c}$$

$$G^{22}_\kappa(r,r')=-ik\frac{E-c^2}{c^2}\times\begin{cases} j_{\bar{l}}(kr)h_{\bar{l}}^{(1)}(kr') & \text{for } r<r' \\ h_{\bar{l}}^{(1)}(kr)j_{\bar{l}}(kr') & \text{for } r>r' \end{cases} . \tag{41d}$$

In the above one should recognize that the off-diagonal radial Green functions G^{12}_κ and G^{21}_κ take the different function forms for the cases $r<r'$ and $r>r'$, i.e., the Green function for $r>r'$ cannot be obtained from that for $r<r'$ by the simple interchange between r and r'. This attributes to the fact that the right- and left-hand-side bispinor solutions Eqs. (8a) and (8b) are, in contrast to the case of the Schrödinger equation, given essentially in different forms. Together with Eqs. (36) we obtain the special relations for the free-electron Green function $G^{(0)}(\mathbf{r},\mathbf{r}';E)$ as

$$G^{(0)}_{22}(\mathbf{r},\mathbf{r}')=\frac{E-c^2}{E+c^2}G^{(0)}_{11}(\mathbf{r},\mathbf{r}') , \tag{42a}$$

$$G^{(0)}_{21}(\mathbf{r},\mathbf{r}')=G^{(0)}_{12}(\mathbf{r},\mathbf{r}') . \tag{42b}$$

The latter relation has been incorrectly stated in many articles following Rose's textbook.[14]

Although any particular assumption was not made on the form of potentials in the derivation of the Green function, it might be a problem to compute the radial solutions directly for the cell potentials, which are zero outside of the cell polyhedron, i.e., a potential jump is introduced at the boundary of the cell in both the radial and angular directions. We expect, therefore, a rather slow convergence in the angular-momentum expansion.[31] Fortunately, this difficulty does not become a real problem in the aim of electronic structure calculations or other applications where we need the Green function only inside of the cell, i.e., $\mathbf{r},\mathbf{r}'\in V_C$. If we introduce an additional potential outside the cell to smooth out the potential jump, then the Dyson equation becomes

$$G(\mathbf{r},\mathbf{r}';E)=G^{(0)}(\mathbf{r},\mathbf{r}';E)+\int_{V_C}G^{(0)}(\mathbf{r},\mathbf{r}'';E)V(\mathbf{r}'')G(\mathbf{r}'',\mathbf{r}';E)d\mathbf{r}''+\int_{\bar{V}_C}G^{(0)}(\mathbf{r},\mathbf{r}'';E)V(\mathbf{r}'')G(\mathbf{r}'',\mathbf{r}';E)d\mathbf{r}'' , \tag{43a}$$

where $\bar{V}_C$ denotes the volume outside the cell. Since $\mathbf{r}$ and $\mathbf{r}'$ are not included in the integral region $\bar{V}_C$, i.e., $G^{(0)}$ and G are the solutions for the homogeneous Dirac equations, the last term on the right-hand side can be transformed into the surface integrals on the boundry of the cell and on the sphere far apart from the cell. Knowing the asymptotic forms of $G^{(0)}$ and G, and $\mathrm{Im}E>0$ for the retarded Green functions, the latter surface integral is found to vanish. After the partial integration, we obtain the expression for the last term as

$$-ic\int_{\partial V_C}G^{(0)}(\mathbf{r},\mathbf{r}'';E)\boldsymbol{\alpha}G(\mathbf{r}'',\mathbf{r}';E)\cdot d\mathbf{S} , \tag{43b}$$

where the surface normal vector $d\mathbf{S}$ is outwardly directed. We recognize now that the potential outside of the cell can be formally eliminated from the Dyson equation.[32] It is worth noting that even this surface integral is to be canceled out with the contribution of the other cells in the multiple-scattering theory. We thus need the radial solutions only for the reasonably smooth cell potentials to construct the Green function.

Taking into account scatterings by the other crystal atoms, the single-site Green function G^{ST} can be written in the form

$$G^{ST}(\mathbf{r},\mathbf{r}';E,\mathbf{k})=\sum_{\substack{\kappa,\mu,\\ \kappa',\mu'}}\langle\mathbf{r}|J^R_{\kappa\mu}\rangle\tau_{\kappa\mu\kappa'\mu'}(E,\mathbf{k})\langle J^L_{\kappa'\mu'}|\mathbf{r}'\rangle + G(\mathbf{r},\mathbf{r}';E) . \tag{44}$$

The determination of $\tau_{\kappa\mu\kappa'\mu'}(E,\mathbf{k})$ is a subject of multiple-scattering theory[33] in which the wave vector $\mathbf{k}$ is three dimensional for the bulk and two dimensional for the surface systems. It should be emphasized, however, that $\langle J^L_{\kappa'\mu'}|$ cannot be generally replaced by $\langle J^R_{\kappa'\mu'}|$ in Eq. (44). It can be done *only if* the energy E is real and the real potential $V(\mathbf{r})$ satisfies the conditions of Eq. (11), and their radial solutions, therefore, can be chosen as real functions. These conditions are far apart from what is called general.

Our procedure to derive the retarded Green function can be applied to other types of Green functions specified by those specific boundary conditions. For example, we obtain the advanced (incoming wave) Green function, if we employ the second kind of spherical

Hankel functions instead of the first kind in Eq. (19b). In the calculation of the ground-state electron structure where we need not specify which waves are incident or scattered, the boundry condition can be chosen at the nucleus. Since the numerical methods to obtain right-hand-side solutions, which also give left-hand-side solutions through Eq. (14), have been thoroughly studied already for various boundary conditions,[34,35] we do not discuss them here.

IV. CONCLUDING REMARKS

The fully relativistic single-site Green function has been rigorously derived for the generally shaped and magnetically polarized complex cell potential. In the derivation we have introduced the identities (the second kind of Wronskian relation) by which the jump condition of the Green function at $r = r'$ has been determined. The obtained expression for the Green function is also correct even if the energy is chosen as complex, so that it can make the application possible to the electronic spectroscopies[36] where the lifetime of electrons may play an important role.

It has been shown that the left-hand-side solutions are the necessary ingredients as well as the right-hand-side solutions, to construct the Green function, which is generally *not* the Hermitian conjugate of the right-hand-side solutions. The importance of recognizing this fact has been demonstrated through the whole of our discussion, in particular, in the explicit expression for the free-electron Green function.

In numerical respect, it has also been shown how to obtain the left-hand-side solutions from the right-hand-side solutions. They are related to each other through successive operations, time reversal, and Hermitian conjugation. This relation provides a proof for the reciprocity of the relativistic Green function.

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