Generalized multiple-scattering theory

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Multiple-scattering theory, as it is applicable to metallic systems, is generalized systematically compared with the usual formulation. The generalization refers to the reference system, which conventionally is free space, but which can be chosen to be much more general. For example, in describing a binary alloy, a defect in a metal, or a finite impurity-cluster model for the latter system, the reference system may be an average medium, the unperturbed metallic host system, or the finite host cluster, respectively. Applications are indicated for the generalized Friedel sum rule, the local density of states, and the transition probability of a Bloch electron. A state in a system is shown to be built up of properly generalized incoming and outgoing waves.

I. INTRODUCTION

Multiple-scattering theory was first applied in solids[1,2] in order to describe the electronic band structure[3] of perfectly crystalline material. It formed an intriguing alternative to the agumented-plane-wave method.[4] In both methods a muffin-tin approximation was used for the electronic potential. Technically, the methods were bound to give the same results.[5] Conceptually, however, the multiple-scattering approach was more appealing in taking full advantage of the special property of a muffin-tin potential of having a constant background potential, the so-called muffin-tin zero. The scattered waves could be followed exactly in a striking way, and consequently the equation for the crystalline electron eigenstates was exact.[6] The muffin-tin zero for an infinite solid, being effectively equivalent to free space, served as a reference system.

It remained that way even in later, more advanced developments of the multiple-scattering approach, aimed at the description of the electronic properties of defects in metals[7-9] and of random binary alloys.[10,11] For example, the former, dilute-alloy systems were described by the Korringa-Kohn-Rostoker (KKR) Green's-function method,[8,12] but both system and unperturbed host were described by the original multiple-scattering theory, with free space as a reference system. Although an initial impulse for using the host system as a reference system can be found in the work of Hamazaki,[13] this line of thought is largely ignored.[14] Ironically enough, in describing the binary-alloy system, the formal condition for the average potential in the KKR coherent-potential approximation is necessarily derived formally using that average medium as a type of reference system. But as soon as that formal condition is set down, it is routinely rewritten[10] in terms of the infinite matrices corresponding to the original binary-alloy system and further elaborated upon in that form.

In the present paper we will show that it is possible to formulate a generalized multiple-scattering theory in that the restriction to free space as a reference system is consequently relaxed. Generalized incoming and outgoing waves are defined, and various examples and applications are given. The generalized theory illustrates nicely the arbitrariness of the choice of reference system. The generalized equations to be derived reduce simply to the equations for the original multiple-scattering theory by taking the limit of free space as a reference system.

In Sec. II a formal treatment is given, with an emphasis on incoming and outgoing waves. In Sec. III formal results are illustrated by elaborating them in the mixed site–angular momentum representation. In Sec. IV a generalized Lloyd formula[14,15] for the density of states of a system, described with respect to a general reference system, is discussed in relation to a theorem by Krein[16] in formal scattering theory. In Sec. V a new expression is derived for the local density of states. Section VI is devoted to transition probabilities. Conclusions and prospects are formulated in Sec. VII.

II. INCOMING AND OUTGOING WAVES. FORMAL TREATMENT

The electronic behavior in a metallic system is determined by a potential to be written as

$$V = \sum_j V_j \, , \tag{1}$$

in which the summation runs over all atomic and vacancy positions in the system. Describing multiple-scattering theory[1-3] it is natural and also permissible to think of a muffin-tin representation of the potential. The original restriction to spherically symmetric single-site potentials can be relaxed, however. The final expressions contain only t matrices and can be derived for nonspherical potentials equally well, leading merely to t matrices which are nondiagonal in angular momentum. For example, the interesting Frenkel pair defect in which two metallic atoms occupy one lattice site in a dumbbell-like way, could be treated straightforwardly[17] in terms of the nondiagonal cluster t matrix of the two atoms. Further, recently[18,19] it has become more and more clear that even full cell potentials can be accounted for if their clearly nondiagonal t matrices are used. Since latter derivations

can be considered complications which can be taken care of at a later stage, the present treatment will be restricted to muffin-tin potentials.

The wave function of an electron in such a metallic system is given by the Lippmann-Schwinger equation

$$|\Psi\rangle = |\phi\rangle + G^r \Delta V |\Psi\rangle \ , \tag{2}$$

and is composed of an incident wave $|\phi\rangle$, being a regular solution of the Schrödinger equation for the reference system at the energy E, and a scattered wave being proportional to the potential difference

$$\Delta V = \sum_j V_j - \sum_j V_j^r \equiv \sum_j \Delta V_j \ . \tag{3}$$

The Green's function of the reference system

$$G^r = (E^+ - H^r)^{-1} \tag{4}$$

contains the energy E explicitly. However, we will write this energy as an argument for G^r only, if it is required for the sake of clarity. The system t matrix described with respect to the reference system, defined by

$$\Delta V |\Psi\rangle = T |\phi\rangle \ , \tag{5}$$

is given by

$$T = \Delta V + \Delta V G^r T = \Delta V + \Delta V G \Delta V \ . \tag{6}$$

The system Green's function $G = (E^+ - H)^{-1}$ is related to G^r by the Lippmann-Schwinger equation

$$G = G^r + G^r \Delta V G = G^r + G^r T G^r \ . \tag{7}$$

The site notation in (3) presupposes a one-to-one correspondence between the sites in the system and those in the reference system. This still includes systems such as binary alloys and dilute substitutional and interstitial alloys. Even possible lattice distortion in the latter systems can be accounted for, but for the moment we will omit this effect, restoring the situation in the final equations by a simple substitution.[14,15,20]

Multiple-scattering theory enters by the definition

$$\Delta V_j |\Psi\rangle = t_{\Delta V}^j |\Psi_j^{\text{inc}}\rangle \tag{8}$$

of an incoming wave at site j, to be distinguished from the incident wave $|\phi\rangle$, using a single-site t matrix defined by

$$t_{\Delta V}^j = \Delta V_j + \Delta V_j G^{rs_j} t_{\Delta V}^j \ . \tag{9}$$

Here G^{rs_j} denotes the Green's function $(E^+ - H_0 - V_j^r)^{-1}$ of a single reference-system potential V_j^r at site j. The kinetic-energy operator, which all Hamiltonians in multiple-scattering theory have in common, is denoted by the free-electron Hamiltonian H_0. The operator $t_{\Delta V}^j$, describing the scattering by a system potential in free space with respect to a reference-system potential at the same site, thus being an operator describing difference-scattering for potentials in free space, will turn out to be the building block of the generalized multiple-scattering theory.

The meaning of definition (8) becomes clearer after

rewriting it with the help of (9):

$$\Delta V_j |\Psi\rangle = \Delta V_j (1 + G^{rs_j} t_{\Delta V}^j) |\Psi_j^{\text{inc}}\rangle \ . \tag{10}$$

Apparently, the system state at site j can be written as a sum of two terms:

$$|\Psi\rangle_j = |\Psi_j^{\text{inc}}\rangle + G^{rs_j} t_{\Delta V}^j |\Psi_j^{\text{inc}}\rangle$$
$$\equiv |\Psi_j^{\text{inc}}\rangle + |\Psi_j^{\text{out}}\rangle \ , \tag{11}$$

the second term being necessarily the outgoing wave at site j. The site label j has to be added at the left-hand side, because the potential factor ΔV_j in (10) projects out only that local part of $|\Psi\rangle$. The composition of the outgoing wave being clear from its definition, insight into the composition of the incoming wave is obtained by reconsidering the system wave function (2) and writing it as

$$|\Psi\rangle = |\phi\rangle + G^r \sum_j \Delta V_j |\Psi\rangle = |\phi\rangle + G^r \sum_j t_{\Delta V}^j |\Psi_j^{\text{inc}}\rangle \ . \tag{12}$$

At site j, one can write

$$|\Psi\rangle_j = |\phi\rangle_j + {}_j G^r \sum_{j'(\neq j)} t_{\Delta V}^{j'} |\Psi_{j'}^{\text{inc}}\rangle$$
$$+ ({}_j G^r - {}_j G^{rs_j}) t_{\Delta V}^j |\Psi_j^{\text{inc}}\rangle + |\Psi_j^{\text{out}}\rangle \ , \tag{13}$$

where the left subscript at the Green's functions denotes at which site one is looking. Comparing this multicenter expansion of the system state with its one-center expansion (11), the incoming wave appears to be composed as follows:

$$|\Psi_j^{\text{inc}}\rangle = |\phi\rangle_j + {}_j G^r \sum_{j'(\neq j)} t_{\Delta V}^{j'} |\Psi_{j'}^{\text{inc}}\rangle$$
$$+ ({}_j G^r - {}_j G^{rs_j}) t_{\Delta V}^j |\Psi_j^{\text{inc}}\rangle \ . \tag{14}$$

For free space as a reference system the third term cancels, because then $G^r = G^{rs_j} = G^0 = (E^+ - H_0)^{-1}$, while the second term describes the contribution from the incoming waves scattered at all other sites, a well-known result reviewed nicely by Faulkner.[3] The second term in (14) in its general form has the same meaning, but the scattered waves at all other sites j' are now propagated to the site j by means of the Green's function of the reference system. The third term in (14) can be identified as a backscattering term. Part of the outgoing wave is scattered backwards by the reference system, to the extent that its Green's function differs from the single-site Green's function G^{rs_j}, contributing anew in this way to the incoming wave.

Since backscattering will be a common feature in all systems as soon as the reference system differs from free space, it is attractive to define a reduced propagator

$$G^{\text{red}} = G^r - G^{rs} \ , \tag{15}$$

which accounts for it automatically. In this definition the propagator G^{rs} works site diagonally only. As for its site properties, one could write (15) more explicitly as

$${}_j G_{j'}^{\text{red}} = {}_j G_{j'}^r - {}_j G^{rs_j} \delta_{jj'} \ . \tag{16}$$

In terms of this reduced propagator, expression (14) for

the incoming wave becomes

$$|\Psi_j^{\mathrm{inc}}\rangle = |\phi\rangle_j + {}_jG^{\mathrm{red}}\sum_{j'} t_{\Delta V}^{j'}|\Psi_{j'}^{\mathrm{inc}}\rangle . \tag{17}$$

For sites $j'\neq j$ the second term of (14) arises again, while the $j'=j$ term gives the third term of (14). In this way scattering of the incoming waves at all sites contributes to the incoming wave at a site j, if propagated properly by G^{red}.

The merit of the one-center form (11) is becoming clear. Outside the muffin-tin sphere the incoming wave is merely composed of regular solutions of the Schrödinger equation of the reference system. The incident wave is one, and G^{red} takes care of another one. The singular solution for the reference system, still contributing to G^r, is cancelled in G^{red} in favor of the outgoing wave, which will be seen explicitly in Sec. III. That means that the multicenter expressions (14) and (17) just connect regular solutions of the reference system. Apparently the multiple scattering, as it occurs in a system described with respect to a reference system, is a matter of the incoming waves. The outgoing wave in (11), being a singular solution for the reference system, simply serves as an extra term in order to complete the local state of the system, which is, of course, a regular solution of its Schrödinger equation.

By now the outgoing wave is written in terms of the incoming wave by Eq. (11), while for the incoming wave a multicenter expansion, in terms of the incident wave and all incoming waves, is given by Eqs. (14) or (17). Looking for scattered wave solutions, it is possible also to write these waves in terms of the incident wave only. A first form follows from Eq. (5) using the decomposition

$$T = \sum_j T_j , \tag{18}$$

and Eq. (3):

$$\Delta V_j |\Psi\rangle = T_j|\phi\rangle . \tag{19}$$

Combining the latter equation with Eq. (8), for the incoming wave in (14) and (17) one finds

$$|\Psi_j^{\mathrm{inc}}\rangle = |\phi\rangle_j + {}_jG^rT|\phi\rangle - {}_jG^{rs_j}T_j|\phi\rangle$$

$$= |\phi\rangle_j + {}_jG^{\mathrm{red}}T|\phi\rangle . \tag{20}$$

The second term in the second member describes the scattering of the incident wave by all centers, after which ${}_jG^r$ takes care of propagation to the center j. Part of the latter incoming wave amplitude is transformed in an outgoing wave, namely the part of $T|\phi\rangle$ which already ended up at site j. The third term corrects for that spurious contribution. The form of the third member is useful as a next step in exposing the different properties of the incoming wave. To that end, a further discussion of the t matrix T is required. In view of Eq. (6), the operator T_j in (18) can be defined as

$$T_j = \Delta V_j + \Delta V_j G^r T , \tag{21}$$

describing all multiple-scattering events finishing at site j. In addition, an operator $T_{jj'}$ can be defined as

$$T_{jj'} = \Delta V_j \delta_{jj'} + \Delta V_j G \Delta V_{j'} , \tag{22}$$

describing all multiple-scattering events starting at site j' and finishing at site j, mediated by the system propagator G.

It is clear from (22) and (21), with (6) and (18), that

$$T_j = \sum_{j'} T_{jj'} . \tag{23}$$

Another operator, denoted by T_j', arises through a summation over the other site label:

$$T_{j'}' = \sum_j T_{jj'} . \tag{24}$$

The latter operator, describing all multiple-scattering events starting at site j', is equal to

$$T_j' = \Delta V_j + TG^r\Delta V_j \tag{25}$$

and has the property (18) as well. With these means the t matrix T is usually written as the so-called multiple-scattering series

$$T = \sum t_j^\Delta + \sum_{j\neq j'} t_j^\Delta G^r t_{j'}^\Delta + \sum_{\substack{j\neq j' \\ j'\neq j''}} t_j^\Delta G^r t_{j'}^\Delta G^r t_{j''}^\Delta + \cdots , \tag{26}$$

in which

$$t_j^\Delta = \Delta V_j + \Delta V_j G^r t_j^\Delta$$

$$= (1-\Delta V_j G^r)^{-1}\Delta V_j = [(\Delta V_j)^{-1}-G^r]^{-1} . \tag{27}$$

Note the difference from the earlier definition of $t_{\Delta V}^j$. For free space as a reference system these two operators are identical. But for the general case the reader is invited to check that, while the operator $t_{\Delta V}^j$ allows for the decomposition (11), including its illuminating interpretation, the operator t_j^Δ does not. Regarding our subject it is therefore more appropriate to write T in terms of $t_{\Delta V}^j$. Using (21) and (16), one finds

$$T_j = \Delta V_j + \Delta V_j G^{\mathrm{red}}T + \Delta V_j G^{rs_j}T_j . \tag{28}$$

Using (9), this can be written in terms of the single-site scattering matrix $t_{\Delta V}^j$ as

$$T_j = t_{\Delta V}^j(1+G^{\mathrm{red}}T) , \tag{29}$$

which reveals that G^{red} mediates between all multiple scattering in the system due to all scattering centers and the center j.

Similarly one finds

$$T_j' = (1+TG^{\mathrm{red}})t_{\Delta V}^j . \tag{30}$$

With this, using (18) for T_j', the incoming wave (20) appears to be given by

$$|\Psi_j^{\mathrm{inc}}\rangle = |\phi\rangle_j + {}_jG^{\mathrm{red}}\sum_{j'}(1+TG^{\mathrm{red}})t_{\Delta V}^{j'}|\phi\rangle \tag{31}$$

as well, completely in terms of the incident wave, the t matrix T with respect to the reference system and the local scattering t matrix $t_{\Delta V}^j$.

For the outgoing wave the operator $T_{jj'}$, occurring in (22) to (24), is useful. This operator can be written as

$$T_{jj'} = [\delta_{jj'} + t^j_{\Delta V}(G^{\text{red}} + G^{\text{red}}TG^{\text{red}})]t^{j'}_{\Delta V} . \tag{32}$$

This follows from (22) by first substituting (7), and then applying (25). This gives

$$T_{jj'} = \Delta V_j \delta_{jj'} + \Delta V_j G^r T'_{j'} . \tag{33}$$

Now using (15) and (24), one finds

$$T_{jj'} = \Delta V_j \delta_{jj'} + \Delta V_j G^{\text{red}} T'_{j'} + \Delta V_j G^{rs_j} T_{jj'} . \tag{34}$$

Result (32) is obtained with the help of (9) and (30). Expression (32) shows that the scattering from a site j' to another site j occurs right away, mediated through the reduced propagator G^{red}, and via all scattering centers in the system, including centers j and j' contained in the full T, represented by the term $G^{\text{red}}TG^{\text{red}}$.

Comparing (31) and (32), it is clear that

$$t^j_{\Delta V}|\Psi^{\text{inc}}_j\rangle = \sum_{j'} T_{jj'}|\phi\rangle = T_j|\phi\rangle , \tag{35}$$

so that the outgoing wave in (11) becomes

$$|\Psi^{\text{out}}_j\rangle = G^{rs_j}\sum_{j'} T_{jj'}|\phi\rangle . \tag{36}$$

Apparently, the incident wave, scattered by all centers, ends up as an amplitude (35) at site j and is transformed to an outgoing wave by the local propagator G^{rs_j}. Of course, Eq. (35) also follows directly from Eqs. (8), (19), and (23). But the interpretation in terms of $T_{jj'}$ given by (32) could be lacking.

For completeness, and with an eye to applying them below, we finally review some results of formal scattering theory,[21] concerning the optical theorem and the S-matrix operator. Using the form

$$T = [(\Delta V)^{-1} - G^r]^{-1} \tag{37}$$

for the t-matrix operator, which is equivalent to Eq. (6), one easily sees that

$$T^{\dagger^{-1}} - T^{-1} = G^r - G^{r\dagger} = 2i \,\text{Im}G^r . \tag{38}$$

The optical theorem in operator form follows after multiplying (38) from the right with T, and from the left with $T^\dagger$:

$$T - T^\dagger = T^\dagger(G^r - G^{r\dagger})T , \tag{39}$$

or, equivalently,

$$\text{Im}T = T^\dagger(\text{Im}G^r)T . \tag{40}$$

The unitary S-matrix operator is defined by

$$S = 1 + 2i(\text{Im}G^r)T = 1 + (G^r - G^{r\dagger})T . \tag{41}$$

Using (38), this operator can also be written as

$$S = T^{\dagger^{-1}}T . \tag{42}$$

This latter equality will be used in Sec. IV in relating the result of Krein[16] and Birman and Krein[22] to a generalized Lloyd formula for the system's density of states.[15]

III. THE MIXED SITE-ANGULAR MOMENTUM REPRESENTATION

The contents of the present section are relatively straightforward, but it is written to illustrate the rather abstract formal results of Sec. II.

The formal equations (2), (11), (14), (31), and (36) for the state $|\Psi\rangle$ and the incoming and outgoing waves will be elaborated using an angular momentum expansion. To that end one needs a one-center expression for $|\Psi\rangle$ in the $\mathbf{r}$ representation:[8]

$$\langle\mathbf{r}|\Psi\rangle \equiv \Psi(\mathbf{r}) = \Psi(\mathbf{x} + \mathbf{R}_j) = \sum_L C^j_{k,L} R^j_L(\mathbf{x}) \tag{43}$$

and an angular momentum expansion of the Green's function of the reference system in the $\mathbf{r}$ representation:[8,13]

$$G^r(\mathbf{r}, \mathbf{r}') = G^r(\mathbf{x} + \mathbf{R}_j, \mathbf{x}' + \mathbf{R}_{j'})$$
$$= R^{r,j}(\mathbf{x}_<)H^{r,j}(\mathbf{x}_>)\delta_{jj'}$$
$$+ R^{r,j}(\mathbf{x})\mathcal{G}^{r,jj'}R^{r,j'}(\mathbf{x}') . \tag{44}$$

At a site j the system wave function $\Psi(\mathbf{r})$ is written in terms of the locally exact solutions $R^j_L(\mathbf{x})$ of the system's Schrödinger equation, which are related to the corresponding solutions for the reference system by

$$R^j_L(\mathbf{x}) = R^{r,j}_L(\mathbf{x}) + \Delta t^j_l H^{r,j}_L(\mathbf{x}) . \tag{45}$$

The latter form reflects the choice of spherical potentials and the neglect of lattice distortion, since

$$\Delta t^j_l = t^j_l - t^{r,j}_l \tag{46}$$

and

$$t^j_l = -\frac{1}{\kappa}\sin\delta^j_l\exp(i\delta^j_l) , \tag{47}$$

in which $\kappa = E^{1/2}$ and δ^j_l are phase shifts.

All $\mathbf{x}$-dependent functions are a product of the form

$$R_L(\mathbf{x}) = R_l(x)Y_L(\hat{\mathbf{x}}) , \tag{48}$$

$Y_L(\mathbf{x})$ being a real spherical harmonic. The singular solution is outside a muffin-tin sphere given by

$$H^r_l(x) = H_l(x) \equiv -i\kappa h^+_l(\kappa x) , \tag{49}$$

the additional factor $-i\kappa$ serving to guarantee an energy-independent Wronskian:

$$[R_l(x), H_l(x)] = \frac{1}{x^2} , \tag{50}$$

and in which $h^+_l(z) = j_l(z) + in_l(z)$ is the standard combination of spherical Bessel and Neumann functions in scattering theory. For a dilute alloy $\mathcal{G}^r$ is the matrix for the unperturbed host system, given by

$$\mathcal{G}^r = B\frac{1}{1 - t^r B} \tag{51}$$

containing the structural matrix B, defined by

$$B^{jj'}_{LL'} = -4\pi\kappa i^{l-l'+1}\sum_{L''} i^{l''}C_{LL'L''}h^+_{L''}(\mathbf{R}_{jj'}) . \tag{52}$$

Using (43) and (44) one readily finds, for (2),

$$\sum_L C_{k,L}^j R_L^j(\mathbf{x}) = \phi(\mathbf{x}+\mathbf{R}_j) + \sum_{j'L} \left[H_L^{r,j}(\mathbf{x})\delta_{jj'} + \sum_{L'} R_L^{r,j}(\mathbf{x})\mathscr{G}_{L'L}^{r,jj'} \right] \Delta t_{j'}^{j'} C_{k,L}^{j'} , \tag{53}$$

in which x is supposed to be larger than the muffin-tin radius at site j. In view of (45) the Hankel function term on the right-hand side cancels such a term on the left-hand side. Writing the incident wave ϕ, being a property of the reference system, in a way similar to (43), and using the Wronskian property (50), one finds the following equation[8] for the expansion coefficients:

$$C_{k,L}^j = C_{k,L}^{r,j} + \sum_{j'L'} \mathscr{G}_{LL'}^{r,jj'} \Delta t_{j'}^{j'} C_{k,L'}^{j'} . \tag{54}$$

At this point it may be clarifying to distinguish scattering solutions of the Schrödinger equation and stationary solutions. Equations (2), (53), and (54) apply to the general case of scattering solutions, in which there is an incident wave, and the special case of stationary states is included. For example, applying (54) to a perfect metal and choosing free space as the reference system, the well-known KKR equation[1,2] follows for the stationary states having no incident wave, i.e., $C^r=0$. In a dilute alloy[20] a host incident wave is present, and equation (54) can be solved for the scattering solutions, i.e., for the system wave-function coefficients in terms of the host coefficients C_k^r, the host Green's-function matrix $\mathscr{G}^r$, and the t-matrix difference Δt.

More interesting are the incoming and outgoing wave equations. The cancellation of the Hankel function terms in (53) always occurs in derivations using the full Lippmann-Schwinger equation (2), but it is just a welcome step in deriving (54). The meaning of that cancellation becomes clear through the multiple-scattering representation (11) of the system state. In view of (14), the following ansatz is prescribed:

$$\Psi_j^{\text{inc}}(\mathbf{x}) = \sum_L C_L^{\text{inc},j} R_L^{r,j}(\mathbf{x}) . \tag{55}$$

The incident wave has this form by definition, and it is only the second term of $G^r(\mathbf{r},\mathbf{r}')$ in expression (44) which contributes to the second and third terms in (14). As for the third term, this becomes clear immediately if one realizes that $G^{rs_j}(\mathbf{r},\mathbf{r}')$ is given by

$$G^{rs_j}(\mathbf{r},\mathbf{r}') = R^{r,j}(\mathbf{r}_<)H^{r,j}(\mathbf{r}_>) , \tag{56}$$

which coincides precisely with the first term of $G^r(\mathbf{r},\mathbf{r}')$ in (44). Substituting (55) into (14) in the r representation, and using (44) and (56), one finds the following equation for the expansion coefficients $C_L^{\text{inc},j}$:

$$C_L^{\text{inc},j} = C_{kL}^{r,j} + \sum_{j'L'} \mathscr{G}_{LL'}^{r,jj'} \Delta t_{j'}^{j'} C_L^{\text{inc},j'} \tag{57}$$

Interestingly, this equation has exactly the same form as (54), which, regarding the one-center expansion (11), the one-center expression (43), and the relation (45), implies an outgoing wave of the form

$$\Psi_j^{\text{out}}(\mathbf{x}) = \sum_L C_L^{\text{inc},j} \Delta t_j^j H_L^{r,j}(\mathbf{x}) . \tag{58}$$

This fully explains the cancellation mentioned above. Solving (57) for the vector C^{inc},

$$C^{\text{inc}} = (1 - \mathscr{G}^r \Delta t)^{-1} C_k^r , \tag{59}$$

and substituting this into (58), comparison with the formal form (36) leads to the expression

$$T = \Delta t \frac{1}{1 - \mathscr{G}^r \Delta t} \tag{60}$$

for the system t matrix described with respect to the reference system.

Although Eqs. (54) and (57) are identical, which could have been anticipated, the reader will admit that the description in terms of incoming and outgoing waves is clarifying and most appealing, similar as it is to original multiple-scattering theory[1,3] with free space as a reference system.

Another example of using a more general reference system than free space is the proof of the relationship

$$\mathscr{G} = \mathscr{G}^r + \mathscr{G}^r \Delta t \mathscr{G} = \mathscr{G}^r + \mathscr{G}^r T \mathscr{G}^r , \tag{61}$$

starting from (7) and using (44) and a similar form for the system Green's function. The main steps of that proof[14] are already found in the early, but not much appreciated work of Hamazaki,[13] and will not be repeated. Nevertheless, it has remained common practice in the literature to derive (61) using the representation

$$\mathscr{G} = B \frac{1}{1 - tB} \tag{62}$$

of the system Green's function matrix described with respect to free space as a reference system. If the right-hand side of (62) is expanded with respect to $\mathscr{G}^r$ given by (51), (61) indeed follows. On the other hand, (61) written in the form

$$\mathscr{G} = \mathscr{G}^r \frac{1}{1 - \Delta t \mathscr{G}^r} \tag{63}$$

illustrates nicely the invariance of the matrix expressions with respect to the choice of the reference system, as expression (60) for the t matrix did already. For free space as a reference system $t^r \to 0$, $\Delta t \to t$ and, according to (51), $\mathscr{G}^r \to B$. It is clear that the free space expressions for $\mathscr{G}$ and T follow from (63) and (60), substituting these limiting values.

An example[14] of a simplification using a more general reference system than free space is found in the derivation of the determining equation for the averaged medium t matrix t^r in the single-site coherent-potential approximation in binary alloys. Using (60) in the form

$$c_A \Delta t^A \frac{1}{1 - \mathscr{G}^r \Delta t^A} + c_B \Delta t^B \frac{1}{1 - \mathscr{G}^r \Delta t^B} = 0 \tag{64}$$

as the self-consistency condition, in which c_A and $c_B = 1 - c_A$ are the concentration of the components A

and B in the alloy, one readily finds the well-known explicit form[10,11]

$$t_r^{-1} = c_A t_A^{-1} + c_B t_B^{-1} + (t_r^{-1} - t_A^{-1}) T^r (t_r^{-1} - t_B^{-1}) . \qquad (65)$$

The t matrix T^r for the average medium, being the reference system in the present case, enters through the equality

$$\mathcal{G}^r = -t_r^{-1} + t_r^{-1} T^r t_r^{-1} . \qquad (66)$$

IV. GENERALIZED LLOYD FORMULA AND KREIN'S THEOREM

The electronic density of states of a system at energy E is given by

$$n(E) = -\frac{2}{\pi} \text{Im} \, \text{Tr} \, G(E) . \qquad (67)$$

The difference in density of states with respect to a reference system

$$\Delta n(E) = n(E) - n^r(E) \qquad (68)$$

has been brought in a very useful form by Lloyd,[23] but for free space as a reference system. The correct form[8,24] as it is used nowadays is

$$\Delta n(E) = \frac{2}{\pi} \text{Im} \frac{d}{dE} \text{Tr} \ln T^s , \qquad (69)$$

in which T^s is a matrix in the mixed-site angular momentum representation of the form (60)

$$T^{0,s} = t \frac{1}{1 - Bt} . \qquad (70)$$

The usefulness of (69) is given by the explicit presence of the energy derivative, implying an explicit expression for the integrated density of states. The latter expression can be used to derive a generalized Friedel sum rule, measuring the local charge neutrality in electronic structure calculations.[9]

The superscript 0 was added in (70) to indicate the reference system. The superscript s, standing for scattering, is required in general in order to cover other reference systems as well. For example, for a dilute alloy described with respect to the unperturbed host system as a reference system, it was shown[14,15] that the t matrix to be substituted in (69) has the form

$$T^{r,s} = t_\Delta \frac{1}{1 - \mathcal{G}^r \Delta t} . \qquad (71)$$

This matrix differs slightly from the matrix (60), in that it contains the difference-scattering t matrix t_Δ, given by

$$t_{\Delta,l}^j = -\frac{1}{\kappa} \sin(\Delta \delta_l^j) e^{i\Delta \delta_l^j} , \qquad (72)$$

which also occurs if scattering of Bloch electrons is described in dilute alloys, as will be seen in Sec. VI. It is clear, that for free space as reference system, $t_\Delta = \Delta t = t$.

The derivation of the generalized Lloyd formula (69) containing (71) was revealing and rigorous,[15] but also quite lengthy. The question was raised of a link with the

general theorems of Krein[16] and Birman and Krein.[22] According to Faulkner[25] these theorems in formal scattering theory amount to the equality

$$\text{Tr}\{G(E) - G^r(E)\} = -\frac{1}{2} \frac{d}{dE} \text{Tr} \ln S(E) , \qquad (73)$$

in which $S(E)$ is the on-the-energy-shell S matrix, while the notation of the present paper is adopted. Substituting (73) into (68) with (67), one obtains

$$\Delta n(E) = \frac{1}{\pi} \text{Im} \frac{d}{dE} \text{Tr} \ln S(E) . \qquad (74)$$

We claim that the link between (74), based on Faulkner's interpretation of Krein's work, is provided by the operator expression derived by the present authors:[14,15]

$$\Delta n(E) = \frac{2}{\pi} \text{Im} \frac{d}{dE} \text{Tr} \ln T , \qquad (75)$$

in which T is still the operator given by (6) or (37), to be combined with equality (42). Since

$$\text{Im} \, \text{Tr} \ln T^\dagger = -\text{Im} \, \text{Tr} \ln T , \qquad (76)$$

Eq. (75) is equivalent to

$$\Delta n(E) = \frac{1}{\pi} \text{Im} \frac{d}{dE} \text{Tr} \ln S , \qquad (77)$$

in which S is still an operator. Reasoning now the other way around, the matrix expression (74) reduces to the generalized Lloyd formula (69). This would mean that the Lloyd formula in its general form (69) holds for all reference systems. The matrix T^s has to be calculated from the operator T, generally given by Eq. (6). This will be done for a dilute alloy in Sec. VI.

V. LOCAL DENSITY OF STATES

In carrying out the trace operation in the r representation, thereby generating an integral over all space, part of such an integral

$$n^j(E) = -\frac{2}{\pi} \text{Im} \int_{\text{cell} j} d^3 r \, G(\mathbf{r}, \mathbf{r}, E) \qquad (78)$$

is defined as the local density of states. For practical purposes the integration in (78) is restricted to a cell, e.g., a Wigner-Seitz cell, around a site j. In deriving the generalized Lloyd formula (69) with (71), the present authors evaluated the integral over all space by summing (78) over all cells.[15] A form for G similar to the form (44) for G^r is used. The integral over a cell can be converted to a surface integral over the cell boundary, and the Green's-function matrix $\mathcal{G}$ can be expanded according to (61). In this way an expression for the local density of states $n^j(E)$ can be derived using ingredients of the latter work, equations in it being referred to in the present section by I. The reader is referred there[15] for details. Our expression follows after substituting Eqs. (I42) and (I43) into the contribution of cell j into Eq. (I40) for the system density of states, which comprises the contributions of all cells,

$$n^j(E) = n^{r,j}(E) - \frac{2}{\pi} \operatorname{Im} \operatorname{tr} \left\{ \alpha_j^r (\mathcal{G}^r T \mathcal{G}^r)^{jj} + \beta_j^r (T\mathcal{G}^r)^{jj} + \tilde{\beta}_j^r (\mathcal{G}^r T)^{jj} + \left[\gamma_j^r + \frac{d(\Delta t^j)^{-1}}{dE} \right] T^{jj} + (\Delta t^j)^{-1} \frac{d\Delta t^j}{dE} - \frac{d\Delta\delta^j}{dE} \right\}.$$

$$(79)$$

The trace operation refers to the angular momentum labels only, and $\tilde{\beta}$ is the transposed with β with respect to these labels. The α^r, β^r, and γ^r matrices come from the integral over a Wigner-Seitz cell. They are Wronskian-like integrals over the cell boundary of the solutions $R_L^{r,j}$ and $H_L^{r,j}$ of the Schrödinger equation for the reference system [see Eqs. (45) and (49)], and their derivatives with respect to the energy. So

$$\alpha_{LL'}^j = W_j \left[\frac{d}{dE} R_L^j, R_{L'}^j \right] \tag{80}$$

and

$$\beta_{LL'}^j = W_j \left[\frac{d}{dE} R_L^j, H_{L'}^j \right], \tag{81}$$

while in γ two singular solutions are combined. The surface integral W_j is defined as

$$W_j \left[\frac{d}{dE} P_L, Q_{L'} \right] = \int d\mathbf{S}_j \cdot \left[\frac{d}{dE} P_L(\mathbf{r}) \nabla Q_{L'}(\mathbf{r}) \right.$$
$$\left. - Q_{L'}(\mathbf{r}) \nabla \frac{d}{dE} P_L(\mathbf{r}) \right].$$

$$(82)$$

All ingredients of expression (79) are known. The matrix $\mathcal{G}^r$ given by (51) is calculated routinely,[9] the matrix T given by (60) follows simply from it, and the surface integrals α^r, β^r, and γ^r have to be calculated once in an iteration procedure, being a property of the reference system. Further, all terms but the α^r term have a natural cutoff in the angular momentum due to the usual cutoff in Δt and $\Delta\delta$. Therefore, only the α^r term requires special attention in the numerical evaluation of (79).

VI. TRANSITION PROBABILITY

A Bloch state can be represented by a form (43) by adding a label r. In calculating a transition probability,[20] one needs the matrix element

$$\langle r, jL | t_j^\Delta | r, jL' \rangle$$
$$\equiv \int d^3x \, d^3x' R_L^{r,j}(\mathbf{x})^* t_j^\Delta(\mathbf{x}, \mathbf{x}') R_L^{r,j}(\mathbf{x}'), \tag{83}$$

in which t_j^Δ, defined by (27), is the building block of the system t-matrix operator T given by (26). In further evaluating T one needs, in view of expression (44) for G^r, the integral

$$\int d^3x \, d^3x' R_L^{r,j}(\mathbf{x}) t_j^\Delta(\mathbf{x}, \mathbf{x}') R_L^{r,j}(\mathbf{x}') = \Delta t_j^j A_{LL'}^j, \tag{84}$$

in which a complex conjugate symbol is missing com-

pared with (83), and the right-hand side of which will be justified readily. For both integrals one needs the matrix A in the equality

$$\int_{\text{cell}} d^3x' t^\Delta(\mathbf{x}, \mathbf{x}') R_L^r(\mathbf{x}') = \Delta V(\mathbf{x}) \sum_{L'} R_{L'}(\mathbf{x}) A_{L'L} \tag{85}$$

connecting a reference-system solution to a linear combination of system solutions. In view of (26) the operator t^Δ holds for a system which deviates from the reference system only at one site, by a potential difference ΔV. The matrix A is nondiagonal, because the environment of the perturbed site is not spherically symmetric. This matrix is obtained by elaborating the Lippmann-Schwinger equation (2) for the present one-site case. Using a matrix notation for the angular momentum labels, one writes[20]

$$R^j(\mathbf{x}) A^j = R^{r,j}(\mathbf{x})$$
$$+ \int_{\text{cell} j} d^3x' G^r(\mathbf{x}, \mathbf{x}') \Delta V(\mathbf{x}') R^j(\mathbf{x}') A^j$$
$$= R^{r,j}(\mathbf{x}) + [H^{r,j}(\mathbf{x}) + R^{r,j}(\mathbf{x}) \mathcal{G}^{r,jj}] \Delta t A^j. \tag{86}$$

The third member is obtained after substituting (44) for G^r, and evaluating the remaining integral, using a standard technique.[20] That technique amounts to the replacement of ΔV by $E - H^r$ due to the Schrödinger equation, after which the kinetic-energy part can be converted into an easily evaluable integral over a spherical surface around ΔV. By that it is precisely the integral in (84) that has been evaluated, so that its right-hand side also is justified by now. In view of (45), it follows from (86) that[14]

$$A^j = (1 - \mathcal{G}^{r,jj} \Delta t^j)^{-1}. \tag{87}$$

The integral (83), being a true Bloch scattering integral, appears to be proportional to the difference-scattering t matrix t_Δ, given by (72). One finds[20]

$$\langle r, jL | t_j^\Delta | r, jL' \rangle = t_{\Delta,l}^j A_{LL'}^j. \tag{88}$$

Now everything is ready for evaluating the full t-matrix operator T. One finds, using (26) and (44),

$$\langle r, jL | T | r, j'L' \rangle = \langle jL | t_\Delta A \frac{1}{1 - \mathcal{G}_{nd}^r \Delta t A} | j'L' \rangle$$
$$= T_{jL,j'L'}^{r,s}, \tag{89}$$

the latter matrix being precisely matrix (71). The matrix $\mathcal{G}^r$ in the denominator in the second member of (89), carrying the nondiagonality subscript, occurs only for different sites, due to the inequality signs in the series (26). The matrix A takes care of the diagonal elements, because, in view of (87),

$$A\frac{1}{1-\mathcal{G}^r_{nd}\Delta t\,A}=\frac{1}{A^{-1}-\mathcal{G}^r_{nd}\Delta t}=(1-\mathcal{G}^r\Delta t)^{-1}\ . \quad (90)$$

For completeness we remark that the integrals (83) and (84) also could have been evaluated using the relation

$$t_j^\Delta=t^j_{\Delta V}+t_j^\Delta G^{red}t^j_{\Delta V}\ , \quad (91)$$

which easily follows from definitions (9), (15), and (27). Since

$$\langle r,jL\,|t^j_{\Delta V}|r,jL'\rangle=t^j_{\Delta,l}\delta_{LL'}\ , \quad (92)$$

and the integral similar to (84) is equal to $\Delta t_j^j\delta_{LL'}$, results (84) and (88) with (87) follow immediately using (15), (44), and (56) for G^{red}.

At this point we wish to clarify the seemingly confusing occurrence of both the difference-scattering t matrix t_Δ and the difference of t matrices Δt. First, for muffin-tin potentials these matrices are related simply by a phase factor, as

$$\Delta t_l^j=e^{2i\delta^{r,j}_l}t^j_{\Delta,l} \quad (93)$$

which easily follows from (46) with (47) and (72). Further, evaluating the Green's-function operator (4) in the r representation, and using Bloch states $|r,k\rangle$ as a complete set of intermediate states, one obtains

$$\langle \mathbf{r}|G^r|\mathbf{r}'\rangle=G^r(\mathbf{x}+\mathbf{R}_j,\mathbf{x}'+\mathbf{R}_{j'})$$

$$=\sum_k\langle\mathbf{r}|r,k\rangle\frac{1}{E^+-E_k^r}\langle r,k|\mathbf{r}'\rangle$$

$$=\sum_{k,L,L'}\frac{C^{r,j}_{k,L}R^{r,j}_L(\mathbf{x})(R^{r,j'}_L(\mathbf{x}')C^{r,j'}_{k,L'})^*}{E^+-E_k^r}\ , \quad (94)$$

in which an expansion like (43) or (55) is used. Note that the scalar r denotes the reference system, and that the energy dependence of the regular solutions is omitted. However, after carrying out the sum over all states, which effectively leads to a contour integral, only on-the-energy-shell states remain. The result must be equivalent to expression (44). Regarding (94), it would have been much more natural (see also Ref. 14) to express the second term of (44) in terms of a regular solution and its complex conjugate, coupled by a matrix $\bar{\mathcal{G}}^{r,jj'}$. Interestingly, this overlined matrix is related to $\mathcal{G}^r$ by

$$\bar{\mathcal{G}}^{r,jj'}_{LL'}=\mathcal{G}^{r,jj'}_{LL'}e^{2i\delta^{r,j'}_{l'}}\ , \quad (95)$$

which is an immediate consequence of the equality

$$R^j_l(\mathbf{x})=e^{2i\delta^j_l}R^j_l(\mathbf{x})^*\ . \quad (96)$$

But now, regarding (88), the elaboration (89) more naturally becomes[14]

$$\langle r,jL\,|T|r,j'L'\rangle=\langle jL\,|t_\Delta A\frac{1}{1-\mathcal{G}^r_{nd}t_\Delta A}|j'L'\rangle$$

$$=t_\Delta\frac{1}{1-\mathcal{G}^r t_\Delta}=T^{r,s}\ , \quad (97)$$

since the term $\mathcal{G}^{r,jj}\Delta t^j$ in A^j given by (87) becomes equal

to $\bar{\mathcal{G}}^{r,jj}t^j_\Delta$. We conclude that it is due only to the conventional choice (44) for the form of the Greens's function in the r representation, that both matrices t_Δ and Δt are required. Also the matrix T given by (60) and occurring in (61), after substituting (95) into (61), would obtain an additional phase factor, thereby attaining the form (97) for $T^{r,s}$. Apparently, it is again due to history that two slightly different system t matrices T and $T^{r,s}$, given by (60) and (71), respectively, occur in the theory.

One might begin to wonder where the choice of (44) stems from. The answer is that an expression for the Green's function for a more complex system than free space has never been derived using the approach of (94). All derivations[8,11,13] follow the multiple-scattering path and end up at the form (44). Interestingly, this form has another nice feature, because it shows clearly the Green's-function symmetry with respect to the interchange of its arguments r and r'. A form according to (94), containing the matrix $\bar{\mathcal{G}}^r$, would hide this symmetry property. The matrix $\mathcal{G}^r$ is a typical symmetrical multiple-scattering matrix, being invariant for the simultaneous interchange of the site and angular momentum labels, while $\bar{\mathcal{G}}^r$ is not.

Finally we wish to comment on a usual short cut[14] followed in finding a (generalized) Lloyd formula (69) starting from the operator form (75). Denoting an on-the-energy-shell eigenstate of the reference system by $|r,k\rangle$, and using (89) and an expansion like (43), one finds

$$\langle r,k|T|r,k\rangle=C_k^{r\dagger}T^{r,s}C_k^r \quad (98)$$

Evaluating the trace operation in (75) with respect to states at the energy E, this equation would reduce to the generalized Lloyd formula (69), because the matrix

$$\sum_k C_k^r C_k^{r\dagger} \quad (99)$$

being Hermitian, does not contribute due to the Im Tr ln operation. However, it is not clear that the restriction to on-the-energy-shell states is allowed. To justify that step, Krein's theorem is required. On the other hand, in describing the scattering of Bloch electrons on the Fermi surface in a dilute alloy, probed experimentally by measuring Dingle temperatures, expression (98) covers all possibilities. It reduces nicely to an old form, applying to one defect in an otherwise perfect metal, derived by one of the present authors.[20]

VII. CONCLUSIONS AND PROSPECTS

Multiple-scattering theory, as was formulated in the early days of Korringa,[1] Kohn, and Rostoker,[2] and as applied ever since,[3,9] has been generalized as far as the reference system is concerned. Originally, and ever since, the reference system has been free space. We have shown that properly generalized incoming and outgoing waves can be defined if more general or more appropriate reference systems are used. The consequent generalization presented, traces of which[12,13] could be found already in the literature, applies to expressions for the generalized Friedel sum, the local density of states, and transition

probabilities. Apart from clarifying certain features of the old description and simplifying old derivations,[10,15,20,26] the generalized multiple-scattering framework may prove useful in studying more and more complex systems. Moreover, viewed from a design stance the framework presented may even prove useful in studying complex artificial neural networks, for which many physical approaches[27,28] already have been tried.

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