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Generalized Lloyd formula for the electron density of states

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An expression is derived for the electron density of states of an arbitrary collection of scattering potentials, described with respect to another, related collection of scatterers. This latter system, serving as a reference system, replaces free space, being the reference system for Lloyd's formula. The expression is very similar in form compared with the original expression. It contains the system t -matrix defined with respect to the reference system. The generalized Lloyd formula is very useful in describing defects in dilute alloys. The derivation is accomplished by evaluating the trace operation in the formal density-of-states expression in the $\mathbf{r}$ representation, by integrating over all space explicitly, and by using a generalized form of the equality due to Jacobs and Zaman.

I. INTRODUCTION

Lloyd's formula¹ for the density of states of an arbitrary collection of nonoverlapping scattering potentials in free space was derived in a period during which it was investigated how far, for electronic properties, an infinite solid could be modeled by a finite collection of atoms. The broadening of the d band, found for transition-metal atoms in a relatively small cluster of atoms compared with a single atom, was promising in an early stage.^{2,3} Later^{4,5} it was found, that a precise comparison with the density of states of a solid remains poor even for very large clusters⁴ of several hundred atoms. Therefore further applications for finite clusters, possibly embedded in some model environment,⁵⁻⁷ were sought in liquid metal systems, in which long-range correlations, typical for a crystalline solid were expected to be averaged out.

Other, more important applications of Lloyd's formula are found in studies of alloys⁸ and the subgroup of dilute alloys.⁹ Although Lloyd's formula gives infinity for an infinite system, a properly normalized expression, e.g., per atom or per unit cell, could be used. In addition, it was shown explicitly¹⁰ that the crystal density-of-states expression for a muffin-tin crystal potential reduces to Lloyd's expression, the corresponding muffin-tin zero for this system potential being equivalent to Lloyd's free space.

In spite of this it seems quite unnatural to use Lloyd's formula for the latter purposes. Regarding the dilute alloy system, for example, both this system and the unperturbed host system are described with respect to free space. It would be much more satisfactory if the dilute alloy system could be described immediately with respect to the unperturbed host as a *reference* system.¹¹ It will be shown that this is indeed possible. A generalized Lloyd formula

$$n(E) = n'(E) + \frac{2}{\pi} \text{Im} \frac{d}{dE} \text{Tr} \ln T(E) \quad (1)$$

can be derived, in which $n(E)$ and $n'(E)$ are the densities of states of the system and the reference system, respectively, and $T(E)$ is the t matrix of the system with respect

to the reference system. The derivation to be given can be considered as a straight generalization of the derivation of Lloyd's formula¹² by one of the present authors. An alternative derivation can be found in Ref. [11], to which we return in Sec. IV.

In Sec. II the system and the reference system will be specified, including some useful definitions, by this preparing the actual derivation of the generalized Lloyd formula to be given in Sec. III. The result will be discussed in Sec. IV. An important equality, required in the derivation of Sec. III, will be proved in an Appendix.

II. THE SYSTEM AND THE REFERENCE SYSTEM

The starting point of the derivation is the formal expression for the density of states at the energy E :

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

$G(E)$ being the Green's-function operator $(E^+ - H)^{-1}$ of the system with Hamiltonian H . The system may be any collection of scatterers, ranging from a finite cluster in free space to a binary alloy, but as a mental help the reader may keep in mind a dilute alloy system. The reference system to be chosen is generally simpler than the system to be described, in that it may have additional symmetry, e.g., translational invariance or extra point symmetry. For example, for a dilute alloy system the unperturbed host is chosen naturally as reference system. Since the trace operation in (2) will be elaborated in the $\mathbf{r}$ representation, leading to an integral over all space, the Green's functions of system and the reference system will be required in this representation. These functions are known^{9,13} to be given by

$$G(\mathbf{x} + \mathbf{R}_j, \mathbf{x}' + \mathbf{R}_{j'}) = R^j(\mathbf{x}_<) H^j(\mathbf{x}_>) \delta_{jj'} + R^j(\mathbf{x}) \mathcal{G}^{jj'} R^{j'}(\mathbf{x}') \quad (3)$$

and

$$G^r(\mathbf{x} + \mathbf{R}_j, \mathbf{x}' + \mathbf{R}_{j'}) = R^{r,j}(\mathbf{x}_<) H^{r,j}(\mathbf{x}_>) \delta_{jj'} + R^{r,j}(\mathbf{x}) \mathcal{G}^{r,jj'} R^{r,j'}(\mathbf{x}') . \quad (4)$$

In these expressions all scatterers in the system are supposed to be disjunct, such that a cell can be indicated for each of them, labeled by a position vector $\mathbf{R}_j$ pointing to the center of the scatterer. A position vector $\mathbf{r}$ inside such a cell is denoted by $\mathbf{x} + \mathbf{R}_j$, while $\mathbf{x}_<$ and $\mathbf{x}_>$ are the shorter and longer vector, respectively, of the pair $(\mathbf{x}, \mathbf{x}')$. A matrix notation is used as for the angular momentum labels $L \equiv (lm)$. The functions $R^j(\mathbf{x})$ and $H^j(\mathbf{x})$ are regular and singular solutions, respectively, of the Schrödinger equation inside the j th cell of the system. So

$$R_L^j(\mathbf{x}) = R_L^j(x) Y_L(\hat{\mathbf{x}}) , \quad (5)$$

$Y_L(\hat{\mathbf{x}})$ being a real spherical harmonic. In the actual derivation to be given, effects due to lattice distortion and nonsphericity of the potentials will be ignored, so that one can think of a muffin-tin representation of the potentials of the systems. It simplifies the derivation, it is well known how to incorporate the effects,^{11,14} and they do not influence¹¹ the general form of the final expressions. In the region outside the muffin-tin sphere which lies inside the j th cell, the regular solution is given by

$$R_L^j(x) = j_L(\kappa x) - i\kappa t_L^j h_L^+(x) , \quad (6)$$

in which $\kappa = E^{1/2}$, the spherical Hankel function $h_L^+(z) \equiv j_L(z) + in_L(z)$ is the standard combination of spherical Bessel and Neumann functions in scattering theory, and

$$t_L^j = -\frac{1}{\kappa} \sin \delta_L^j \exp(i\delta_L^j) , \quad (7)$$

δ_L^j being phase shifts. The singular function is outside the j th muffin-tin sphere given by

$$H_L^j(x) \equiv -i\kappa h_L^+(x) , \quad (8)$$

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

$$[R_L^j(x), H_L^j(x)] = \frac{1}{x^2} . \quad (9)$$

The main information about the systems is stored in the $\mathcal{G}$ matrices. They are given by

$$\mathcal{G}^r = B \frac{1}{1 - t^r B} \quad (10)$$

and

$$\mathcal{G} = B \frac{1}{1 - tB} = B \frac{1}{1 - t^r B - (\Delta t)B} = \mathcal{G}^r + \mathcal{G}^r \Delta t \mathcal{G} \quad (11)$$

containing the structural matrices B , defined by

$$B_{LL'}^{jj'} = -4\pi\kappa i^{l-l'+1} \sum_{L''} i^{l''} C_{LL'L''} h_{L''}^+(\mathbf{R}_{jj'}) \quad (12)$$

and

$$\Delta t \equiv t - t^r . \quad (13)$$

If one would like to give the whole derivation, including

the lattice distortion, in the definition of $\mathcal{G}^r$ a matrix B^r instead of B should be used.

By iterating Eq. (11), one finds

$$\mathcal{G} = \mathcal{G}^r + \mathcal{G}^r \mathcal{T} \mathcal{G}^r \quad (14)$$

in which the t matrix

$$\mathcal{T} = \Delta t \frac{1}{1 - \mathcal{G}^r \Delta t} = \frac{1}{(\Delta t)^{-1} - \mathcal{G}^r} \quad (15)$$

is closely related to the t matrix $T(E)$ in the final generalized Lloyd expression (1).

We finally remark about Eqs. (3) and (4) that

$$H_L^j(x) = H_L^j(x) \quad (16)$$

and that, in view of (6), (8), (13), and (16) the regular solutions $R_L^j(x)$ and $R_L^{r,j}(x)$, in the region between the muffin-tin sphere and cell boundary, are related by¹¹

$$R_L^j(x) = R_L^{r,j}(x) + \Delta t_L^j H_L^j(x) . \quad (17)$$

In carrying out the space integration according to Eq. (2), it is most convenient¹² to rewrite the Hankel function terms in (3) and (4) using a real regular solution, defined by

$$\bar{R}_L^j(x) \equiv e^{-i\delta_L^j} R_L^j(x) = \cos \delta_L^j j_L(\kappa x) - \sin \delta_L^j n_L(\kappa x) , \quad (18)$$

and denoted by a line over it. The second member is valid everywhere inside the j th cell, while the third member is valid only outside the j th muffin-tin sphere. Correspondingly,

$$\bar{H}_L^j(x) \equiv e^{i\delta_L^j} H_L^j(x) = -i\kappa [\bar{R}_L^j(x) + i\bar{S}_L^j(x)] , \quad (19)$$

in which the overlined singular solution outside the muffin-tin sphere is given by

$$\bar{S}_L^j(x) = \cos \delta_L^j n_L(\kappa x) + \sin \delta_L^j j_L(\kappa x) , \quad (20)$$

and is also a real function. It is clear that, in taking the imaginary part, only the overlined regular solutions remain.

Similar to Eq. (17), the following property can be derived:¹¹

$$\bar{R}_L^j(x) = \cos(\Delta \delta_L^j) \bar{R}_L^{r,j}(x) - \sin(\Delta \delta_L^j) \bar{S}_L^{r,j} . \quad (21)$$

One more definition is required. The trace operation in Eq. (2), carried out in $\mathbf{r}$ space, will lead to integrals of products $P_L(\mathbf{r}) Q_{L'}(\mathbf{r})$ over a cell or over a subvolume inside a cell, $P_L(\mathbf{r})$ and $Q_{L'}(\mathbf{r})$ being solutions of the Schrödinger equation. Such an integral reduces to a kind of generalized Wronskian, defined as

$$\begin{aligned} \int d^3r P_L(\mathbf{r}) Q_{L'}(\mathbf{r}) &= \int d\mathbf{A} \cdot \left[\frac{d}{dE} P_L(\mathbf{r}) \nabla Q_{L'}(\mathbf{r}) \right. \\ &\quad \left. - Q_{L'}(\mathbf{r}) \nabla \frac{d}{dE} P_L(\mathbf{r}) \right] \\ &\equiv W_A \left[\frac{d}{dE} P_L, Q_{L'} \right] , \end{aligned} \quad (22)$$

in which A denotes the surface or boundary of the volume over which the integral on the left-hand side runs. This property was proved by one of the present authors,¹² and rederived independently 12 years later by Zhang and Butler.¹⁵

III. THE ACTUAL DERIVATION

In elaborating Eq. (2), the trace operation is taken in the $\mathbf{r}$ representation. This leads to an integral over all space, which can be split up in a sum of integrals over all cells. So Eq. (2) becomes

$$n(E) = -\frac{2}{\pi} \text{Im} \sum_j \int d^3x G(\mathbf{x} + \mathbf{R}_j, \mathbf{x} + \mathbf{R}_j). \quad (23)$$

Substituting expression (3) in Eq. (23), and using (18) and (19), one finds

$$n(E) = \frac{2\kappa}{\pi} \sum_j \bar{\alpha}_j - \frac{2}{\pi} \text{Im} \sum_j \alpha_j g^{jj}. \quad (24)$$

A similar expression is found for the reference system using (4):

$$n'(E) = \frac{2\kappa}{\pi} \sum_j \bar{\alpha}'_j - \frac{2}{\pi} \text{Im} \sum_j \alpha'_j g'^{jj}. \quad (25)$$

The matrix α is defined by

$$\alpha_{LL'}^j = W_j \left[\frac{d}{dE} R_L^j, R_{L'}^j \right] \quad (26)$$

in which use has been made of (22). The surface integral over the boundary of the j th cell is denoted by the label j . The matrices $\bar{\alpha}$, α' , and $\bar{\alpha}'$ are defined similarly, by placing the additional symbols in (26) at the appropriate places. As for the angular momentum labels, a trace operation, which is omitted for the sake of survey ability, should be applied to the right-hand sides of (24) and (25). For example,

$$\alpha_j g^{jj} = \sum_{LL'} \alpha_{LL'}^j g_{LL'}^{jj} \quad (27)$$

and in the first term with the overlined matrices only diagonal elements occur.

$$n(E) = \frac{2\kappa}{\pi} \sum_j \left[\cos^2(\Delta\delta^j) \bar{\alpha}'_j - \cos(\Delta\delta^j) \sin(\Delta\delta^j) (\bar{\beta}_j^{r,RS} + \bar{\beta}_j^{r,SR}) + \sin^2(\Delta\delta^j) \bar{\gamma}'_j + \frac{1}{\kappa} \frac{d\Delta\delta^j}{dE} \right] - \frac{2}{\pi} \text{Im} \sum_j \left[\{ \alpha'_j + \beta_j^{r,RH} \Delta t^j + \Delta t^j (\beta_j^{r,HR} + \gamma_j^r \Delta t^j) \} (g^r + g^r T g^r)^{jj} - \frac{d\Delta t^j}{dE} g^{jj} \right]. \quad (33)$$

Comparing (33) with (25), one recognizes in the density-of-states expression (33) for the system the expression for the reference system, the additional terms (33) being zero if $\Delta\delta^j=0$, which holds outside the perturbed regions of the system. But at the present stage of the derivation the reader will hardly believe that something simple will result. To that end three equalities are required. Two of them,

First Eqs. (17) and (21) are used to express the α matrices in terms of matrices for the reference system. One finds

$$\alpha_j = \alpha'_j + \beta_j^{r,RH} \Delta t^j + \Delta t^j (\beta_j^{r,HR} + \gamma_j^r \Delta t^j) + \frac{d\Delta t^j}{dE} W_j(H^r, R^r) \quad (28)$$

and

$$\bar{\alpha}_j = \cos^2(\Delta\delta^j) \bar{\alpha}'_j - \cos(\Delta\delta^j) \sin(\Delta\delta^j) (\bar{\beta}_j^{r,RS} + \bar{\beta}_j^{r,SR}) + \sin^2(\Delta\delta^j) \bar{\gamma}'_j - \sin(\Delta\delta^j) \frac{d \cos(\Delta\delta^j)}{dE} W_j(\bar{R}, \bar{S}) - \cos(\Delta\delta^j) \frac{d \sin(\Delta\delta^j)}{dE} W_j(\bar{S}, \bar{R}). \quad (29)$$

The matrices β and γ are integrals over a cell boundary of form (22), combining a regular and singular solution, respectively, with a singular solution. While α and γ are insensitive to the order of the functions in the generalized Wronskian expression (22), the β matrix is sensitive to it, because of which the order is indicated by a superscript. The overlined matrices are defined similarly. In writing Eqs. (28) and (29), terms are omitted which are zero. For example,

$$W_j(R, R) = W_j(H, H) = 0, \quad (30)$$

which becomes clear immediately if one realizes that a generalized Wronskian for solutions of the Schrödinger equation is independent of the closed surface over which it is calculated, and if one evaluates it over a sphere with a radius equal to or slightly larger than the muffin-tin radius. In the same way generalized Wronskians combining equal overlined solutions $\bar{R}$ and $\bar{S}$ are zero. One also finds this way that

$$W_j(H^r, R^r) = -1 \quad (31)$$

and

$$W_j(\bar{R}, \bar{S}) = -W_j(\bar{S}, \bar{R}) = \kappa^{-1}. \quad (32)$$

Substituting (28) with (31), (29) with (32), and (14) in expression (24) for $n(E)$, one finds

$$\Delta t g^r T = T - \Delta t \quad (34)$$

and

$$T g^r \Delta t = T - \Delta t, \quad (35)$$

are closely related, and both derivable from (15) by multiplying it from the left or from the right with $(\Delta t)^{-1} - g^r$. The third equality is a property of the reference system.

It reads as

$$\begin{aligned} \frac{d}{dE} \mathcal{G}^{r,jj'} = & -\gamma_j^r \delta_{jj'} - \sum_{j''} \mathcal{G}^{r,jj''} \alpha_{j''}^r \mathcal{G}^{r,j''j'} \\ & - \beta_j^{r,HR} \mathcal{G}^{r,jj'} - \mathcal{G}^{r,jj'} \beta_j^{r,RH} \end{aligned} \quad (36)$$

and can be considered a generalization of the equality by Jacobs and Zaman,¹⁶ holding for the free-space structural matrix B as defined in Eq. (12). The latter equality was rederived by one of the present authors,¹² at which opportunity an implicit property of the equality was discovered which had been overlooked by Jacobs and Zaman. The same derivation was given recently by Zhang and Butler¹⁵ and Kaprzyk and Bansil.¹⁷ The derivation of the generalized equality (36) is given in an Appendix.

$$\begin{aligned} n(E) = n^r(E) + \frac{2\kappa}{\pi} \sum_j \left[-\sin^2(\Delta\delta^j)(\bar{\alpha}_j^r - \gamma_j^r) - \cos(\Delta\delta^j)\sin(\Delta\delta^j)(\bar{\beta}_j^{r,RS} + \bar{\beta}_j^{r,SR}) + \frac{1}{\kappa} \frac{d\Delta\delta^j}{dE} \right] \\ - \frac{2}{\pi} \text{Im} \sum_j \left[\alpha_j^r (\mathcal{G}^r \mathcal{T} \mathcal{G}^r)^{jj} + \beta_j^{r,RH} (\mathcal{T} \mathcal{G}^r)^{jj} + \beta_j^{r,HR} (\mathcal{G}^r \mathcal{T})^{jj} + \gamma_j^r (\mathcal{T}^{jj} - \Delta t^j) - \frac{d\Delta t^j}{dE} \mathcal{G}^{jj} \right]. \end{aligned} \quad (40)$$

Employing the generalized equality (36) leads to a considerable reduction of the second j summation in (40). It becomes equal to

$$\frac{2}{\pi} \text{Im} \text{Tr} \left\{ \mathcal{T} \frac{d\mathcal{G}^r}{dE} + \gamma^r \Delta t + \frac{1}{1 - \mathcal{G}^r \Delta t} \mathcal{G}^r \frac{d\Delta t}{dE} \right\}, \quad (41)$$

in which the trace operation applies to (jL) labels, the position label in it running over the perturbed region in the system, with $\Delta t^j \neq 0$, only. Equation (11) is used to replace $\mathcal{G}$ in the third term.

Now the matrix γ^r , using (19) applied to the reference system, is to be written as

$$\gamma^r = -\kappa^2 e^{-2i\delta_l^r} (\bar{\alpha}^r + i\bar{\beta}^{r,RS} + i\bar{\beta}^{r,SR} - \bar{\gamma}^r), \quad (42)$$

while

$$e^{-2i\delta_l^r} \Delta t_l \equiv t_{\Delta,l} = -\frac{1}{\kappa} \sin(\Delta\delta_l) e^{i\Delta\delta_l}. \quad (43)$$

Substituting (41)–(43) in (40), and using the definition (15) of $\mathcal{T}$, a further reduction

$$n(E) = n^r(E) - \frac{2}{\pi} \frac{d}{dE} \text{Im} \text{Tr} \ln(1 - \mathcal{G}^r \Delta t) + \frac{2}{\pi} \text{Tr} \left\{ \frac{d\Delta\delta}{dE} \right\} \quad (44)$$

is found. In the meantime the difference-scattering t matrix t_Δ has been introduced by (43), which will turn out to be an essential ingredient¹¹ of the final expression for the density of states, in addition to the difference of t matrices Δt . Note the similarity between t_Δ and the potential scattering t matrix t given in Eq. (7), which in fact illuminates the name given to the former matrix. Now, finally, after writing the third term in (44) in terms t_Δ , the

By now the simplification of (33) can be realized quickly. Using (34) and (35), one finds the equalities

$$\Delta t^j (\mathcal{G}^r + \mathcal{G}^r \mathcal{T} \mathcal{G}^r)^{jj} = (\mathcal{T} \mathcal{G}^r)^{jj}, \quad (37)$$

$$(\mathcal{G}^r + \mathcal{G}^r \mathcal{T} \mathcal{G}^r)^{jj} \Delta t^j = (\mathcal{G}^r \mathcal{T})^{jj}, \quad (38)$$

and

$$\Delta t^j (\mathcal{G}^r + \mathcal{G}^r \mathcal{T} \mathcal{G}^r)^{jj} \Delta t^j = \mathcal{T}^{jj} - \Delta t^j. \quad (39)$$

Substituting these equalities into (33), using expression (25) for the density of states of the reference system $n^r(E)$, and employing explicitly the fact that the matrices can be cyclically exchanged because of the trace operation with respect to the angular momentum, one finds

expression for the system density of states obtains the form

$$n(E) = n^r(E) + \frac{2}{\pi} \frac{d}{dE} \text{Im} \text{Tr} \ln \left\{ t_\Delta \frac{1}{1 - \mathcal{G}^r \Delta t} \right\}. \quad (45)$$

The t matrix $T(E)$ of the system with respect to the reference system being given by¹¹

$$T(E) = t_\Delta \frac{1}{1 - \mathcal{G}^r \Delta t}, \quad (46)$$

Eq. (45) is apparently the generalized Lloyd formula (1) we were looking for, by which its derivation has been achieved. Expression (45) was obtained earlier by one of the present authors,¹¹ starting from the operator equation (52) to be discussed below.

IV. DISCUSSION

By now having derived the generalized Lloyd formula (1) for the density of states of a system $n(E)$ described with respect to the density of states of a general reference system, some comments are in order.

First of all, for free space as a reference system, the t matrix (46) in it reduces to the t matrix

$$T^0(E) = t \frac{1}{1 - Bt}, \quad (47)$$

leading to the correct form^{9,12} of the original Lloyd formula.¹ This follows immediately by evaluating t_Δ , Δt , and $\mathcal{G}^r$, defined by Eq. (43), (13), and (10), for $t^r = \delta^r = 0$.

Second, its practical importance should be stressed. In all previous treatments (see, e.g., Refs. 9, 12, 15, 17, and 18) the original Lloyd formula formed the starting point, implying an infinitely large t matrix (47) for the systems

considered, like a binary alloy. The dimension of the t matrix (46) in the generalized formula is limited, and determined by those parts of the system which deviate from the reference system.¹¹ For a binary alloy described by the single-site coherent-potential approximation only one site contributes, and for a dilute alloy the dimension is restricted to the atoms in a relatively small impurity cluster, due to possible charge transfer and lattice distortion¹⁴ around the impurity.

Third, expression (46) for the t matrix to be substituted in (1) reveals the general structure of a Lloyd formula. Apart from appropriate t matrices, the Green's-function matrix of the reference system is a vital ingredient. Its origin is clear from the derivation. This observation also forms the answer to a question raised in the previous paper.¹⁸ In applying the original Lloyd formula to both the system and the reference system, some ambiguity showed up. Two forms could be derived for $n(E) - n'(E)$, but one of these forms contained a deficiency. The origin of it was not clear. Regarding the present paragraph, the deficient form is a reduced form compared with the other, general form. The latter form indeed explicitly contained the Green's-function matrix of the reference system.

Finally, in the derivation given above the lattice distortion was not accounted for, and the interstitial-impurity case was not covered explicitly either. However, one of the authors has shown¹¹ that a simple substitution, using a purely geometrical matrix $J(\Delta)$ (Ref. 14) describing lattice distortion, leads to a more general expression which includes the latter effect as well. The substitution amounts to

$$\begin{aligned} \mathcal{G}^r &\rightarrow \tilde{\mathcal{G}}^r \equiv J(\Delta) \mathcal{G}^r J(-\Delta), \\ \Delta t &\rightarrow \Delta \tilde{t} \equiv t - J(\Delta) t' J(-\Delta), \end{aligned} \quad (48)$$

containing the displacement vector $\Delta_j = \mathbf{R}_j - \mathbf{R}_j^r$ which measures the position $\mathbf{R}_j$ of an atom in the system with respect to the corresponding position in the reference system. The matrix $J(\Delta)$ reduces to unity for $\Delta=0$. As for the interstitial-impurity case, although not covered explicitly using expressions (3) and (4) for the Green's functions, technically it is included. One just has to subdivide the system and the reference system into cells, such that some cell volume is left at an interstice, implying smaller (reference) system atom cells just around the interstice. This can be done without restriction, because no use is made of possible symmetry properties of the reference system such as translational invariance. An appropriately generalized equality of Jacobs and Zaman follows along the same lines, having the same form as (36), but with site labels which include the position of the interstice. The expressions for the Green's functions to be used have the same form as (3) and (4), and are available in the literature.¹⁹ The final form (45) with (46) is unaffected. The only difference is the site label which now includes the position of the impurity in the interstice.

It is tempting to look for possible roots of the possibility to find generalizations of the Lloyd formula, by starting from a well-known operator form of the Lloyd formula.

1a. The Green's-function operator $G(E) = (E^+ - H)^{-1}$ in Eq. (2) can be written as

$$\begin{aligned} G(E) &= G'(E) + G'(E) \Delta V G(E) \\ &= G'(E) + G'(E) \Delta V \frac{1}{1 - G'(E) \Delta V} G'(E) \\ &= G'(E) + G'(E) \frac{1}{(\Delta V)^{-1} - G'(E)} G'(E), \end{aligned} \quad (49)$$

in which $H = H^r + \Delta V$ is used, and which allows for the usual definition of the t operator

$$T^{\text{op}}(E) = \Delta V \frac{1}{1 - G'(E) \Delta V} = \frac{1}{(\Delta V)^{-1} - G'(E)}. \quad (50)$$

Substituting (49) into (2), using the property of cyclic invariance of operator products with respect to a trace operation, and employing equality (A1) given in the Appendix, which holds for $G'(E)$ as well, one finds

$$\begin{aligned} n(E) &= n'(E) - \frac{2}{\pi} \text{Im Tr} \left\{ G'(E) \frac{1}{(\Delta V)^{-1} - G'(E)} G'(E) \right\} \\ &= n'(E) + \frac{2}{\pi} \text{Im Tr} \left\{ \frac{1}{(\Delta V)^{-1} - G'(E)} \frac{dG'(E)}{dE} \right\} \\ &= n'(E) - \frac{2}{\pi} \text{Im} \frac{d}{dE} \text{Tr} \ln \{ (\Delta V)^{-1} - G'(E) \}. \end{aligned} \quad (51)$$

With (50) this leads immediately¹¹ to

$$n(E) = n'(E) + \frac{2}{\pi} \text{Im} \frac{d}{dE} \text{Tr} \ln T^{\text{op}}(E). \quad (52)$$

Although the similarity to the Lloyd formula (1), containing a matrix instead of an operator, is striking, it is by no means simple to reduce (52) to (1). By implementing the trace operator, one is faced by one of two problems. Either one uses a complete set of states, e.g., Bloch functions in the case of a dilute alloy, but then off-the-energy-shell matrix elements of $T^{\text{op}}(E)$ are generated, which do not lead to simple forms. Or, regarding the final equation (1), containing only on-the-energy-shell t -matrix elements, one seems invited to use only the subset of states at the energy E . But then one introduces an additional energy dependence under the energy derivative in (52), and it is not clear whether this is allowed.

There may be a way out of the latter problems if one returns to the work of Krein²⁰ and Birman and Krein²¹ in the field of formal scattering theory, pointed at by Faulkner.²² Faulkner has explored the link between Birman and Krein's S -matrix form²¹ and Lloyd's original formula. Regarding the result of the present paper it is challenging to investigate how far it is possible to extend Faulkner's contribution in the direction of a more general description using a general reference system.

The generalized Lloyd formula (1) with (46) is just one example of a generalization of the original multiple-scattering theory.^{23,24} The formulation of multiple-scattering theory in a system, described with respect to a

more general reference system¹¹ than free space, will be the subject of a subsequent paper.²⁵

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APPENDIX

Equality (36) will be proved starting from the operator equality

$$\frac{dG(E)}{dE} = -G(E)G(E), \quad (A1)$$

which is easily shown to hold for any Green's-function operator of the form $(E^+ - H)^{-1}$. Jacobs and Zaman derived their equality¹⁶ for the B matrices defined by (12) starting from the operator equality for the free-electron Green's-function operator $G^0(E)$. We will apply (A1) to the Green's-function operator $G^r(E)$ of the reference system. In the $\mathbf{r}$ representation the operator equality can be written as

$$\begin{aligned} \frac{d}{dE} G^r(\mathbf{x} + \mathbf{R}_j, \mathbf{x}' + \mathbf{R}_{j'}) \\ = - \sum_{j''} \int_{\text{cell } j''} d^3x'' G^r(\mathbf{x} + \mathbf{R}_j, \mathbf{x}'' + \mathbf{R}_{j''}) \\ \times G^r(\mathbf{x}'' + \mathbf{R}_{j''}, \mathbf{x}' + \mathbf{R}_{j'}) \end{aligned} \quad (A2)$$

in which the internal integration over all space is split up in integrals over cell volumes. Expression (4) will be used in the elaboration of (A2). From now on the label r will be omitted, which in fact is irrelevant for the derivation. The left-hand side (LHS) of (A2) is equal to

$$\begin{aligned} \text{LHS} = & \left[\frac{dR^j(\mathbf{x})}{dE} H^j(\mathbf{x}') + R^j(\mathbf{x}) \frac{d}{dE} H^j(\mathbf{x}') \right] \\ & \times \delta_{jj'} + R^j(\mathbf{x}) \frac{d\mathcal{G}^{jj'}}{dE} R^{j'}(\mathbf{x}') \\ & + \frac{dR^j(\mathbf{x})}{dE} \mathcal{G}^{jj'} R^{j'}(\mathbf{x}') + R^j(\mathbf{x}) \mathcal{G}^{jj'} \frac{d}{dE} R^{j'}(\mathbf{x}'), \end{aligned} \quad (A3)$$

in which the choice $x < x'$ has been made. It will turn out to be convenient to make a choice, but the derivation will appear to be insensitive to which choice is made. The right-hand side of (A2) is equal to

$$\text{RHS} = - \sum_{j''} \int_{\text{cell } j''} d^3x'' [R^j(\mathbf{x}_<) H^j(\mathbf{x}_>) \delta_{jj''} + R^j(\mathbf{x}) \mathcal{G}^{jj''} R^{j''}(\mathbf{x}'')][R^{j'}(\mathbf{x}_<) H^{j'}(\mathbf{x}_>) \delta_{j''j'} + R^{j''}(\mathbf{x}'') \mathcal{G}^{j''j'} R^{j'}(\mathbf{x}')] . \quad (A4)$$

Which variables must be substituted for $\mathbf{x}_<$ and $\mathbf{x}_>$, namely either one of the pair $(\mathbf{x}, \mathbf{x}'')$ or one of the pair $(\mathbf{x}'', \mathbf{x}')$, will be clear from the context. Some integrals in (A4) over a cell volume j can be written in terms of the matrix α_j , defined by (26) with (22). In addition, matrices $\alpha_j(x)$, β_j^{RH} , $\beta_j^{RH}(x)$, γ_j , and $\gamma_j(x)$ will show up. These matrices can be defined relatively concisely if the matrix α_j is written more explicitly as

$$\alpha_j = W_{j,A}(R'_E, R), \quad (A5)$$

in which A stands for the cell surface, and the derivative with respect to the energy is denoted in a slightly different way. If the surface integral is to be taken over an inscribed sphere with radius x , the character x will be written instead of A . The matrices mentioned above are now defined as

$$\alpha_j(x) = W_{j,x}(R'_E, R), \quad \beta_j^{RH} = W_{j,A}(R'_E, H), \quad \beta_j^{RH}(x) = W_{j,x}(R'_E, H), \quad \gamma_j = W_{j,A}(H'_E, H), \quad \gamma_j(x) = W_{j,x}(H'_E, H). \quad (A6)$$

Written in terms of these matrices, (A4) looks like

$$\begin{aligned} \text{RHS} = & - \{ H^j(\mathbf{x}) \alpha_j(x) H^j(\mathbf{x}') + R^j(\mathbf{x}) [\beta_j^{HR}(\mathbf{x}') - \beta_j^{HR}(x)] H^j(\mathbf{x}') + R^j(\mathbf{x}) [\gamma_j - \gamma_j(x')] R^j(\mathbf{x}') \} \delta_{jj'} \\ & - \{ H^j(\mathbf{x}) \alpha_j(x) + R^j(\mathbf{x}) [\beta_j^{HR} - \beta_j^{HR}(x)] \} \mathcal{G}^{jj'} R^{j'}(\mathbf{x}') \\ & - R^j(\mathbf{x}) \mathcal{G}^{jj'} \{ \alpha_j(x') H^{j'}(\mathbf{x}') + [\beta_j^{RH} - \beta_j^{RH}(x')] R^{j'}(\mathbf{x}') \} - R^j(\mathbf{x}) \sum_{j''} \mathcal{G}^{jj''} \alpha_{j''} \mathcal{G}^{j''j'} R^{j'}(\mathbf{x}'). \end{aligned} \quad (A7)$$

In the order of the terms the reader will recognize that again use has been made of the choice $x < x'$. Now it can be proved that

$$H^j(\mathbf{x}) \alpha_j(x) - R^j(\mathbf{x}) \beta_j^{HR}(x) = - \frac{d}{dE} R^j(\mathbf{x}), \quad (A8)$$

and that

$$\beta_j^{HR}(x) H^j(\mathbf{x}) - \gamma_j(x) R^j(x) = - \frac{dH^j(\mathbf{x})}{dE}. \quad (A9)$$

A first step in the proof is to make use of the property that matrices α , β , and γ in (A8) and (A9) are diagonal in angular momentum. This is due to the fact that a Wronskian expression (22) over a spherical surface with radius

x reduces to an ordinary scalar Wronskian as, e.g.,

$$\alpha_{LL'}(x) = x^2 \left[\frac{dR_l(x)}{dE}, R_l(x) \right] \delta_{LL'}, \quad (\text{A10})$$

in which the j label has been skipped. The factor x^2 comes from the surface integration element.

This means that in (A8) the order in a product of a solution of the Schrödinger equation and an α or β matrix can be changed, which is useful to keep in mind in applying it to (A7). Writing the angular momentum label explicitly and skipping the j label, (A8) and (A9) are equivalent to

$$x^2 H_l(x) \left[\frac{dR_l(x)}{dE}, R_l(x) \right] - x^2 R_l(x) \left[\frac{dH_l(x)}{dE}, R_l(x) \right] = -\frac{d}{dE} R_l(x) \quad (\text{A11})$$

and

$$x^2 \left[\frac{dH_l(x)}{dE}, R_l(x) \right] H_l(x) - x^2 \left[\frac{dH_l(x)}{dE}, H_l(x) \right] R_l(x) = -\frac{dH_l(x)}{dE}, \quad (\text{A12})$$

respectively. The latter equality is found immediately by writing out the Wronskians and applying the Wronskian property (9), given in the main text, once. The proof of (A11) requires a substitution of the equality

$$\left[\frac{dH_l(x)}{dE}, R_l(x) \right] = \left[\frac{dR_l(x)}{dE}, H_l(x) \right] \quad (\text{A13})$$

first, after which it follows immediately as well. Equality (A13) is found by differentiating the Wronskian property (9) with respect to the energy. By the way, this equality shows that in (A8) the superscript HR could be RH as well.

Apply now equalities (A8) and (A9) to (A7), and combine the expression reduced in this way for the RHS with expression (A3) for the LHS. One finds, due to an impressive cancellation of terms, the following equality:

$$R^j(\mathbf{x}) \frac{d\mathcal{G}^{jj'}}{dE} R^{j'}(\mathbf{x}') = -R^j(\mathbf{x}) \left[\gamma_j \delta_{jj'} + \beta_j^{HR} \mathcal{G}^{jj'} + \mathcal{G}^{jj'} \beta_j^{RH} + \sum_{j''} \mathcal{G}^{jj''} \alpha_{j''} \mathcal{G}^{j''j'} \right] R^{j'}(\mathbf{x}'). \quad (\text{A14})$$

The internal matrix relation reduces to an identity

$$\frac{d\mathcal{G}^{jj'}}{dE} = -\gamma_j \delta_{jj'} - \beta_j^{HR} \mathcal{G}^{jj'} - \mathcal{G}^{jj'} \beta_j^{RH} - \sum_{j''} \mathcal{G}^{jj''} \alpha_{j''} \mathcal{G}^{j''j'}, \quad (\text{A15})$$

which follows from the fact that equality (A14) holds continuously in a finite volume in $\mathbf{x}$ space, but which also can be proved explicitly by taking inner products with the spherical harmonics $Y_L(\hat{\mathbf{x}})$ and $Y_L(\hat{\mathbf{x}}')$ and by subsequently applying the Wronskian property (9) twice.

Equality (A15) is a generalized equality compared with the one derived by Jacobs and Zaman.¹⁶ Restoring the superscript r again, referring to the reference system, it gives precisely the equality (36) we were looking for.

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¹P. Lloyd, Proc. Phys. Soc. **90**, 207 (1967).

²P. House and P. V. Smith, J. Phys. F **3**, 753 (1973).

³D. B. B. Rijsenbrij and A. Lodder, J. Phys. F **6**, 1053 (1976).

⁴G. Ries and H. Winter, J. Phys. F **9**, 1589 (1979).

⁵C. E. van Dijkum and A. Lodder, Phys. Status Solidi B **106**, 107 (1981).

⁶W. John and W. Keller, J. Phys. F **7**, L223 (1977).

⁷R. Lenk, Phys. Status Solidi B **86**, 603 (1978).

⁸L. Schwartz and A. Bansil, Phys. Rev. B **10**, 3261 (1974).

⁹G. Lehmann, Phys. Status Solidi B **70**, 737 (1975).

¹⁰A. Lodder and C. E. van Dijkum, Phys. Lett. **74A**, 110 (1979).

¹¹P. J. Braspenning, Ph.D. thesis, Vrije Universiteit, Amsterdam, 1982, available on request.

¹²A. Lodder, J. Phys. F **10**, 1117 (1980).

¹³M. Hamazaki, S. Asano, and J. Yamshita, J. Phys. Soc. Jpn. **41**, 378 (1976).

¹⁴A. Lodder, J. Phys. F **6**, 1885 (1976).

¹⁵X.-G. Zhang and W. H. Butler, Phys. Rev. B **46**, 7433 (1992).

¹⁶R. L. Jacobs and N. Zaman, J. Phys. F **7**, 283 (1977).

¹⁷S. Kaprzyk and A. Bansil, Phys. Rev. B **42**, 7358 (1990).

¹⁸A. Lodder and J. P. Dekker, preceding paper, Phys. Rev. B **49**, 10 206 (1994).

¹⁹P. M. Oppeneer and A. Lodder, J. Phys. F **17**, 1885 (1987).

²⁰M. G. Krein, Matem. Sborn. **33**, 597 (1953).

²¹M. L. Birman and M. G. Krein, Sov. Math. Dokl. **3**, 740 (1962).

²²J. S. Faulkner, J. Phys. C **10**, 4661 (1977).

²³J. Korrynga, Physica **13**, 392 (1947).

²⁴W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

²⁵P. J. Braspenning and A. Lodder, following paper, Phys. Rev. B **49**, 10 222 (1994).