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# An elementary derivation of Lloyd's formula valid for full-potential multiple-scattering theory

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## Abstract

Lloyd's formula is an elegant tool in multiple-scattering theory. It implicitly provides an analytical integration over energy and over all space and directly gives the number of states as a function of energy. The usual derivations of Lloyd's formula are involved and the range of their applicability is not obvious. It is the purpose of this paper to give a derivation which requires only elementary mathematical manipulations. The result is valid for potentials of general shape and for arbitrary complex energies.

## 1. Introduction

Lloyd's formula [1, 2] is an important concept in the Korringa–Kohn–Rostoker (KKR) multiple-scattering theory [2–4], since it provides an analytical integration over energy and over all space, and directly gives the number of electronic states as a function of energy. Its mathematical derivation is involved and has been the subject of many investigations [1, 2, 5–23]. Unfortunately, because of mathematical difficulty some of the derivations are incorrect or of limited applicability. Kaprzyk and Bansil [19] argue that Lloyd's formula in the previous literature contains spurious singularities, which must be subtracted in an ad hoc manner. Lehmann [10] points out a mistake made by Lloyd [1] and John and Ziesche [5]. Terakura refers to a shortcoming in the formulation of Lasseter and Soven [7]. Lodder and van Dijkum [15] and Faulkner and Stocks [16] criticize Jacobs and Zaman [13] because they left out certain critical terms. Furthermore, most of the existing derivations are restricted to real energies and to potentials of muffin-tin type. This is a serious limitation in view of the recent developments of the KKR Green-function method [24], which now routinely uses the general shape of the potential and complex energies contours with finite temperatures [25] for energy integrations necessary to obtain charge densities and total energies.

The extension of Lloyd's formula to complex energies has been treated by Drittler *et al* [18], Kaprzyk and Bansil [19], and Akai and Dederichs [26]. The situation in the literature with

respect to the muffin-tin approximation can be characterized by a statement given by Zhang and Butler [21], who state that they believe that their result is valid for full-cell potentials, although they had to use some steps in their derivation which are not valid for this case. According to Dederichs [27] a treatment of potentials of general shape requires a careful separation into single-scattering and multiple-scattering terms. The formal operator expression  $\text{Tr} \ln(1 - gV)$ , where  $g$  is the free space Green function and  $V$  is the potential, can be written as a sum of  $\text{Tr} \ln(1 - g_b \tau)$  and  $\text{Tr} \ln(1 - g_s V)$ , where  $\tau$  is defined as  $\tau = V(1 - g_s V)^{-1}$  and  $g_b$  and  $g_s$  are the back-scattering and single-scattering parts of  $g$ . The logarithms can be expanded into infinite series, where each term can be integrated over space. The resulting series can be summed to obtain matrix logarithms and yields Lloyd's formula [20, 28] in the form used in the Jülich full-potential KKR computer programs [24].

Although these formal manipulations lead to the correct result, the range of validity is not obvious, since the formal series for the multivalued complex logarithms probably diverge for most potentials. It would be desirable to derive Lloyd's formula more straightforwardly and it is the purpose of this paper to give such a derivation, which uses no more mathematics than the product rule of differentiation, the separation of integrals over all space into integrals over atomic cells and simple substitutions. No use is made of boundary conditions at infinity, of Wronskians or of surface integrals over complicated cell boundaries. Real-part contributions are not neglected and no plausibility arguments are necessary to remove rapidly oscillating terms. The present derivation differs from most previous ones, which use differential equations for the multiple-scattering wavefunction, by the use of integral equations for the multiple-scattering Green function. The advantage of integral equations is that boundary conditions are built in, whereas these boundary conditions require an explicit treatment in differential equations.

The outline of the paper is as follows. Section 2 describes the basic theory and gives Lloyd's formula in the notation of Drittler *et al* [18, 28], which is valid for complex energies and for non-overlapping potentials of arbitrary shape. Section 3 contains the full-potential multiple-scattering equations, which are necessary for the elementary derivation of Lloyd's formula. The derivation in section 4 is based on the integral equation (Dyson equation), which connects two Green functions for two different potentials. The trace of the difference in the Green functions is separated into the contributions arising from single-site scattering, back-scattering and cross terms. These terms are simplified by various substitutions and are shown to lead to the correct form of Lloyd's formula. Section 5 contains the conclusions and the appendices contain necessary details for the derivation in section 4.

## 2. Basic theory

For a system of non-interacting electrons the electronic density of states can formally be expressed as

$$n(E) = -\frac{1}{\pi} \text{Im Tr } G(E). \quad (1)$$

Here the energy  $E$  is in general complex and  $G(E) = (E - H)^{-1}$  is the Green-function operator for the Hamiltonian  $H$  of the single-particle Schrödinger equation  $H = -\nabla^2 + V$  (using atomic units  $\hbar^2/2m = 1$ ). From (1) the standard result for the density of states at real energies follows by taking the limit  $\text{Im } E \rightarrow +0$ . The difference between the density of states for two systems characterized by two Green-function operators  $G(E)$  and  $g(E)$  is given by

$$\Delta n(E) = -\frac{1}{\pi} \text{Im Tr}[G(E) - g(E)]$$

$$\begin{aligned}
&= -\frac{1}{\pi} \operatorname{Im} \operatorname{Tr}[g(E)VG(E)] \\
&= -\frac{1}{\pi} \operatorname{Im} \operatorname{Tr} \left[ g(E)V \frac{1}{1-g(E)V} g(E) \right]
\end{aligned} \tag{2}$$

where the second and last line follow from the fundamental operator equation

$$G(E) = g(E) + g(E)VG(E) = \frac{1}{1-g(E)V}g(E). \tag{3}$$

Here and below  $V$  denotes the difference between the two potentials. Because of

$$g(E)g(E) = -\frac{d}{dE}g(E) \tag{4}$$

the last line of (2) can be expressed as

$$\Delta n(E) = -\frac{1}{\pi} \operatorname{Im} \operatorname{Tr} \frac{d}{dE} \ln(1-g(E)V). \tag{5}$$

The difference between the integrated density of states is thus given by

$$\Delta N(E) = -\frac{1}{\pi} \operatorname{Im} \operatorname{Tr} \ln(1-g(E)V). \tag{6}$$

The essential achievement of Lloyd's formula is the fact that by multiple-scattering theory the formal operator  $\operatorname{Tr} \ln(1-gV)$  can be converted into a computationally useful matrix form

$$\Delta N(E) = \frac{1}{\pi} \operatorname{Im} \sum_n \ln \det |\alpha_{LL'}^n(E)| - \frac{1}{\pi} \operatorname{Im} \ln \det \left| \delta_{LL'}^{nn'} - \sum_{L''} g_{LL''}^{nn'}(E)t_{L''L}^{n'}(E) \right| \tag{7}$$

where the first term represents the single-scattering and the second term the back-scattering contributions. In (7) the notation of Drittler *et al* [18, 20] is used, which is valid for complex energies and non-overlapping potentials of arbitrary shape. The first term contains a sum over all single-scattering sites and a determinant over the angular-momentum indices. The second term contains a determinant over the combined angular-momentum and site indices. If the potentials are such that higher angular momenta can be neglected, then the determinants can be evaluated from matrices of finite dimensions in the angular-momentum indices and (7) gives the exact result for the difference of the number of electronic states. It should be noted that for an infinite number of sites, for instance for an infinite periodic crystal, (7) gives an infinite result [23]. Then it is useful to define the density of states per unit cell and to exploit the periodicity by Fourier transformation and Brillouin-zone integration. This treatment is rather straightforward and will be omitted here.

### 3. Full-potential multiple-scattering equations

In real space the operator equation (3) is an integral equation of the form

$$G(\mathbf{x}, \mathbf{x}'; E) = g(\mathbf{x}, \mathbf{x}'; E) + \int d\mathbf{x}'' g(\mathbf{x}, \mathbf{x}''; E)V(\mathbf{x}'')G(\mathbf{x}'', \mathbf{x}'; E) \tag{8}$$

or of the equivalent form

$$G(\mathbf{x}, \mathbf{x}'; E) = g(\mathbf{x}, \mathbf{x}'; E) + \int d\mathbf{x}'' G(\mathbf{x}, \mathbf{x}''; E)V(\mathbf{x}'')g(\mathbf{x}'', \mathbf{x}'; E) \tag{9}$$

where the integrals are over all space and  $\mathbf{x}$  and  $\mathbf{x}'$  are arbitrary points in space. For free space with vanishing potential, the Green function is explicitly known as

$$g(\mathbf{x}, \mathbf{x}'; E) = -\frac{\exp(i\kappa|\mathbf{x} - \mathbf{x}'|)}{4\pi|\mathbf{x} - \mathbf{x}'|}, \quad \kappa = \sqrt{E} \tag{10}$$

which obviously satisfies the symmetry  $g(\mathbf{x}, \mathbf{x}'; E) = g(\mathbf{x}', \mathbf{x}; E)$ . By use of (8) and (9) it can be shown that the Green function for non-vanishing potentials also satisfies  $G(\mathbf{x}, \mathbf{x}'; E) = G(\mathbf{x}', \mathbf{x}; E)$ . This symmetry will be used in the derivation given below.

Multiple-scattering theory provides a decomposition of the Green function into single-scattering quantities, which depend on the potentials of the single individual atomic cells, and into energy and site dependent structure constants, which describe the multiple-scattering properties. In the notation of [24, 29] the Green functions can be written as

$$G(\mathbf{r} + \mathbf{R}^n, \mathbf{r}' + \mathbf{R}^{n'}; E) = \delta_{nn'} G_s^n(\mathbf{r}, \mathbf{r}'; E) + \sum_{LL'} R_L^n(\mathbf{r}; E) G_{LL'}^{nn'}(E) R_{L'}^{n'}(\mathbf{r}'; E) \quad (11)$$

$$g(\mathbf{r} + \mathbf{R}^n, \mathbf{r}' + \mathbf{R}^{n'}; E) = \delta_{nn'} g_s^n(\mathbf{r}, \mathbf{r}'; E) + \sum_{LL'} J_L^n(\mathbf{r}; E) g_{LL'}^{nn'}(E) J_{L'}^{n'}(\mathbf{r}'; E) \quad (12)$$

where site-centred coordinates  $\mathbf{r} = \mathbf{x} - \mathbf{R}^n$ ,  $\mathbf{r}' = \mathbf{x}' - \mathbf{R}^{n'}$  are introduced and  $\mathbf{R}^n$  and  $\mathbf{R}^{n'}$  denote the scattering sites. The notation in (12) for the Green function  $g$  resembles the usual one for free space, where the single-scattering wavefunctions  $J_L^n$  are given by products of spherical Bessel functions  $j_l$  and spherical harmonics  $Y_L$  and do not depend on  $n$ . By using the explicit superscript  $n$  the present derivation is valid for any reference system [23], not just for the free-space reference system. The first terms on the right-hand sides of (11) and (12) contain the single-site Green functions, which are connected by the integral equations

$$G_s^n(\mathbf{r}, \mathbf{r}'; E) = g_s^n(\mathbf{r}, \mathbf{r}'; E) + \int_n d\mathbf{r}'' g_s^n(\mathbf{r}, \mathbf{r}''; E) V^n(\mathbf{r}'') G_s^n(\mathbf{r}'', \mathbf{r}'; E) \quad (13)$$

$$G_s^n(\mathbf{r}, \mathbf{r}'; E) = g_s^n(\mathbf{r}, \mathbf{r}'; E) + \int_n d\mathbf{r}'' G_s^n(\mathbf{r}, \mathbf{r}''; E) V^n(\mathbf{r}'') g_s^n(\mathbf{r}'', \mathbf{r}'; E) \quad (14)$$

where  $V^n(\mathbf{r})$  is the potential difference restricted to the atomic cell  $n$  and where the integrals over the cell are denoted with explicit subscripts. The second terms on the right-hand sides of (11) and (12) are the back-scattering contributions. They contain the structure constants  $G_{LL'}^{nn'}$  and  $g_{LL'}^{nn'}$ , and the single-scattering wavefunctions  $R_L^n$  and  $J_L^n$ , which are connected by the integral equation

$$R_L^n(\mathbf{r}; E) = J_L^n(\mathbf{r}; E) + \int_n d\mathbf{r}' g_s^n(\mathbf{r}, \mathbf{r}'; E) V^n(\mathbf{r}') R_L^n(\mathbf{r}'; E). \quad (15)$$

The resolvent kernel for this integral equation is  $G_s^n(\mathbf{r}, \mathbf{r}'; E) V^n(\mathbf{r}')$  according to the identity

$$(1 + G_s^n V)(1 - g_s^n V) = 1 + G_s^n V - g_s^n V - G_s^n V g_s^n V = 1 \quad (16)$$

which is valid because of (14). In terms of the resolvent kernel the solution of (15) is

$$R_L^n(\mathbf{r}; E) = J_L^n(\mathbf{r}; E) + \int_n d\mathbf{r}' G_s^n(\mathbf{r}, \mathbf{r}'; E) V^n(\mathbf{r}') J_L^n(\mathbf{r}'; E). \quad (17)$$

The structure constants in (11) and (12) are connected by an algebraic Dyson equation

$$G_{LL'}^{nn'}(E) = g_{LL'}^{nn'}(E) + \sum_{n''} \sum_{L''L'''} g_{LL''}^{nn''}(E) t_{L''L'''}^{n''}(E) G_{L''L'''}^{n''n'}(E). \quad (18)$$

The  $t$  matrix, which appears here and in Lloyd's formula (7), is defined by

$$t_{LL'}^n(E) = \int_n d\mathbf{r} J_L^n(\mathbf{r}; E) V^n(\mathbf{r}) R_{L'}^n(\mathbf{r}; E). \quad (19)$$

By inserting (17) into (19) and using  $G_s^n(\mathbf{r}, \mathbf{r}'; E) = G_s^n(\mathbf{r}', \mathbf{r}; E)$  the symmetry

$$t_{L'L}^n(E) = t_{LL'}^n(E) \quad (20)$$

of the  $t$  matrix follows, which allows us to rewrite (18) as

$$G_{LL'}^{nn'}(E) = g_{LL'}^{nn'}(E) + \sum_{n''} \sum_{L''L'''} G_{LL''}^{nn''}(E) t_{L''L'''}^{n''}(E) g_{L''L'''}^{n''n'}(E). \quad (21)$$

It remains to define the  $\alpha$  matrix, which appears in Lloyd's formula (7). This matrix describes the different behaviour of the single-scattering solutions  $R_L^n$  and  $J_L^n$  at the origin

$$R_L^n(\mathbf{r}, E) = \sum_{L'} J_{L'}^n(\mathbf{r}, E) \alpha_{L'L}^n(E) \quad \text{for } r \rightarrow 0 \quad (22)$$

and is defined as

$$\alpha_{LL'}^n(E) = \delta_{LL'} + \int_n d\mathbf{r} H_L^n(\mathbf{r}, E) V^n(\mathbf{r}) R_{L'}^n(\mathbf{r}, E). \quad (23)$$

Here  $H_L^n$  is the irregular wavefunction of the reference system with the Green function  $g_s^n(\mathbf{r}, \mathbf{r}'; E)$ , which agrees with  $-i\kappa h_l^{(1)}(\kappa r) Y_L(\hat{\mathbf{r}})$  outside the sphere circumscribed around cell  $n$ , where  $r = |\mathbf{r}|$  denotes the length of vector  $\mathbf{r}$ . The irregular wavefunction of the system with the Green function  $G_s^n(\mathbf{r}, \mathbf{r}'; E)$  will be denoted by  $S_L^n$ . It agrees with  $H_L^n$  outside the sphere circumscribed around cell  $n$  and satisfies the integral equation

$$S_L^n(\mathbf{r}; E) = \sum_{L'} \beta_{LL'}^n(E) H_{L'}^n(\mathbf{r}; E) + \int_n d\mathbf{r}' g_s^n(\mathbf{r}, \mathbf{r}'; E) V^n(\mathbf{r}') S_L^n(\mathbf{r}'; E) \quad (24)$$

with the solution

$$S_L^n(\mathbf{r}; E) = \sum_{L'} \beta_{LL'}^n(E) \left[ H_{L'}^n(\mathbf{r}; E) + \int_n d\mathbf{r}' G_s^n(\mathbf{r}, \mathbf{r}'; E) V^n(\mathbf{r}') H_{L'}^n(\mathbf{r}'; E) \right]. \quad (25)$$

The matrix  $\beta$  is defined by

$$\beta_{LL'}^n(E) = \delta_{LL'} - \int_n d\mathbf{r} S_L^n(\mathbf{r}, E) V^n(\mathbf{r}) J_{L'}^n(\mathbf{r}, E) \quad (26)$$

and is the inverse of the  $\alpha$  matrix. This can be seen by inserting (17) into (23) and then using (25) to eliminate  $H_L^n$  in favour of  $S_L^n$ , which leads to

$$\alpha_{LL'}^n(E) = \delta_{LL'} + \sum_{L''} [\beta^{-1}]_{LL''}^n(E) \int_n d\mathbf{r} S_{L''}^n(\mathbf{r}, E) V^n(\mathbf{r}) J_{L'}^n(\mathbf{r}, E). \quad (27)$$

Here the integral can be written as  $\delta_{L''L'} - \beta_{L''L'}^n$  because of (26) and  $\alpha = \beta^{-1}$  follows. It should be noted that the integral equations given above for the single-site Green functions and wavefunctions define these functions in all space. Equations (13) and (14) are valid if  $\mathbf{r}$  and  $\mathbf{r}'$  are replaced by  $\mathbf{x}$  and  $\mathbf{x}'$ , and (15), (17), (24) and (25) are valid if  $\mathbf{r}$  is replaced by  $\mathbf{x}$ .

#### 4. Elementary derivation

In order to simplify the notation the energy variable will be suppressed in the following derivation, which starts from (8) by replacing  $G(\mathbf{x}'', \mathbf{x}')$  on the right-hand side by the right-hand side of (9). The result is

$$G(\mathbf{x}, \mathbf{x}''') - g(\mathbf{x}, \mathbf{x}''') = \int d\mathbf{x}' g(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') g(\mathbf{x}', \mathbf{x}''') \\ + \int d\mathbf{x}' \int d\mathbf{x}'' g(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') G(\mathbf{x}', \mathbf{x}'') V(\mathbf{x}'') g(\mathbf{x}'', \mathbf{x}'''). \quad (28)$$

The trace in (2) means an integration over space after setting  $\mathbf{x}''' = \mathbf{x}$ . This leads to

$$\text{Tr}(G - g) = - \int d\mathbf{x}' \dot{g}(\mathbf{x}', \mathbf{x}') V(\mathbf{x}') - \int d\mathbf{x}' \int d\mathbf{x}'' \dot{g}(\mathbf{x}'', \mathbf{x}') V(\mathbf{x}') G(\mathbf{x}', \mathbf{x}'') V(\mathbf{x}'') \quad (29)$$

where the relation (4) in the form

$$\int d\mathbf{x} g(\mathbf{x}'', \mathbf{x}; E) g(\mathbf{x}, \mathbf{x}'; E) = -\dot{g}(\mathbf{x}'', \mathbf{x}'; E) \quad (30)$$

was used. Here and below the dot means differentiation with respect to energy. The last relation is a fundamental property of the Green functions and is valid for any energy independent potential as shown in appendix B. With site-centred coordinates  $\mathbf{r}' = \mathbf{x}' - \mathbf{R}^{n'}$  and  $\mathbf{r}'' = \mathbf{x}'' - \mathbf{R}^n$  equation (29) can be written as

$$\begin{aligned} \text{Tr}(G - g) = & - \sum_n \int_n d\mathbf{r}' \dot{g}(\mathbf{r}' + \mathbf{R}^n, \mathbf{r}' + \mathbf{R}^n) V^n(\mathbf{r}') - \sum_{nn'} \int_{n'} d\mathbf{r}' \int_n d\mathbf{r}'' \\ & \times \dot{g}(\mathbf{r}'' + \mathbf{R}^n, \mathbf{r}' + \mathbf{R}^{n'}) V^{n'}(\mathbf{r}') G(\mathbf{r}' + \mathbf{R}^{n'}, \mathbf{r}'' + \mathbf{R}^n) V^n(\mathbf{r}'') \end{aligned} \quad (31)$$

where the integrals are written as sums of integrals over the cells. The potential  $V(\mathbf{x})$  is thus partitioned into a sum of non-overlapping potentials  $V^n(\mathbf{r})$ . Into (31) the Green-function representations (11) and (12) can be inserted. Both consist of a single-scattering and a back-scattering part. The single integral in (31) thus leads to a sum of two terms and the double integral to a sum of four terms. By combining these terms as described below,  $\text{Tr}(G - g)$  can be written as sum of four terms

$$\text{Tr}(G - g) = A + B + C + D. \quad (32)$$

Term  $A$  arises from the back-scattering parts of (11) and (12) and is given by

$$\begin{aligned} A = & - \sum_{nn'} \int_{n'} d\mathbf{r}' \int_n d\mathbf{r}'' \sum_{LL'L''L'''} \frac{d}{dE} [J_L^n(\mathbf{r}'') g_{LL'L''L'''}^{nn'} J_{L'}^{n'}(\mathbf{r}')] \\ & \times V^{n'}(\mathbf{r}') R_{L'''}^{n'}(\mathbf{r}') G_{L''L'''}^{n'n} R_{L''}^n(\mathbf{r}'') V^n(\mathbf{r}''). \end{aligned} \quad (33)$$

Appendix C shows that  $A$  can be rewritten as

$$\begin{aligned} A = & - \sum_{nn'} \sum_{LL'L''L'''} \dot{g}_{LL'L''L'''}^{nn'} t_{L''L'''}^n t_{L''L'''}^n \\ & - \sum_n \int_n d\mathbf{r}'' \sum_{LL'''} j_L^n(\mathbf{r}'') G_{LL'''}^{nn} R_{L'''}^n(\mathbf{r}'') V^n(\mathbf{r}'') \\ & + \sum_n \int_n d\mathbf{r}'' \sum_{LL'''} j_L^n(\mathbf{r}'') g_{LL'''}^{nn} R_{L'''}^n(\mathbf{r}'') V^n(\mathbf{r}'') \\ & - \sum_{n'} \int_{n'} d\mathbf{r}' \sum_{L'L''} j_{L'}^{n'}(\mathbf{r}') V^{n'}(\mathbf{r}') R_{L''}^{n'}(\mathbf{r}') G_{L''L'}^{n'n'} \\ & + \sum_{n'} \int_{n'} d\mathbf{r}' \sum_{L'L''} j_{L'}^{n'}(\mathbf{r}') V^{n'}(\mathbf{r}') R_{L''}^{n'}(\mathbf{r}') g_{L''L'}^{n'n'}. \end{aligned} \quad (34)$$

Cross term  $B$  arises from the back-scattering part of (12) and the single-scattering part of (11) and is given by

$$\begin{aligned} B = & - \sum_n \int_n d\mathbf{r}' \sum_{LL'} \frac{d}{dE} [J_L^n(\mathbf{r}') g_{LL'}^{nn} J_{L'}^n(\mathbf{r}')] V^n(\mathbf{r}') \\ & - \sum_n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' \sum_{LL'} \frac{d}{dE} [J_L^n(\mathbf{r}'') g_{LL'}^{nn} J_{L'}^n(\mathbf{r}')] V^n(\mathbf{r}') G_s^n(\mathbf{r}', \mathbf{r}'') V^n(\mathbf{r}'') \end{aligned} \quad (35)$$

where due to the Kronecker symbols  $\delta_{nn'}$  in (11) the sum over  $n'$  was eliminated. Appendix C shows that  $B$  can be rewritten as

$$\begin{aligned} B = & - \sum_n \sum_{LL'} t_{L'L}^n \dot{g}_{LL'}^{nn} \\ & - \sum_n \int_n d\mathbf{r}'' \sum_{LL'} j_L^n(\mathbf{r}'') g_{LL'}^{nn} R_{L'}^n(\mathbf{r}'') V^n(\mathbf{r}'') \end{aligned}$$

$$- \sum_n \int_n d\mathbf{r}' \sum_{LL'} R_L^n(\mathbf{r}') g_{LL'}^{nn} J_{L'}^n(\mathbf{r}') V^n(\mathbf{r}'). \quad (36)$$

Cross term  $C$  arises from the single-scattering part of (12) and the back-scattering part of (11) and is given by

$$C = - \sum_n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' \sum_{LL'} \dot{g}_s^n(\mathbf{r}'', \mathbf{r}') V^n(\mathbf{r}') R_L^n(\mathbf{r}') G_{LL'}^{nn} R_{L'}^n(\mathbf{r}'') V^n(\mathbf{r}''). \quad (37)$$

Appendix C shows that  $C$  can be rewritten as

$$C = \sum_n \int_n d\mathbf{r}'' \sum_{LL'} J_L^n(\mathbf{r}'') G_{LL'}^{nn} R_{L'}^n(\mathbf{r}'') V^n(\mathbf{r}'') - \sum_n \int_n d\mathbf{r}' \sum_{LL'} V^n(\mathbf{r}') \dot{R}_L^n(\mathbf{r}') G_{LL'}^{nn} J_{L'}^n(\mathbf{r}'). \quad (38)$$

Term  $D$  arises from the single-scattering parts of (11) and (12) and is given by

$$D = - \sum_n \int_n d\mathbf{r}' \dot{g}_s^n(\mathbf{r}', \mathbf{r}') V^n(\mathbf{r}') - \sum_n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' \dot{g}_s^n(\mathbf{r}'', \mathbf{r}') V^n(\mathbf{r}') G_s^n(\mathbf{r}', \mathbf{r}'') V^n(\mathbf{r}''). \quad (39)$$

This term is a sum of single-scattering contributions  $D = \sum_n D^n$  with

$$D^n = \int_n d\mathbf{r}' \int d\mathbf{x} g_s^n(\mathbf{x}, \mathbf{r}') V^n(\mathbf{r}') g_s^n(\mathbf{r}', \mathbf{x}) + \int_n d\mathbf{r}' \int_n d\mathbf{r}'' \int d\mathbf{x} g_s^n(\mathbf{x}, \mathbf{r}') V^n(\mathbf{r}') G_s^n(\mathbf{r}', \mathbf{r}'') V^n(\mathbf{r}'') g_s^n(\mathbf{r}'', \mathbf{x}) \quad (40)$$

where the relation (30) for the single-site Green function  $g_s^n$  was used. Here (13) can be used to eliminate the integral over  $\mathbf{r}''$ , and then (14) can be used to eliminate the integral over  $\mathbf{r}'$ . The result is

$$D^n = \int_n d\mathbf{r}' \int d\mathbf{x} G_s^n(\mathbf{x}, \mathbf{r}') V^n(\mathbf{r}') g_s^n(\mathbf{r}', \mathbf{x}) = \int d\mathbf{x} [G_s^n(\mathbf{x}, \mathbf{x}) - g_s^n(\mathbf{x}, \mathbf{x})]. \quad (41)$$

It is important to note that the last integral is over all space. Thus  $D$  differs from the result which would be obtained if the single-site parts of (11) and (12) are inserted into the left-hand side of (28). By integration this would lead to a sum of integrals over the cells instead of a sum of integrals over all space and a clear separation of Lloyd's formula into single-scattering and the back-scattering parts would be impossible.

$D^n$  can be expressed by a logarithmic derivative of the  $\alpha$  matrix (23).

$$D^n = \frac{d}{dE} \sum_L [\ln \alpha^n]_{LL}. \quad (42)$$

By integration over energy and summation over  $n$  the single-scattering contribution of Lloyd's formula (7) follows from (42). For spherical potentials the validity of (42) was shown by Drittler *et al* [18]. Later [20] the proof was extended to potentials of general shape by expanding the single-scattering wavefunctions  $R_L^n(\mathbf{x})$  and  $S_L^n(\mathbf{x})$  into spherical harmonics, for instance,  $R_L^n(\mathbf{x}) = \sum_{L'} R_{LL'}^n(x) Y_{L'}(\hat{\mathbf{x}})$ . The convergence behaviour of such expansions has been extensively debated in the literature [30] and care must be taken with respect to the order of summations over  $L$  and  $L'$ . Appendix A shows that such spherical-harmonics expansions for the single-scattering wavefunctions are not necessary to establish the validity of (42).



It remains to show that the sum of (34), (36) and (38) leads to the back-scattering part of Lloyd's formula. The sum is given by

$$\begin{aligned}
 A + B + C = & - \sum_{nn'} \sum_{LL'L''L'''} \dot{g}_{LL'L'L''}^{nn'} t_{L'L''}^{n'} G_{L''L'''}^{n'n} t_{L''L}^n - \sum_n \sum_{LL'} t_{L'L}^n \dot{g}_{LL'}^{nn} \\
 & - \sum_{n'} \int_{J_{n'}} d\mathbf{r}' \sum_{L'L''} \mathbf{j}_{L'}^{n'}(\mathbf{r}') V^{n'}(\mathbf{r}') R_{L''}^{n'}(\mathbf{r}') G_{L''L'}^{n'n'} \\
 & - \sum_n \int_{J_n} d\mathbf{r}' \sum_{LL'} V^n(\mathbf{r}') \dot{R}_L^n(\mathbf{r}') G_{LL'}^{nn} J_{L'}^n(\mathbf{r}') \quad (43)
 \end{aligned}$$

since the second term of (34) cancels against the first term of (38), the third term of (34) against the second term of (36) and the last term of (34) against the last term of (36). Differentiation of (19) with respect to energy shows that the remaining integrals in (43) can be expressed by the energy derivative of the  $t$  matrix. The result is

$$A + B + C = - \sum_n \sum_{LL'} t_{L'L}^n \dot{g}_{LL'}^{nn} - \sum_{nn'} \sum_{LL'L''L'''} \dot{g}_{LL'L'L''}^{nn'} t_{L'L''}^{n'} G_{L''L'''}^{n'n} t_{L''L}^n - \sum_n \sum_{LL'} \dot{t}_{L'L}^n G_{LL'}^{nn} \quad (44)$$

or in concise matrix notation

$$A + B + C = - \text{Tr}[t \dot{g} + t \dot{g} t G + \dot{t} g + \dot{t} g t G] = - \text{Tr}[(t \dot{g} + \dot{t} g)(1 + t G)] \quad (45)$$

where  $G = g + g t G$  was used to replace the last  $G$  in (44). The last result can be rewritten by use of the identity  $(1 - t g)(1 + t G) = 1$  as

$$\begin{aligned}
 A + B + C &= - \text{Tr}[(t \dot{g} + \dot{t} g)(1 - t g)^{-1}] \\
 &= \frac{d}{dE} \text{Tr} \ln(1 - t g). \quad (46)
 \end{aligned}$$

Energy integration and use of the matrix identity  $\text{Tr} \ln M = \ln \det M$  directly lead to the back-scattering contribution of Lloyd's formula (7).

## 5. Conclusion

The main conclusion of this paper is that Lloyd's formula, which in multiple-scattering theory directly gives the energy integrated density of states, can be derived by elementary mathematical means. The basic relation used is that a spatial integral over the product of two identical Green functions can be obtained by differentiating this Green function with respect to energy. The derivation given is rather general and covers both real and complex potentials. The form of the potentials is not restricted to the muffin-tin approximation, but can be of general shape within non-overlapping cells around the atomic scattering sites. Thus Lloyd's formula is generally valid in full-potential multiple-scattering theory. The derivation given also makes no assumption for the energy and is thus valid both for real and complex energies. The validity for complex energies is important for the use of Lloyd's formula in electronic-structure calculations, which use energy integrations along contours in the energy plane. A further result of this paper is that Lloyd's formula can be derived without an additional expansion of the single-scattering wavefunctions in terms of spherical harmonics. Thus the question, whether such an expansion converges or how fast it converges, is avoided in the present derivation.

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**Appendix A. Single-site Green function**

The purpose of this appendix is to show that the single-site Green functions  $g_s^n$  and  $G_s^n$  can be written in semi-separable form

$$G_s(\mathbf{x}, \mathbf{x}') = \sum_L R_L(\mathbf{x}_<) S_L(\mathbf{x}_>) \tag{A.1}$$

$$g_s(\mathbf{x}, \mathbf{x}') = \sum_L J_L(\mathbf{x}_<) H_L(\mathbf{x}_>) \tag{A.2}$$

where  $\mathbf{x}_<$  and  $\mathbf{x}_>$  denote the vectors  $\mathbf{x}$  and  $\mathbf{x}'$  with smaller and larger length and where, as in the rest of this appendix, the cell superscript  $n$  is suppressed to simplify the notation. The proof is based on a technique explained by Rall [31, 32] and starts from the Fredholm integral equation

$$y(\mathbf{x}) = f(\mathbf{x}) + \int d\mathbf{x}' g_s(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') y(\mathbf{x}') \tag{A.3}$$

for an arbitrary function  $f(\mathbf{x})$ , which in terms of the resolvent kernel has the solution

$$y(\mathbf{x}) = f(\mathbf{x}) + \int d\mathbf{x}' G_s(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') f(\mathbf{x}'). \tag{A.4}$$

The proof establishes that  $G_s$  can be written in the form (A.1), if  $g_s$  can be written in the form (A.2). Since the validity of (A.2) is well known for the free-space Green function (10), where  $J_L$  and  $H_L$  are products of spherical Bessel and Hankel functions and spherical harmonics, this shows that single-site Green functions can always be written in the semi-separable forms (A.1) and (A.2). The proof applies (A.2) to convert Fredholm integral equations into Volterra integral equations. For instance, by adding and subtracting appropriate terms (24) can be converted into

$$S_L(\mathbf{x}) = H_L(\mathbf{x}) + \int d\mathbf{x}' k_s(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') S_L(\mathbf{x}') \tag{A.5}$$

with

$$k_s(\mathbf{x}, \mathbf{x}') = \Theta(x - x') \sum_L [J_L(\mathbf{x}') H_L(\mathbf{x}) - J_L(\mathbf{x}) H_L(\mathbf{x}')] \tag{A.6}$$

where  $\Theta(x)$  is the Heaviside step function. The solution of (A.5) is

$$S_L(\mathbf{x}) = H_L(\mathbf{x}) + \int d\mathbf{x}' K_s(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') H_L(\mathbf{x}') \tag{A.7}$$

containing the resolvent Volterra kernel  $K_s(\mathbf{x}, \mathbf{x}') V(\mathbf{x}')$ , which satisfies

$$K_s(\mathbf{x}, \mathbf{x}') = k_s(\mathbf{x}, \mathbf{x}') + \int d\mathbf{x}'' k_s(\mathbf{x}, \mathbf{x}'') V(\mathbf{x}'') K_s(\mathbf{x}'', \mathbf{x}'). \tag{A.8}$$

(A.3) can also be converted into Volterra form by adding and subtracting terms.

$$y(\mathbf{x}) = f(\mathbf{x}) + \sum_L c_L J_L(\mathbf{x}) + \int d\mathbf{x}' k_s(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') y(\mathbf{x}'). \tag{A.9}$$

This equation has the solution

$$y(\mathbf{x}) = f(\mathbf{x}) + \sum_L c_L J_L(\mathbf{x}) + \int d\mathbf{x}' K_s(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') \left[ f(\mathbf{x}') + \sum_L c_L J_L(\mathbf{x}') \right]. \tag{A.10}$$

The coefficients  $c_L$  depend on the unknown solution  $y(x)$  and are given by

$$c_L = \int d\mathbf{x} H_L(\mathbf{x}) V(\mathbf{x}) y(\mathbf{x}). \quad (\text{A.11})$$

Equation (A.11) can be rewritten as

$$y(\mathbf{x}) = F(\mathbf{x}) + \sum_L c_L U_L(\mathbf{x}) \quad (\text{A.12})$$

with the definitions

$$F(\mathbf{x}) = f(\mathbf{x}) + \int d\mathbf{x}' K_s(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') f(\mathbf{x}') \quad (\text{A.13})$$

$$U_L(\mathbf{x}) = J_L(\mathbf{x}) + \int d\mathbf{x}' K_s(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') J_L(\mathbf{x}'). \quad (\text{A.14})$$

The last equation is the solution of the Volterra integral equation

$$U_L(\mathbf{x}) = J_L(\mathbf{x}) + \int d\mathbf{x}' k_s(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') U_L(\mathbf{x}'). \quad (\text{A.15})$$

Here (A.6) and (A.2) can be used to obtain

$$U_L(\mathbf{x}) = \sum_{L'} J_{L'}(\mathbf{x}) \tilde{\beta}_{L'L} + \int d\mathbf{x}' g_s(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') U_L(\mathbf{x}') \quad (\text{A.16})$$

where the  $\tilde{\beta}$  matrix is given by

$$\tilde{\beta}_{LL'} = \delta_{LL'} - \int d\mathbf{x} H_{L'}(\mathbf{x}) V(\mathbf{x}) U_L(\mathbf{x}). \quad (\text{A.17})$$

Comparison of (A.16) with (15) shows the connection

$$U_L(\mathbf{x}) = \sum_{L'} R_{L'}(\mathbf{x}) \tilde{\beta}_{L'L} \quad (\text{A.18})$$

which inserted into (A.17) leads to  $\tilde{\beta} = 1 - (\alpha - 1)\tilde{\beta}$ , from which  $\tilde{\beta} = \alpha^{-1} = \beta$  follows. The coefficients  $c_L$  are determined by inserting (A.12) into (A.11) and by replacing the functions  $U_L$  in favour of  $R_L$  with the help of (A.18). The result is

$$c_L = \int d\mathbf{x} H_L(\mathbf{x}) V(\mathbf{x}) F(\mathbf{x}) + \sum_{L'} c_{L'} \int d\mathbf{x} H_L(\mathbf{x}) V(\mathbf{x}) \sum_{L''} R_{L''}(\mathbf{x}) \beta_{L''L'}. \quad (\text{A.19})$$

This is a system of linear equations for the coefficients  $c_L$ . By use of (23) the second integral can be expressed by  $\alpha - 1$  and because of  $(\alpha - 1)\beta = 1 - \beta$  the solution of (A.19) is given by

$$c_L = \sum_{L'} \beta_{LL'}^{-1} \int d\mathbf{x} H_{L'}(\mathbf{x}) V(\mathbf{x}) F(\mathbf{x}) \quad (\text{A.20})$$

or by

$$c_L = \sum_{L'} \beta_{LL'}^{-1} \int d\mathbf{x} S_{L'}(\mathbf{x}) V(\mathbf{x}) f(\mathbf{x}) \quad (\text{A.21})$$

where the last result is a consequence of (A.13) and (A.7). Inserting (A.13) and (A.21) into (A.12) leads to

$$y(\mathbf{x}) = f(\mathbf{x}) + \int d\mathbf{x}' \left[ K_s(\mathbf{x}, \mathbf{x}') V(\mathbf{x}') + \sum_{LL'} U_L(\mathbf{x}) \beta_{LL'}^{-1} S_{L'}(\mathbf{x}') V(\mathbf{x}') \right] f(\mathbf{x}'). \quad (\text{A.22})$$

Here (A.18) can be used to eliminate  $U_L$  in favour of  $R_L$ . The comparison with (A.4) shows

$$G_s(\mathbf{x}, \mathbf{x}') = K_s(\mathbf{x}, \mathbf{x}') + \sum_L R_L(\mathbf{x}) S_L(\mathbf{x}'). \quad (\text{A.23})$$

According to (A.6) the Volterra kernel vanishes for  $x < x'$ . This implies  $K_s(x, x') = 0$  for  $x < x'$  and

$$G_s(x, x') = \sum_L R_L(x) S_L(x') \quad \text{for } x < x'. \quad (\text{A.24})$$

By the symmetry  $G_s(x, x') = G_s(x', x)$  the last result directly leads to (A.1), which completes the proof.

### Appendix B. Proof of $\dot{G} = -GG$ and $\dot{K} = -KK$

For the free-space Green function the fundamental relation (30) is a standard result, which can be obtained, for instance, by Fourier transformation. For a system with potential  $V$  the relation (30) for the Green function  $G$  can be derived from (8) by differentiation. This leads to

$$\dot{G} = \dot{g} + \dot{g}VG + gV\dot{G} \quad (\text{B.1})$$

where all variables and integrals are suppressed to simplify the notation. Since  $\dot{g} = -gg$  is valid for the free-space Green function, (B.1) can be rewritten as

$$\dot{G} = -gg - ggVG + gV\dot{G} \quad (\text{B.2})$$

and because of (8) as

$$(1 - gV)\dot{G} = -gG. \quad (\text{B.3})$$

The identity (16) then implies

$$\dot{G} = -(1 + GV)gG = -GG \quad (\text{B.4})$$

where the last result is obtained because of (9). Since  $k$  and  $K$  are connected by (A.8) in the same way as  $g$  and  $G$  by (8), the consideration above also shows that  $\dot{k} = -kk$  implies  $\dot{K} = -KK$ . Therefore it is sufficient to consider free space, where  $k$  can be expressed by spherical harmonics and Bessel and Neumann functions of index  $\nu = l + 1/2$  as

$$k(x, x'; \kappa) = \frac{\pi}{2\sqrt{xx'}} \Theta(x - x') \sum_L [J_\nu(\kappa x') N_\nu(\kappa x) - J_\nu(\kappa x) N_\nu(\kappa x')] Y_L(\hat{\mathbf{x}}) Y_L(\hat{\mathbf{x}}'). \quad (\text{B.5})$$

Angular integration over spherical harmonics then gives

$$\begin{aligned} \int d\mathbf{x} k(x'', \mathbf{x}; \kappa) k(x, x'; \kappa) &= \frac{\pi^2}{4\sqrt{x'x''}} \sum_L \left[ N_\nu(\kappa x'') J_\nu(\kappa x') \int_{x'}^{x''} x dx J_\nu(\kappa x) N_\nu(\kappa x) \right. \\ &\quad - J_\nu(\kappa x'') J_\nu(\kappa x') \int_{x'}^{x''} x dx N_\nu(\kappa x) N_\nu(\kappa x) \\ &\quad - N_\nu(\kappa x'') N_\nu(\kappa x') \int_{x'}^{x''} x dx J_\nu(\kappa x) J_\nu(\kappa x) \\ &\quad \left. \times J_\nu(\kappa x'') N_\nu(\kappa x') \int_{x'}^{x''} x dx N_\nu(\kappa x) J_\nu(\kappa x) \right] Y_L(\hat{\mathbf{x}}'') Y_L(\hat{\mathbf{x}}') \Theta(x'' - x'). \quad (\text{B.6}) \end{aligned}$$

Here the terms which arise from the upper limit  $x''$  and multiply  $N_\nu(\kappa x')$  can be simplified according to

$$\begin{aligned} J_\nu(\kappa x'') \int_{x'}^{x''} x dx J_\nu(\kappa x) N_\nu(\kappa x) - N_\nu(\kappa x'') \int_{x'}^{x''} x dx J_\nu(\kappa x) J_\nu(\kappa x) \\ = \frac{x''^2}{4} J_\nu[2J_\nu N_\nu - J_{\nu-1} N_{\nu+1} - J_{\nu+1} N_{\nu-1}] - \frac{x''^2}{4} N_\nu[2J_\nu J_\nu - 2J_{\nu-1} J_{\nu+1}] \end{aligned}$$

$$\begin{aligned}
&= \frac{x''^2}{4} J_{v+1} [J_{v-1} N_v - J_v N_{v-1}] - \frac{x''^2}{4} J_{v-1} [J_v N_{v+1} - J_{v+1} N_v] \\
&= -\frac{x''}{2\pi\kappa} [J_{v+1} - J_{v-1}] = \frac{1}{\pi\kappa} \frac{d}{d\kappa} J_v(\kappa x'') \quad (\text{B.7})
\end{aligned}$$

where in the intermediate steps the argument  $\kappa x''$  of Bessel and Neumann functions was omitted and where the standard formulae

$$\begin{aligned}
&\int x \, dx \, w_v(\kappa x) W_v(\kappa x) \\
&= \frac{x^2}{4} [2w_v(\kappa x) W_v(\kappa x) - w_{v-1}(\kappa x) W_{v+1}(\kappa x) - w_{v+1}(\kappa x) W_{v-1}(\kappa x)] \quad (\text{B.8})
\end{aligned}$$

and

$$J_{v-1}(x) N_v(x) - J_v(x) N_{v-1}(x) = -\frac{2}{\pi x} \quad (\text{B.9})$$

were used. These formulae, where  $w_v$  and  $W_v$  can be either  $J_v$  or  $N_v$ , are given as 7.14.1(10) and 7.11(35) in [33]. Similarly the terms, which arise from the upper limit  $x''$  and multiply  $J_v(\kappa x')$ , and the terms which arise from the lower limit  $x'$ , can be simplified according to

$$\begin{aligned}
N_v(\kappa x'') \int_{x'}^{x''} x \, dx \, N_v(\kappa x) J_v(\kappa x) - J_v(\kappa x'') \int_{x'}^{x''} x \, dx \, N_v(\kappa x) N_v(\kappa x) \\
= -\frac{1}{\pi\kappa} \frac{d}{d\kappa} N_v(\kappa x'') \quad (\text{B.10})
\end{aligned}$$

$$\begin{aligned}
J_v(\kappa x') \int_{x'} x \, dx \, J_v(\kappa x) N_v(\kappa x) - N_v(\kappa x') \int_{x'} x \, dx \, J_v(\kappa x) J_v(\kappa x) \\
= -\frac{1}{\pi\kappa} \frac{d}{d\kappa} J_v(\kappa x') \quad (\text{B.11})
\end{aligned}$$

$$\begin{aligned}
N_v(\kappa x') \int_{x'} x \, dx \, N_v(\kappa x) J_v(\kappa x) - J_v(\kappa x') \int_{x'} x \, dx \, N_v(\kappa x) N_v(\kappa x) \\
= \frac{1}{\pi\kappa} \frac{d}{d\kappa} N_v(\kappa x'). \quad (\text{B.12})
\end{aligned}$$

By inserting (B.7) and (B.10)–(B.12) in (B.6) the result

$$\begin{aligned}
\int d\mathbf{x} k(\mathbf{x}'', \mathbf{x}; \kappa) k(\mathbf{x}, \mathbf{x}'; \kappa) &= -\frac{\pi}{2\kappa \sqrt{x'x''}} \Theta(x'' - x') \sum_L Y_L(\hat{\mathbf{x}}'') Y_L(\hat{\mathbf{x}}') \\
&\times \frac{d}{d\kappa} [N_v(\kappa x'') J_v(\kappa x') - N_v(\kappa x') J_v(\kappa x'')] \\
&= -\frac{1}{2\kappa} \frac{d}{d\kappa} k(\mathbf{x}'', \mathbf{x}'; \kappa) \quad (\text{B.13})
\end{aligned}$$

follows, which completes the proof.

### Appendix C. Simplification of the back-scattering terms

By the product rule for differentiation term  $A$  can be written as a sum of the following three contributions

$$\begin{aligned}
A_1 &= -\sum_{nn'} \int_{n'} d\mathbf{r}' \int_n d\mathbf{r}'' \\
&\times \sum_{L'L''L'''} J_L^n(\mathbf{r}'') \dot{g}_{LL'}^{nn'} J_{L'}^{n'}(\mathbf{r}') V^{n'}(\mathbf{r}') R_{L''}^{n'}(\mathbf{r}') G_{L''L'''}^{n'n} R_{L'''}^n(\mathbf{r}'') V^n(\mathbf{r}'') \quad (\text{C.1})
\end{aligned}$$

$$A_2 = - \sum_{nn'} \int_{n'} d\mathbf{r}' \int_n d\mathbf{r}'' \times \sum_{LL'L''L'''} J_L^n(\mathbf{r}'') g_{LL'}^{nn'} J_{L'}^{n'}(\mathbf{r}') V^{n'}(\mathbf{r}') R_{L''}^{n'}(\mathbf{r}') G_{L''L'''}^{n'n} R_{L'''}^n(\mathbf{r}'') V^n(\mathbf{r}'') \quad (\text{C.2})$$

$$A_3 = - \sum_{nn'} \int_{n'} d\mathbf{r}' \int_n d\mathbf{r}'' \times \sum_{LL'L''L'''} J_L^n(\mathbf{r}'') g_{LL'}^{nn'} J_{L'}^{n'}(\mathbf{r}') V^{n'}(\mathbf{r}') R_{L''}^{n'}(\mathbf{r}') G_{L''L'''}^{n'n} R_{L'''}^n(\mathbf{r}'') V^n(\mathbf{r}''). \quad (\text{C.3})$$

The integrals over  $\mathbf{r}'$  and  $\mathbf{r}''$  in (C.1) can be expressed by  $t$  matrices given in (19) and (20). Thus  $A_1$  gives the first term of (34). Similarly the integral over  $\mathbf{r}'$  in (C.2) and the integral over  $\mathbf{r}''$  in (C.3) can be expressed by  $t$  matrices. This leads to

$$A_2 = - \sum_{nn'} \int_n d\mathbf{r}'' \sum_{LL'L''L'''} J_L^n(\mathbf{r}'') g_{LL'}^{nn'} t_{L'L''}^{n'} G_{L''L'''}^{n'n} R_{L'''}^n(\mathbf{r}'') V^n(\mathbf{r}'') \quad (\text{C.4})$$

$$A_3 = - \sum_{nn'} \int_{n'} d\mathbf{r}' \sum_{LL'L''L'''} g_{LL'}^{nn'} J_{L'}^{n'}(\mathbf{r}') V^{n'}(\mathbf{r}') R_{L''}^{n'}(\mathbf{r}') G_{L''L'''}^{n'n} t_{L''L}^n. \quad (\text{C.5})$$

Because of (18) and (21) the sums over  $n'$  and  $L'L''$  in (C.4) and over  $n$  and  $L''L$  in (C.5) can be substituted by differences of structure constants  $G_{LL'}^{nn'} - g_{LL'}^{nn'}$ , and  $A_2$  and  $A_3$  give the last four terms of (34).

Term  $B$  can also be written as a sum of three contributions

$$B_1 = - \sum_n \int_n d\mathbf{r}' \sum_{LL'} J_L^n(\mathbf{r}') \dot{g}_{LL'}^{nn} J_{L'}^n(\mathbf{r}') V^n(\mathbf{r}') - \sum_n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' \sum_{LL'} J_L^n(\mathbf{r}'') \dot{g}_{LL'}^{nn} J_{L'}^n(\mathbf{r}') V^n(\mathbf{r}') G_s^n(\mathbf{r}', \mathbf{r}'') V^n(\mathbf{r}'') \quad (\text{C.6})$$

$$B_2 = - \sum_n \int_n d\mathbf{r}' \sum_{LL'} J_L^n(\mathbf{r}') g_{LL'}^{nn} J_{L'}^n(\mathbf{r}') V^n(\mathbf{r}') - \sum_n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' \sum_{LL'} J_L^n(\mathbf{r}'') g_{LL'}^{nn} J_{L'}^n(\mathbf{r}') V^n(\mathbf{r}') G_s^n(\mathbf{r}', \mathbf{r}'') V^n(\mathbf{r}'') \quad (\text{C.7})$$

$$B_3 = - \sum_n \int_n d\mathbf{r}' \sum_{LL'} J_L^n(\mathbf{r}') g_{LL'}^{nn} J_{L'}^n(\mathbf{r}') V^n(\mathbf{r}') - \sum_n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' \sum_{LL'} J_L^n(\mathbf{r}'') g_{LL'}^{nn} J_{L'}^n(\mathbf{r}') V^n(\mathbf{r}') G_s^n(\mathbf{r}', \mathbf{r}'') V^n(\mathbf{r}''). \quad (\text{C.8})$$

The integral over  $\mathbf{r}'$  in the second term of (C.6) can be eliminated because of (17) and the result is

$$B_1 = - \sum_n \int_n d\mathbf{r}'' \sum_{LL'} J_L^n(\mathbf{r}'') \dot{g}_{LL'}^{nn} R_{L'}^n(\mathbf{r}'') V^n(\mathbf{r}''). \quad (\text{C.9})$$

Because of (19) the last result can be further simplified and gives the first term of (36). The integrals over  $\mathbf{r}'$  in (C.7) and over  $\mathbf{r}''$  in (C.8) can similarly be eliminated. This leads to the second and third term of (36).

Term  $C$  depends on the derivative  $\dot{g}_s^n$ , which can be eliminated in terms of  $\dot{R}_L^n$  and  $\dot{J}_L^n$  by differentiating (15) with respect to energy. The differentiation leads to

$$\int_n d\mathbf{r}' \dot{g}_s^n(\mathbf{r}'', \mathbf{r}') V^n(\mathbf{r}') R_L^n(\mathbf{r}') = \dot{R}_L^n(\mathbf{r}'') - \dot{J}_L^n(\mathbf{r}'') - \int_n d\mathbf{r}' g_s^n(\mathbf{r}'', \mathbf{r}') V^n(\mathbf{r}') \dot{R}_L^n(\mathbf{r}') \quad (\text{C.10})$$

which used in (37) gives

$$\begin{aligned}
C &= \sum_n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' \sum_{LL'} g_s^n(\mathbf{r}'', \mathbf{r}') V^n(\mathbf{r}') \dot{R}_L^n(\mathbf{r}') G_{LL'}^{nn} R_{L'}^n(\mathbf{r}'') V^n(\mathbf{r}'') \\
&\quad - \sum_n \int_n d\mathbf{r}'' \sum_{LL'} \dot{R}_L^n(\mathbf{r}'') G_{LL'}^{nn} R_{L'}^n(\mathbf{r}'') V^n(\mathbf{r}'') \\
&\quad + \sum_n \int_n d\mathbf{r}'' \sum_{LL'} J_L^n(\mathbf{r}'') G_{LL'}^{nn} R_{L'}^n(\mathbf{r}'') V^n(\mathbf{r}''). \tag{C.11}
\end{aligned}$$

In the first line the integral over  $\mathbf{r}''$  can be expressed by a difference of  $R_{L'}^n(\mathbf{r})$  and  $J_{L'}^n(\mathbf{r})$ . Only the contribution arising from  $J_{L'}^n(\mathbf{r})$  remains, since the contribution from  $R_{L'}^n(\mathbf{r})$  cancels against the second term of (C.11). The result then gives (38).

#### Appendix D. Simplification of the single-scattering term

$D^n$  can be expressed by a logarithmic derivative of the  $\alpha$  matrix (23). This can be shown as follows. The starting point is the product  $R_L^n(\mathbf{x}) S_L^n(\mathbf{x})$ , which by introducing  $\gamma^n = (1 - \beta^n)^{-1}$  and using  $\gamma^n - \gamma^n \beta^n = 1$  can be written as

$$\begin{aligned}
R_L^n(\mathbf{x}) S_L^n(\mathbf{x}) &= \sum_{L'} R_L^n(\mathbf{x}) \gamma_{LL'}^n S_{L'}^n(\mathbf{x}) - \sum_{L'L''} R_L^n(\mathbf{x}) \beta_{LL''}^n \gamma_{L''L'}^n S_{L'}^n(\mathbf{x}) \\
&= \sum_{L'} [R_L^n(\mathbf{x}) - J_L^n(\mathbf{x})] \gamma_{LL'}^n S_{L'}^n(\mathbf{x}) \\
&\quad - \sum_{L'L''} R_L^n(\mathbf{x}) \beta_{LL''}^n \gamma_{L''L'}^n [S_{L'}^n(\mathbf{x}) - H_{L'}^n(\mathbf{x})] \\
&\quad + \sum_{L'} J_L^n(\mathbf{x}) \gamma_{LL'}^n S_{L'}^n(\mathbf{x}) - \sum_{L'L''} R_L^n(\mathbf{x}) \beta_{LL''}^n \gamma_{L''L'}^n H_{L'}^n(\mathbf{x}) \tag{D.1}
\end{aligned}$$

where the terms appearing in the last line were added and subtracted. Similarly the product  $J_L^n(\mathbf{x}) H_L^n(\mathbf{x})$  can be expressed as

$$\begin{aligned}
J_L^n(\mathbf{x}) H_L^n(\mathbf{x}) &= \sum_{L'} J_L^n(\mathbf{x}) \gamma_{LL'}^n H_{L'}^n(\mathbf{x}) - \sum_{L'L''} J_L^n(\mathbf{x}) \gamma_{LL''}^n \beta_{L''L'}^n H_{L'}^n(\mathbf{x}) \\
&= \sum_{L'} J_L^n(\mathbf{x}) \gamma_{LL'}^n [H_{L'}^n(\mathbf{x}) - S_{L'}^n(\mathbf{x})] \\
&\quad + \sum_{L'L''} [R_L^n(\mathbf{x}) - J_L^n(\mathbf{x})] \gamma_{LL''}^n \beta_{L''L'}^n H_{L'}^n(\mathbf{x}) \\
&\quad + \sum_{L'} J_L^n(\mathbf{x}) \gamma_{LL'}^n S_{L'}^n(\mathbf{x}) - \sum_{L'L''} R_L^n(\mathbf{x}) \beta_{LL''}^n \gamma_{L''L'}^n H_{L'}^n(\mathbf{x}) \tag{D.2}
\end{aligned}$$

where  $\gamma^n \beta^n = \beta^n \gamma^n$  was used in the last line. The last lines of (D.1) and (D.2) are identical and thus the difference of (D.1) and (D.2) is given by

$$\begin{aligned}
&\sum_L [R_L^n(\mathbf{x}) S_L^n(\mathbf{x}) - J_L^n(\mathbf{x}) H_L^n(\mathbf{x})] \\
&= \sum_{LL'L''} [R_L^n(\mathbf{x}) - J_L^n(\mathbf{x})] \gamma_{LL''}^n [\delta_{L''L'} S_{L'}^n(\mathbf{x}) - \beta_{L''L'}^n H_{L'}^n(\mathbf{x})] \\
&\quad - \sum_{LL'L''} [R_L^n(\mathbf{x}) \beta_{LL''}^n - J_L^n(\mathbf{x}) \delta_{LL''}] \gamma_{L''L'}^n [S_{L'}^n(\mathbf{x}) - H_{L'}^n(\mathbf{x})]. \tag{D.3}
\end{aligned}$$

Here wavefunction differences can be replaced by integrals by using (15) and (24) in the first line and (A.18), (A.14) and (A.7) in the second line. The result is

$$\sum_L [R_L^n(\mathbf{x}) S_L^n(\mathbf{x}) - J_L^n(\mathbf{x}) H_L^n(\mathbf{x})]$$

$$\begin{aligned}
&= \sum_{LL'} \gamma_{LL'}^n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' R_L^n(\mathbf{r}') V^n(\mathbf{r}') g_s^n(\mathbf{r}', \mathbf{x}) g_s^n(\mathbf{x}, \mathbf{r}'') V^n(\mathbf{r}'') S_{L'}^n(\mathbf{r}'') \\
&\quad - \sum_{LL'} \gamma_{LL'}^n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' J_L^n(\mathbf{r}') V^n(\mathbf{r}') K_s^n(\mathbf{r}', \mathbf{x}) K_s^n(\mathbf{x}, \mathbf{r}'') V^n(\mathbf{r}'') H_{L'}^n(\mathbf{r}'').
\end{aligned} \tag{D.4}$$

Integration over  $\mathbf{x}$  leads to

$$\begin{aligned}
D^n &= - \sum_{LL'} \gamma_{LL'}^n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' R_L^n(\mathbf{r}') V^n(\mathbf{r}') \dot{g}_s^n(\mathbf{r}', \mathbf{r}'') V^n(\mathbf{r}'') S_{L'}^n(\mathbf{r}'') \\
&\quad + \sum_{LL'} \gamma_{LL'}^n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' J_L^n(\mathbf{r}') V^n(\mathbf{r}') \dot{K}_s^n(\mathbf{r}', \mathbf{r}'') V^n(\mathbf{r}'') H_{L'}^n(\mathbf{r}'')
\end{aligned} \tag{D.5}$$

where (A.1), (A.2) and (41) were used on the left-hand side and where the right-hand side occurs because of (30) and the result

$$\int d\mathbf{x} K_s^n(\mathbf{x}'', \mathbf{x}) K_s^n(\mathbf{x}, \mathbf{x}') = -\dot{K}_s^n(\mathbf{x}'', \mathbf{x}') \tag{D.6}$$

of appendix B. In (D.5) the energy derivatives of  $g_s^n$  and  $K_s^n$  can be eliminated by (C.10) and by a similar equation which is obtained by differentiating (A.7) with respect to energy. The result is

$$\begin{aligned}
D^n &= \sum_{LL'} \gamma_{LL'}^n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' \dot{R}_L^n(\mathbf{r}') V^n(\mathbf{r}') g_s^n(\mathbf{r}', \mathbf{r}'') V^n(\mathbf{r}'') S_{L'}^n(\mathbf{r}'') \\
&\quad - \sum_{LL'} \gamma_{LL'}^n \int_n d\mathbf{r}' [\dot{R}_L^n(\mathbf{r}') - J_L^n(\mathbf{r}')] V^n(\mathbf{r}') S_{L'}^n(\mathbf{r}') \\
&\quad - \sum_{LL'} \gamma_{LL'}^n \int_n d\mathbf{r}' \int_n d\mathbf{r}'' J_L^n(\mathbf{r}') V^n(\mathbf{r}') K_s^n(\mathbf{r}', \mathbf{r}'') V^n(\mathbf{r}'') \dot{H}_{L'}^n(\mathbf{r}'') \\
&\quad + \sum_{LL'} \gamma_{LL'}^n \int_n d\mathbf{r}' J_L^n(\mathbf{r}') V^n(\mathbf{r}') [\dot{S}_{L'}^n(\mathbf{r}') - \dot{H}_{L'}^n(\mathbf{r}')].
\end{aligned} \tag{D.7}$$

Here (24) can be used in the first two lines to eliminate  $g_s^n$  and (A.14) together with (A.18) in the last two lines to eliminate  $K_s^n$ . This leads to

$$\begin{aligned}
D^n &= - \sum_{LL'} \gamma_{LL'}^n \int_n d\mathbf{r}' \dot{R}_L^n(\mathbf{r}') V^n(\mathbf{r}') \sum_{L''} \beta_{L'L''}^n H_{L''}^n(\mathbf{r}') \\
&\quad + \sum_{LL'} \gamma_{LL'}^n \int_n d\mathbf{r}' J_L^n(\mathbf{r}') V^n(\mathbf{r}') S_{L'}^n(\mathbf{r}') \\
&\quad - \sum_{LL'} \gamma_{LL'}^n \int_n d\mathbf{r}' \sum_{L''} R_{L''}^n(\mathbf{r}') \beta_{L'L''}^n V^n(\mathbf{r}') \dot{H}_{L'}^n(\mathbf{r}') \\
&\quad + \sum_{LL'} \gamma_{LL'}^n \int_n d\mathbf{r}' J_L^n(\mathbf{r}') V^n(\mathbf{r}') \dot{S}_{L'}^n(\mathbf{r}').
\end{aligned} \tag{D.8}$$

Since  $\beta$  and  $\gamma$  are commutative matrices, the expression  $\gamma_{LL'}^n \beta_{L'L''}^n$  in the third line can be replaced by  $\beta_{L'L''}^n \gamma_{L''L}^n$ . A cyclic interchange of the  $L$ -summation indices in the first line then shows that the sum of the integrals in the first and third line leads to the energy derivative of the  $\alpha$  matrix (23). Similarly, the sum of the integrals in the second and fourth line leads to the energy derivative of the  $\beta$  matrix (26) and

$$D^n = - \sum_{LL'L''} \gamma_{L''L}^n \beta_{L'L''}^n \dot{\alpha}_{L'L''}^n - \sum_{LL'} \gamma_{LL'}^n \dot{\beta}_{L'L}^n \tag{D.9}$$



follows. By use of  $\dot{\beta} = -\beta^2 \dot{\alpha}$  and  $\gamma\beta - \gamma\beta^2 = \beta$  the final results are obtained as

$$D^n = - \sum_{LL'} \beta_{LL'}^n \dot{\alpha}_{LL'}^n \quad (\text{D.10})$$

which because of  $\beta = \alpha^{-1}$  directly gives (42).

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