Exact distorted-wave approach to multiple-scattering theory for general potentials

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We present a new approach to real-space multiple-scattering theory for molecules and clusters, based on the two-potential (distorted-wave) Lippmann-Schwinger equation formalism. Our approach uses a recently developed form [D. L. Foulis, Phys. Rev. A 70, 022706 (2004)], for the partial-wave expansions of the exact time-independent single-particle Green function for a general potential, to solve exactly the scattering problem for the distortion potential. The multiple-scattering problem for the full multicenter molecular potential is then developed along familiar lines, within a partition of space consisting of non-overlapping atomic spheres, but relative to the distorting potential. To achieve this some new general Green-function re-expansion formulas are derived, as well as further developments of our earlier partial-wave expansions. In passing, we make use of some of our results to derive a complete solution to the single-scattering problem for an arbitrary noncentral potential, and investigate some of the algebraic properties of Gaunt coefficients which arise frequently in our formulas. Based on the division of the multicenter molecular potential into the non-singular distorting potential and a remaining singular part we develop explicitly the secular equations of our approach and prove a result concerning the symmetry of the atomic matrices. The new secular equations are similar in overall form to those of related methods, but do not require any volume integrals. In our approach the computational burden consists essentially of the solution of the coupled radial Schrödinger equations for each atomic center, once in the actual atomic potential, and twice (giving the regular and irregular solutions) in the distorting potential; followed by integrals of combinations of these solutions over the atomic-sphere surfaces. We comment on key aspects of the numerical implementation, notably issues related to the choice of distorting potential. We treat both continuum (scattering) states and bound states within the same framework, and consider also the case of an outer sphere.

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I. INTRODUCTION

In previous work [1] the author has derived partial-wave expansions for the exact time-independent Green function of a general noncentral one-electron potential in terms of matrix solutions of the coupled radial Schrödinger equations for that potential. Although hopefully of interest in its own right to quantum-scattering theorists, the motivation was, in fact, to provide a key result in a new approach to multiple-scattering theory for general potentials, which is intended to be less cumbersome, more transparent, and more amenable to accurate numerical implementation than alternative approaches. In this article the full development of our new approach is presented.

We consider here multiple-scattering theory in the restricted sense of the well known multiple-scattered-wave (MSW) theory of Johnson, Slater and co-workers (see for example Ref. [2]) for bound states, extended by others [3] to continuum states and scattering, as well as photoionization [4]. It is expected, nevertheless, that some of the results developed below will have wider application. The MSW theory is itself an adaptation to finite clusters and molecules of the famous KKR method from solid-state physics. Although we concentrate here on methods for finite systems, where the practical applications are varied and numerous, it is expected that the approach of this present work may be adapted to the original case of periodic systems.

As is well known, the main limitation for the original MSW and KKR methods was the requirement of the so called “muffin-tin” (MT) approximation for the potential. In this approximation space is partitioned into disjoint atomic spheres and a remaining interstitial region. The atomic potentials are taken to be spherically symmetric and the interstitial potential constant, so that the motion of an electron in the potential may be described in terms of free propagation between distinct atomic scattering events, for which the associated $T$ matrices are diagonal. There have been considerable efforts over many years to extend these multiple-scattering methods to more general potentials, which began to bear fruit towards the end of the 1980s, and have led to some computational implementations.

One of the main reasons that so much work has been done in this area, despite the fact that a variety of alternative, non-scattering methods have become available (in certain fields of application), is that few, if any, of these alternatives have all the attractive features of the MSW/KKR approach. In particular, these are real-space, non-basis-set methods which combine a rapidly convergent partial-wave representation of multicenter wavefunctions with an accurate treatment of atomic cores. Furthermore, both bound and continuum states may be treated within the same framework, making the methods applicable to a wide range of problems. An attractive feature (of the original formalism at least), both from a conceptual and a practical point of view, is the separation between geometry and scattering that...
is manifest in the secular equations of the method.

The approach we shall present here has roots in the work of Natoli, Benfatto, and Doniach [5] who developed a particularly clear formulation of MSW theory for general potentials, applied to molecules and clusters, drawing themselves on the work of Beleznay and Lawrence [6], and Lloyd and Smith [7]. In their approach the atomic $T$ matrices are generalized to describe scattering from a non-spherical atomic potential, achieved by integrating the coupled radial Schrödinger equations in matrix form. The resulting $T$ matrices then have non-zero off-diagonal elements. The effect of a varying interstitial potential on the electron scattering is taken into account via an extra term in the MSW secular matrix, related to a $T$ matrix for the interstitial potential.

This full-potential (FP) MSW method was implemented by the present author and colleagues [8] as the suite of computer codes FPX, and tested for analytically known bound-state and continuum problems as well as realistic molecular systems [9] [in the context of ab initio calculations in X-ray absorption fine-structure spectroscopy (XAFS)]. The codes have proved a useful pathway in exploring the benefits of full-potential calculations and have produced results [10] which remain a benchmark [11] in the field. They were designed to accommodate arbitrary molecular geometries, although optimized for symmetric systems, implementing the algebra of Ref. [8] completely, except for the interstitial $T$ matrix which is calculated in the Born approximation. They have also had a useful general role in clarifying the relative importance of elements in the hierarchy of approximations underlying XAFS calculations.

In practice, the FPX codes have proved of limited applicability, primarily because of the Born approximation for the interstitial $T$ matrix, and the associated scaling behavior resulting from the volume integrals. A scheme to calculate the full interstitial $T$ matrix was developed by Wästberg [12], and implemented for bound states of diatomic molecules. It is also a volume integral method relying on the use of an accurate quadrature grid for the interstitial region. Had development of the FPX codes been continued his scheme would undoubtedly have been incorporated.

Other schemes to extend MSW/KKR methods to non-MT potentials have been developed, notably the “cellular method” in the context of band structure calculations for periodic systems, proposed by Williams and Morgan [13], developed in a variety of forms and worked on by many others. (To find a way into the literature of this approach see Refs. [1,14,15] and further references therein.)

Despite a measure of progress, represented by the above approaches (among others), it appears still to be the case that non-MT MSW/KKR methods have been less widely taken up than might be expected. It is true, in general, that all of these extensions are significantly more complicated algebraically than the original MT-based methods, and their numerical implementation correspondingly more challenging. We shall not consider here in detail the reasons for the poor take-up of these methods, although it seems likely to this author that they are not unrelated to the latter observations.

It is perhaps not immediately obvious how to improve the situation. The experience of the present author suggests that the emphasis should be on reducing the computational burden and, if not reducing algebraic complexity, at least increasing the transparency of the theoretical approach. Also crucially important are the details of the numerical implementation; although these will, of course, be dictated to a great extent by the theory. This present work is an attempt to develop a theory with reduced computational requirements, which is also well adapted to an accurate numerical implementation.

Our particular approach has grown from the simple notion, mentioned in Ref. [1], that a Green function better adapted than the free Green function, to the case of an electron propagating in a varying potential, should play a central role in the theory. This leads naturally to a consideration of the distorted-wave Lippmann-Schwinger equation and how it may be adapted to the multiple-scattering problem, and thus to the development of the necessary mathematical machinery. As will be seen below the resulting method retains the partition of space with distinct spherical atomic volumes, but requires no volume integrals. The computational burden is mainly the integration of coupled radial Schrödinger equations for each atomic center, and the evaluation of surface integrals over the atomic spheres. It is hoped that the algebraic development may be considered transparent and convincing, and perhaps conceptually simpler than other approaches in this field.

II. THEORY

We consider a molecule or finite cluster of $N$ atoms with nuclear positions given by the vectors $\mathbf{R}_i$ (for $i = 1, \ldots, N$) relative to some origin. Associated with the molecule is a one-electron potential $V(\mathbf{r})$, arising perhaps in the context of Hartree-Fock or density-functional calculations, of a multicenter character, i.e., with singularities at the nuclear sites, which tends to zero (or some constant value) at infinity. We are interested in solutions, both scattering (continuum) and bound-state, of the Schrödinger equation,

$$\left[\nabla^2 + E - V(\mathbf{r})\right] \psi(\mathbf{r}) = 0,$$

associated with the potential $V(\mathbf{r})$. (As in Ref. [1] we use the Rydberg atomic units.)
As usual in multiple-scattering theory we shall partition the molecular space as follows: each atomic center \( i \) is enclosed in a spherical region \( \tau_i \) of radius \( b_i \) centered on \( R_i \),

\[
\tau_i \equiv \{ \mathbf{r} \in \mathbb{R}^3 : |\mathbf{r} - \mathbf{R}_i| < b_i \} ,
\]

(2)
taken to be mutually disjoint (non-overlapping), so that \( b_i + b_j \leq |R_i - R_j| \) for all \( i \) and \( j \) not equal. The surface of atomic sphere \( i \) will be denoted by \( \partial \tau_i \), i.e.,

\[
\partial \tau_i \equiv \{ \mathbf{r} \in \mathbb{R}^3 : |\mathbf{r} - \mathbf{R}_i| = b_i \} .
\]

(3)

We shall consider later a modified partition which includes also an outer sphere \( \tau_0 \) of radius \( b_0 \) centered on some position \( R_0 \), which contains all the atomic spheres, i.e.,

\[
\tau_0 \equiv \{ \mathbf{r} \in \mathbb{R}^3 : |\mathbf{r} - \mathbf{R}_0| \leq b_0 \} ,
\]

(4)
such that \( \tau_i \subset \tau_0 \) for all \( i \). In this case the region outside the outer sphere, denoted by \( \tau_0^c \) (the complement of \( \tau_0 \)), will be treated in effect as an atomic center.

### A. The distorted-wave Lippmann-Schwinger equation

In the usual multiple-scattering methods derivation of the central equations frequently begins with the Lippmann-Schwinger equation for scattering states \( \psi(\mathbf{r}) \) in a multicenter potential \( V(\mathbf{r}) \),

\[
\psi(\mathbf{r}) = \phi_0(\mathbf{r}) + \int G_0^+(\mathbf{r},s)V(s)\psi(s)\,d^3s ,
\]

(5)

where \( \phi_0(\mathbf{r}) \) is a plane wave and \( G_0^+(\mathbf{r},s) \) is the time-independent free Green function with outgoing-wave boundary conditions. (An integral in which the region is not specified should be taken over the whole range of the variable of integration; e.g., in the foregoing equation this is therefore over all space.)

The key to the approach we present here is the splitting of our multicenter molecular potential into two parts: a finite non-singular potential \( V_I(\mathbf{r}) \) which coincides with \( V(\mathbf{r}) \) in the interstitial region; and a remaining part \( V_A(\mathbf{r}) \) which is zero in the interstitial region, but contains atomic potential singularities. Thus,

\[
V(\mathbf{r}) = V_I(\mathbf{r}) + V_A(\mathbf{r}) ,
\]

(6)

with

\[
V_I(\mathbf{r}) \equiv \begin{cases} 
V_{IA}(\mathbf{r}) & \text{if } \mathbf{r} \in \bigcup_{i=1}^{N} \tau_i \\
V(\mathbf{r}) & \text{otherwise}
\end{cases} .
\]

(7)

It is not necessary for our immediate purpose to define \( V_{IA}(\mathbf{r}) \) other than that it lead to a non-singular, well behaved, and finite \( V_I(\mathbf{r}) \). One possible choice is to set it to be identically zero. Alternatively, one might choose a form which joins continuously or smoothly to \( V(\mathbf{r}) \) at the atomic-sphere surfaces. Clearly the actual choice will be significant when one considers the numerical implementation of the methods we present here and is a point which we shall consider in more detail later on.

Having made this split of the potential our approach to the multiple-scattering problem will be via “distorted-wave” theory [16], otherwise known as the case of additive potentials, or the two-potential formula [17, 18], which we shall use here without approximation. In this theory, instead of taking the zeroth-order hamiltonian to be the kinetic energy operator,

\[
H_0 \equiv -\nabla^2 ,
\]

(8)

and the scattering potential to be \( V(\mathbf{r}) \), leading to the usual Lippmann-Schwinger equation (5), we take it to be

\[
H_I \equiv -\nabla^2 + V_I ;
\]

(9)

with the full hamiltonian being

\[
H \equiv -\nabla^2 + V .
\]

(10)
We may then obtain the desired outgoing-wave scattering solutions $\psi^+$ of the full Hamiltonian by solving the Lippmann-Schwinger equation

$$\psi^+(r) = \chi^+(r) + \int G^+_I(r, s)V_A(s)\psi^+(s) \, d^3s, \quad (11)$$

where $G^+_I$ is the Green function relative to the potential $V_I$, with outgoing-wave boundary conditions, and the “distorted wave” $\chi^+(r)$ satisfies the Lippmann-Schwinger equation for the “distorting” potential $V_I(r)$, i.e.,

$$\chi^+(r) = \phi_0(r) + \int G^+_0(r, s)V_I(s)\chi^+(s) \, d^3s. \quad (12)$$

As is well known (see Ref. [17] page 132) this may be replaced by the explicit form

$$\chi^+(r) = \phi_0(r) + \int G^+_I(r, s)V_I(s)\phi_0(s) \, d^3s, \quad (13)$$

from which, if one knows the explicit form of $G^+_I$, one may evaluate $\chi^+$ directly. However, our previous work [1] gives us precisely this, as we shall see in detail below.

**B. Partial-wave Green-function expansions**

In Ref. [1] the author has derived an expression for the partial-wave expansions of the exact time-independent Green functions, at positive and negative energies, for an arbitrary single-particle potential $V(r)$ (within certain limitations). Since the results of this section will be completely general we shall, until further notice, take $V(r)$ not to be our multicenter potential, introduced earlier. In fact, the results of Ref. [1], and some immediate consequences which we develop below, will be applied to the more well behaved part $V_I(r)$ of the multicenter potential, providing us with explicit forms for $G^+_I(r, s)$, therefore allowing us to attack the multicenter problem via the integral equations (11) and (13).

The Green functions that we require are solutions of the equation

$$[\nabla^2_r + E - V(r)] G(r, s) = \delta^3(r - s), \quad (14)$$

together with the appropriate boundary conditions. The potential $V(r)$ is given as a well behaved convergent expansion in spherical harmonics about some point which we take as the origin of coordinates, so that

$$V(r) \equiv \sum_L v_L(r)Y_L(\hat{r}), \quad (15)$$

where the compound index $L$ represents, as usual, the pair $(l, m)$ and the summation over $L$ is given by

$$\sum_L \equiv \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \quad (16)$$

Again to simplify the algebra we shall make use of real spherical harmonics (where the index $m$ is negative for sine and positive or zero for cosine spherical harmonics). As is well known they may be obtained from complex spherical harmonics by a unitary transformation which preserves the orthonormality property and the addition theorem.

The Green functions may be expressed in terms of solutions of the coupled radial Schrödinger equations. These may derived from Eq. (1) by considering the solution of Schrödinger’s equation as a spherical-harmonic expansion,

$$\psi(r) \equiv \sum_L \phi_L(r)Y_L(\hat{r}), \quad (17)$$

with which one quickly finds that

$$\left[ \frac{1}{r^2} \left( \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \right) - \frac{l(l+1)}{r^2} + E \right] \phi_L(r) - \sum_{L'} w_{LL'}(r)\phi_{L'}(r) = 0; \quad (18)$$
where we have used spherical-harmonic orthonormality and defined the potential matrix elements

\[ w_{LL'}(r) \equiv \sum_{L''} I(L, L', L'') v_{L''}(r) \]  

(with the Gaunt coefficients for real spherical harmonics given by

\[ I(L, L', L'\prime) \equiv \int Y_L(\hat{r}) Y_{L'}(\hat{r}) Y_{L'\prime}(\hat{r}) \, d\Omega \]  

which are manifestly symmetric under any permutation of the indices \( L, L', \) and \( L'' \). It is obvious that the quantities \( w_{LL'} \) are real, for a real potential, and symmetric in the indices.

The general form of the Green function may be now written as follows [1]:

\[
G(\mathbf{r}, \mathbf{s}) = \sum_{LL_1L_2L_1'\prime L_2'} \left[ p_{LL_1}(r) \begin{bmatrix} M^{-1} \end{bmatrix}_{L_1L_1'} q_{L_2L_2}(s)\theta(s-r) \right. \\
+ q_{LL_1}(r) \begin{bmatrix} M^{-1} \end{bmatrix}_{L_1L_2} p_{L_2L_2'}(s)\theta(r-s) \left. \right] Y_\mathbf{L}(\mathbf{r}) Y_\mathbf{L'}(\mathbf{s}), \tag{21}
\]

where the \( p_{LL'}(r) \) constitute a set of real linearly independent vector solutions to the radial Schrödinger equations [18], indexed by \( L' \), and regular at \( r = 0 \); the \( q_{LL'}(r) \) constitute similarly a set of vector solutions, regular at infinity, whose boundary conditions at this limit determine which Green function we have; and \( M_{LL'} \) is a constant matrix derived from the Wronskian of these two sets of functions, as we describe below. Since the potential will, in general, have non-zero higher multipole components, the potential matrix \( w_{LL'} \) will have non-zero off-diagonal elements. Consequently the solution matrices will not be diagonal.

It is interesting to note that the problem of an explicit form for the partial-wave expansions of the Green function of a noncentral potential appears to have been rarely treated. One example we have found is Ref. [14], where the authors consider the problem in their Appendix, using the phase-functional formalism with particular boundary conditions. They develop an expression without an explicit matrix \( M_{LL'} \), which seems not readily adapted to the further development we shall present later.

It is useful before proceeding further to introduce some notation. In particular we represent our infinite matrices and vectors by sans-serif letters. Therefore we may write equations without explicit reference to indices and summations. Thus, in an obvious way, our set of radial matrix solutions may be represented by \( \mathbf{p}(r) \) and \( \mathbf{q}(r) \), and the constant matrix by \( M \).

Our general result may be now written more clearly as

\[
G(\mathbf{r}, \mathbf{s}) = Y(\hat{r})^T \begin{bmatrix} \mathbf{p}(r) (M^{-1})^T \mathbf{q}(s)^T & \mathbf{q}(s)^T \theta(s-r) + \mathbf{q}(r)M^{-1}\mathbf{p}(s)^T \theta(r-s) \end{bmatrix} Y(\hat{s}), \tag{22}
\]

where \( Y(\hat{r}) \) is a column vector with elements \( Y_L(\hat{r}) \), the superscript \( T \) denotes the matrix transpose, and, as was shown in Ref. [1] using a well known argument, we have

\[
\mathbf{p}'(r)^T \mathbf{q}(r) - \mathbf{p}(r)^T \mathbf{q}'(r) = -\frac{1}{r^2} M. \tag{23}
\]

In fact the argument is valid for any pair of matrix solutions, leading to a different constant matrix in each case. When the two matrix solutions are the same, further argument shows, at least for \( \mathbf{p} \) and \( \mathbf{q} \) individually, that the constant matrix is zero, so that

\[
\mathbf{p}(r)^T \mathbf{p}'(r) = \mathbf{p}'(r)^T \mathbf{p}(r), \tag{24}
\]

and

\[
\mathbf{q}(r)^T \mathbf{q}'(r) = \mathbf{q}'(r)^T \mathbf{q}(r), \tag{25}
\]

provided that, in the latter case, \( \mathbf{q} \) tends to a diagonal form in the asymptotic limit, which will usually be the case if the potential tends to zero quickly enough asymptotically. These two equations would have been automatically true in the case of diagonal matrices when the potential is spherically symmetric.

In the course of the derivation of our main result other relations between these matrices arise. In particular, we have

\[
\mathbf{p}(r) (M^{-1})^T \mathbf{q}(r)^T = \mathbf{q}(r)M^{-1}\mathbf{p}(r)^T, \tag{26}
\]
and
\[ q'(r)M^{-1}p(r)^T - p'(r) (M^{-1})^T q(r)^T = \frac{1}{r^2}I, \]  
both of which will be useful later on.

The choice of particular Green function depends on the boundary conditions, which are imposed on the asymptotic behavior of \( q \). For positive energies, \( E > 0 \) (with \( k > 0 \) such that \( E = k^2 \)), and Green functions suitable for scattering problems, we have two choices for \( q \). Firstly, the choice of outgoing-wave boundary conditions and the retarded Green function is obtained with \( q^+(r) \), defined to be the solutions of the coupled radial Schrödinger equations [18] which approach asymptotically, as \( r \to \infty \), the corresponding free-electron solutions
\[ q^+_f(r) = -ih^+(kr), \]  
where the diagonal spherical Hankel-function matrix has elements given by
\[ h^+_{LL'}(x) \equiv h^+_l(x)\delta_{LL'} . \]  
We define here similarly spherical Bessel- and Neumann-function matrices \( j \) and \( n \), respectively, by
\[ j_{LL'}(x) \equiv j_l(x)\delta_{LL'}, \]  
and
\[ n_{LL'}(x) \equiv n_l(x)\delta_{LL'} ; \]  
so that
\[ h^+(x) = j(x) + i n(x). \]  
It is useful to define the diagonal unitary matrices \( \xi \) and \( \eta \) by
\[ [\xi]_{LL'} \equiv i^l\delta_{LL'} \quad \text{and} \quad [\eta]_{LL'} \equiv (-1)^l\delta_{LL'}, \]  
from which we may see that
\[ \xi^2 = \eta \quad \text{and} \quad \xi^4 = \eta^2 = I. \]  
With this notation we may write the famous plane-wave expansion as
\[ e^{ikr} = 4\pi \mathcal{Y}(\hat{k})^T j(kr) \xi \mathcal{Y}(\hat{r}). \]  

The choice of incoming-wave boundary conditions and the advanced Green function is obtained with \( q^-(r) \), defined to be the complex conjugate of \( q^+(r) \);
\[ q^-(r) = q^+(r)^*. \]  
The constant matrices \( M \) from Eq. (23), for the retarded and advanced Green functions, are denoted \( M_+ \) and \( M_- \) respectively. It is easily seen from Eq. (23), since \( p \) is real, that
\[ M_+ = M_-^*. \]  
By the argument which led to Eq. (23) we have a similar equation for the Wronskian between \( q^+(r) \) and \( q^-(r) \), however, the constant matrix may be evaluated by considering the limit as \( r \to \infty \), and making use of the well known relation for spherical Bessel and Neumann functions [19],
\[ j'_l(x)n_l(x) - j_l(x)n'_l(x) = -\frac{1}{x^2}. \]  
Thus we find that
\[ q^+(r)^T q^-(r) - q^+(r)q^-(r)^T = \frac{2i}{kkr_2}I. \]
When the potential vanishes we have, of course, the free-electron case and can take $p$ and $q$ to be, respectively,

$$p_f(r) \equiv j(\kappa r)$$

(40)

and $q_f^{(+)}(r)$ from Eq. (28), leading to constant matrix

$$M_+f \equiv (1/k)I,$$

(41)

and free retarded Green function

$$G_0^+(r, s) = -ik \sum_L \left[ j_i(\kappa r)h_i^+(\kappa s)\theta(s - r) + h_i^+(\kappa r)j_i(\kappa s)\theta(r - s) \right] Y_L(\hat{r})Y_L(\hat{s}),$$

(42)

with its famous closed-form representation

$$G_0^+(r, s) = -\frac{e^{ik|r-s|}}{4\pi |r - s|}. 

(43)$$

For negative energies, $E < 0$ (with $\kappa > 0$ such that $E = \kappa^2$), we have only one acceptable set of functions $q_f$ regular at infinity, which tends asymptotically to a diagonal exponentially decaying form. In general, the singularity of the Green function at a bound-state energy comes about through the singularity of the constant matrix $M_f$ at that energy.

In the free-electron case we can take $p$ and $q$ to be, respectively,

$$p_f(r) \equiv i(\kappa r)$$

(44)

and

$$q_f(r) \equiv k^+(\kappa r),$$

(45)

where, as above, we have defined matrices for the usual modified spherical Bessel and Hankel functions as

$$i_{LL'}(x) \equiv i_t(x)\delta_{LL'},$$

(46)

and

$$k^+_{LL'}(x) \equiv k^+_{t}(x)\delta_{LL'}. 

(47)$$

These definitions lead to constant matrix

$$M_f \equiv -(1/\kappa)\eta,$$

(48)

and Green function

$$G_0(r, s) = -\kappa \sum_L (-1)^l \left[ i_l(\kappa r)k^+_l(\kappa s)\theta(s - r) + k^+_l(\kappa r)i_l(\kappa s)\theta(r - s) \right] Y_L(\hat{r})Y_L(\hat{s}),$$

(49)

with closed-form representation

$$G_0(r, s) = -\frac{e^{-\kappa|r-s|}}{4\pi |r - s|}. 

(50)$$

To finish this section we note that the standard symmetries of the general Green function (see for example [20] and [21]),

$$G^+(r, s) = G^-(s, r)^*$$

(51)

(stemming from the reality of $V(r)$), and,

$$G^+(r, s) = G^+(s, r),$$

(52)

may be be verified from the main formula (22).
1. Further developments

In the foregoing section we have reproduced the main results from Ref. [1] together with some useful incidental formulas, and set up some notation which will be used in the remainder of this work. In this section we develop some immediate consequences of these results. Returning to the positive-energy scattering situation, we derive first an important relation between the radial Schrödinger equation solutions \( p, q^{(+)} \), and \( q^{(-)} \).

Since \( q^{(+)} \) and \( q^{(-)} \) are the two linearly independent radial-solution matrices regular at infinity, then any other solution must be expressible as a linear combination of them. This applies therefore to \( p \). (We note that all three sets of solutions are well defined at all radii, determined by inward or outward integration of the coupled radial equations from suitable boundary conditions; except for \( q^{(+)} \) and \( q^{(-)} \) which may be singular at \( r = 0 \).) Thus, given any constant vector \( X \) (with elements \( X_L \)), there must exist constant vectors \( Z^+ \) and \( Z^- \) such that, for general \( r \),

\[
p(r)X = q^{(+)}(r)Z^+ + q^{(-)}(r)Z^- .
\]

Evidently we may differentiate both sides with respect to \( r \) to get a similar relation between their derivatives. Thus we may form the matrix Wronskians of both sides with \( q^{(+)} \), \( q^{(-)} \), and \( p \), successively, and make use of Eqs. (23), (24), (25), and (39), to obtain, respectively, (with some minor rearrangement) three new relations:

\[
Z^- = -\left(\frac{ik}{2}\right) M_+^+ X ,
\]

\[
Z^+ = \left(\frac{ik}{2}\right) M_-^- X ,
\]

and

\[
M_+ Z^+ + M_- Z^- = 0 .
\]

(Note that \( Z^+ \) and \( Z^- \) are complex conjugate only if \( X \) is real.) We may use the first two of these relations to eliminate \( Z^+ \) and \( Z^- \) from our original equation (53), and also from the third above, to obtain, noting that \( X \) is arbitrary,

\[
p(r) = \frac{ik}{2} \left[ q^{(+)}(r)M_--^- - q^{(-)}(r)M_+^+ \right] ,
\]

and

\[
M_+ M_-^- = M_- M_+^+ .
\]

From the latter equation we see that the combination \( M_- M_+^+ \) is hermitian. Since \( M_- \) and \( M_+ \) are complex conjugate, then \( M_- M_+^+ \) is hermitian. Therefore it is also real.

We note, in the positive-energy case, that the relations (26) and (27), between combinations of the radial functions and their derivatives, are valid separately for \( q^{(+)} \) and \( q^{(-)} \). It will be useful for later reference to prove a further, similar relation. So, given \( p \) and \( q \), let us define \( y \) and \( z \) by

\[
y(r) = rp(r) \quad \text{and} \quad z(r) = rq(r) .
\]

Define also \( u(r) \), as in Ref. [1], by

\[
u_{LL'}(r) = w_{LL'}(r) + \frac{l(l+1)}{r^2} \delta_{LL'} - E \delta_{LL'} ,
\]

noting definition (19) and the radial Schrödinger equation (18), from which it may be easily seen that

\[
y''(r) = u(r)y(r) \quad \text{and} \quad z''(r) = u(r)z(r) .
\]

With these definitions it is not difficult to show, using Eqs. (26) and (27), that

\[
z'(r)M^{-1}y(r)^T - y'(r) \left( M^{-1} \right)^T z(r)^T = 1 .
\]
Taking the derivative of this with respect to \( r \), eliminating second derivatives with Eq. \((65)\), and using Eq. \((26)\) to make cancellations, leads to

\[
z'(r)M^{-1}y'(r)^T = y'(r) (M^{-1})^T z'(r)^T.
\]

If we now substitute for \( y \) and \( z \) from Eq. \((50)\), and make some cancellations with Eqs. \((26)\) and \((27)\), then we obtain our result:

\[
q'(r)M^{-1}p'(r)^T = p'(r) (M^{-1})^T q'(r)^T.
\]  

With our most important result \((64)\) from earlier in this section it is possible to eliminate \( V \) in the above equation with \( \phi_0 \), and continue to use \( V \) to represent an arbitrary potential.

\[
M_-^T (M_+^{-1})^T = M_+^{-1}M_-, \tag{60}
\]

showing incidentally that the combination \( M_-^T (M_+^{-1})^T \), which will prove important in the next section, is a symmetric matrix. One may proceed straightforwardly now to obtain, respectively,

\[
q^{(+)T}(r)q^{(-)T}(r) = q^{(-)T}(r)q^{(+)T}(r), \tag{61}
\]

\[
q^{(+)T'}(r)q^{(-)T}(r) - q^{(-)T'}(r)q^{(+)T}(r) = -\frac{2i}{kr^2}, \tag{62}
\]

which may be compared with the Wronskian \((69)\), and

\[
q^{(+)T'}(r)q^{(-)T'}(r) = q^{(-)T'}(r)q^{(+)T'}(r). \tag{63}
\]

### C. Single scattering and the distorted wave

Our approach to the multiple-scattering problem is via the distorted-wave Lippmann-Schwinger equation \((11)\). This requires, of course, that we have an explicit expression for the distorted wave \( \chi^+ \); which means, in effect, a complete solution to the single-scattering problem for the distorting potential \( V_I \). The fact that we have a formula for the Green function \( G^+_I \), from our earlier results, enables precisely that. Since the results of this section can be applied to any general, noncentral potential (within the limitations discussed in Ref. \([1]\)), we drop the subscript \( I \), and continue to use \( V \) to represent an arbitrary potential.

To find \( \chi^+ \) then, we use the explicit version \((13)\) of the Lippmann-Schwinger equation

\[
\chi^+(r) = \phi_0(r) + \int G^+(r,s)V(s)\phi_0(s) \, ds, \tag{64}
\]

with

\[
\phi_0(r) \equiv e^{ik \cdot r}. \tag{65}
\]

Now because of the inhomogeneous equation \((14)\) satisfied by \( G^+ \), and the symmetry \((52)\), we can replace the product \( G^+V \) in the above equation with \( (\nabla_s^2 + E) G^+(r,s) - \delta^3(r-s) \). Canceling the inhomogeneous part with the delta-function term we therefore obtain

\[
\chi^+(r) = \int \phi_0(s) (\nabla_s^2 + E) G^+(r,s) \, ds. \tag{66}
\]

Since \( \phi_0 \) satisfies the free-particle Schrödinger equation,

\[
(\nabla^2 + E) \phi_0(r) = 0, \tag{67}
\]

we can add an extra term to the right-hand side (rhs) to get

\[
\chi^+(r) = \int [\phi_0(s) (\nabla_s^2 + E) G^+(r,s) - G^+(r,s) (\nabla_s^2 + E) \phi_0(s)] \, ds. \tag{68}
\]
To transform the volume integral into a surface integral, we now wish to use Green’s theorem in the form (see Ref. [3])
\[
\int_T \left[ P (\nabla^2 + E) Q - Q (\nabla^2 + E) P \right] d\tau = \int_{\partial T} (P \nabla Q - Q \nabla P) \cdot \hat{n} d\sigma ,
\]
where \(\partial T\) is the surface enclosing the volume \(T\), and \(\hat{n}\) is the outward-pointing normal to the surface. It should be noted here that, since \(\phi_0\) is not a proper normalizable vector in the Hilbert space of physical states, the volume integral in Eq. (58) is not zero. When transformed by Green’s theorem to a surface integral, the “surface at infinity” provides a non-zero contribution which is the quantity we seek.

To find this quantity we first consider the volume integral of Eq. (68) as being over a spherical region with large radius \(R\), and then allow \(R\) to go to infinity. Using Green’s theorem then leads to
\[
\chi^+(r) = \lim_{R \to \infty} \int_0^R \left\{ \phi_0(s) \frac{\partial}{\partial s} \left[ G^+(r,s) - G^+(r,s) \frac{\partial \phi_0(s)}{\partial s} \right] \right\} \bigg|_{s=R} \frac{R^2}{2} d\Omega_s ,
\]
where we have made use of the fact that \(\hat{n} \cdot \nabla_s = \partial / \partial s\). Now if \(R\) is larger than \(r\), then we can take the Green function to consist of only the first term of Eq. (22), with the choice of outgoing waves \(q^{(+)}\). The plane wave \(\phi_0\) may also be expressed as the expansion (55). Substituting both expressions into the above equation for \(\chi^+\) leads, with some rearrangement, to
\[
\chi^+(r) = 4\pi Y(\hat{r})^T p(r) \left( M^{-1}_- \right)^T \left\{ \lim_{R \to \infty} R^2 \left[ q^{(+)}(R) T j(kR) - q^{(+)}(R) T k' j(kR) \right] \right\} \xi Y(\hat{k}) ,
\]
where we have used the orthonormality of spherical harmonics,
\[
\int Y(\hat{s}) Y(\hat{s})^T d\Omega_s = 1 ,
\]
and to remove the angular integral. To evaluate the limit of the Wronskian expression we make use of the asymptotic form of \(q^{(+)}\) and invoke the formula (55). The result for the expression inside the braces is easily found to be \((1/k)\).

Our final result is then
\[
\chi^+(r) = (4\pi/k) Y(\hat{r})^T p(r) \left( M^{-1}_+ \right)^T \xi Y(\hat{k}) ,
\]
the general form of the scattering state arising from a plane wave in a noncentral potential.

1. Single scattering: complete solution

Our equation (23) contains all the information required for the solution of the single-scattering problem for a general potential, but is not usable for this purpose in its present form since it contains the set of radial solutions \(p\) regular at \(r = 0\). From the scattering point of view we are more interested in the asymptotic region. With this in mind we remove \(p\) by using the formula (54). This gives us straightforwardly
\[
\chi^+(r) = 2\pi i Y(\hat{r})^T \left[ q^{(+)}(r) \hat{A} - q^{(-)}(r) \right] \xi Y(\hat{k}) ,
\]
where we define
\[
\hat{A} \equiv M^{-T}_- \left( M^{-1}_+ \right)^T ,
\]
the symmetric matrix that we encountered earlier. We note therefore that
\[
\hat{A}^T = \hat{A}^* = M^{-T}_+ \left( M^{-1}_- \right)^T = \hat{A}^{-1} ;
\]
i.e., \(\hat{A}\) is unitary.

Since the asymptotic behavior of \(\chi^+\) is more interesting for the single-scattering problem, we consider the form of \(\chi^+\) at large distances where, by construction, \(q^{(+)}\) and \(q^{(-)}\) approach their free-particle counterparts. Thus, at large \(r\),
\[
\chi^+(r) \sim 2\pi i Y(\hat{r})^T \left[ q^{(+)}_f(r) \hat{A} - q^{(-)}_f(r) \right] \xi Y(\hat{k}) .
\]
If we note that the plane-wave expansion can be written
\[ e^{ikr} = 2\pi i \mathbf{Y}(\hat{\mathbf{r}})^T \left[q_f^{(+)}(r) - q_f^{(-)}(r)\right] \xi \mathbf{Y}(\hat{\mathbf{k}}), \] (77)
then it is plain that we may write
\[ \chi^+(r) \sim \phi_0(r) + 2\pi i \mathbf{Y}(\hat{\mathbf{r}})^T q_f^{(+)}(r) \left[A - \mathbb{I}\right] \xi \mathbf{Y}(\hat{\mathbf{k}}). \]
We now use the asymptotic form of the spherical Hankel function,
\[ h_i^+(x) = \frac{1}{x} e^{-\frac{x}{2}(1+i)\pi} \text{ as } r \to \infty, \]
to show that, at large \(r\),
\[ q_f^{(+)}(r) \sim \frac{1}{kr} e^{ikr\xi^t}. \]
We may then write finally
\[ \chi^+(r) \sim \phi_0(r) + \left(\frac{2\pi i}{k}\right) \mathbf{Y}(\hat{\mathbf{r}})^T \left[A - \mathbb{I}\right] \mathbf{Y}(\hat{\mathbf{k}}) \left\{ \frac{e^{ikr}}{r} \right\}, \] (78)
where we have defined
\[ A \equiv \xi^t \hat{\mathbf{A}} \xi = \xi^t \mathbf{M}_-^T \left(\mathbf{M}_+^{-1}\right)^T \xi, \] (79)
also plainly a unitary matrix.

Having expressed the asymptotic form of \(\chi^+\) in this way we recognize immediately that the usual scattering amplitude is given by
\[ f(\mathbf{k}', \mathbf{k}) = (2\pi i/k) \mathbf{Y}((\hat{\mathbf{k}}')^T \left[I - A\right] \mathbf{Y}(\hat{\mathbf{k}}), \] (80)
where \(\mathbf{k}'\) is of the same magnitude as \(\mathbf{k}\), but whose direction \(\hat{\mathbf{r}}\) is that at which one observes the scattering from the incoming wave of direction \(\hat{\mathbf{k}}\). We note here that this result agrees essentially with the corresponding expression in the interesting work of Ziegler [22]. It can be fairly easily shown that our matrix \(A\) is the same, within some simple matrix factors, as his \(\Gamma\). His development is a direct approach in terms of asymptotic forms of the solutions of the coupled radial Schrödinger equations, rather than, as here, a straightforward application of our explicit general Green-function formula. It should be noted, however, that the most important result of our present development is not so much the asymptotic form [78] of \(\chi^+\), which is well known and may be derived from more general principles, but the formula [79] for the matrix \(A\) expressing it in terms of directly calculable quantities.

Of course, it is not always necessary to have an explicit form for \(A\) to derive some useful results. It is therefore interesting to verify the usual well known properties of \(f\) directly from the formula [80]. Thus, to show the reciprocity theorem (see [21] page 135) we note that
\[ f(-\mathbf{k}, -\mathbf{k}') = (2\pi i/k) \mathbf{Y}((-\hat{\mathbf{k}})^T \left[I - A\right] \mathbf{Y}(-\hat{\mathbf{k}}') \]
\[ = (2\pi i/k) \mathbf{Y}((\hat{\mathbf{k}})^T \eta \left[I - A\right] \eta \mathbf{Y}(\hat{\mathbf{k}}') \]
\[ = (2\pi i/k) \mathbf{Y}(\hat{\mathbf{k}}')^T \left[I - \eta A^T \eta\right] \mathbf{Y}(\hat{\mathbf{k}}) \]
\[ = f(\mathbf{k}', \mathbf{k}); \] (81)
where, in the first step we used the parity of spherical harmonics, in the second we took the matrix transpose, and we justify the final step by observing that
\[ \eta A^T \eta = \eta \xi^t \hat{\mathbf{A}}^t \xi^t \eta = \xi^t \hat{\mathbf{A}}^t \xi = A, \]
using the symmetry of \(\hat{\mathbf{A}}\) and the properties of \(\xi\) and \(\eta\) [Eqs. [11] and [12]].

Furthermore we have that
\[ \int f(\mathbf{k}_r, \mathbf{k}')^* f(\mathbf{k}_r, \mathbf{k}) \, d\Omega_{\mathbf{k}_r} = (4\pi^2/k^2) \int \mathbf{Y}(\hat{\mathbf{k}}')^T \left[I - A^t\right] \mathbf{Y}(\hat{\mathbf{k}}) \mathbf{Y}(\hat{\mathbf{k}})^T \left[I - A^t\right] \mathbf{Y}(\hat{\mathbf{k}}) \, d\Omega_{\mathbf{k}} = (4\pi^2/k^2) \mathbf{Y}(\hat{\mathbf{k}}')^T \left[I - A^t - A + I\right] \mathbf{Y}(\hat{\mathbf{k}}) = (2\pi i/k) [f(\mathbf{k}, \mathbf{k}')^* - f(\mathbf{k}', \mathbf{k})]; \] (82)
where, in the first equality we have matrix transposed the (scalar) \( f^* \) term; for the next step we used spherical-harmonic orthonormality, multiplied out the matrix terms and used the unitarity of \( A \); and in the last step split the linear sum into two parts. We recognize in this result the generalized optical theorem. As is well known, setting \( \mathbf{k}' \) to \( \mathbf{k} \) in this result, and observing that the differential cross section is given by

\[
\sigma(\mathbf{k}_r, \mathbf{k}) = |f(\mathbf{k}_r, \mathbf{k})|^2,
\]
leads directly to an expression for the total elastic scattering cross section,

\[
\sigma_{\text{tot}} = \int \sigma(\mathbf{k}_r, \mathbf{k}) \, d\Omega_{\mathbf{k}_r} = (4\pi/k) \, \text{Im} \, f(\mathbf{k}, \mathbf{k}),
\]
the famous optical theorem.

D. Green-function origin translations and re-expansions

The mathematical elaboration of multiple-scattering theory relies to a large extent on the translation of expansions of various functions, most notably the Green function, from one scattering center to another. Since the Green function used is normally the free Green function this poses no problems as it is translationally invariant, and its expansions and re-expansions in partial waves are well known. In our case the problem is more complicated since our potential need have no translational or rotational symmetry, and this will be reflected in the Green function associated with it. It is nevertheless necessary to know how the functional form of the Green function appears seen from different centers. It is useful in this context therefore to highlight here a couple of basic mathematical issues that underpin the justification for some of the steps in our arguments below.

The first point that we need to deal with is uniqueness of the Green function. It is, of course, well known that the inhomogeneous Schrödinger equation \([14]\) does not specify the Green function uniquely, since the boundary conditions must be imposed. It is easy to show that a solution of Eq. \([14]\), viewed from a translated origin, will also be a solution of the corresponding equation with the original potential viewed from the new origin. Intuitively one suspects that, since the boundary conditions are imposed at \( r \to \infty \), and are the same in both cases, the resulting solutions will be just different points of view of one unique Green function; however, this needs to be shown formally.

In fact it is the Lippmann-Schwinger equation for the Green function,

\[
G^+(\mathbf{r}, \mathbf{s}) = G^+_0(\mathbf{r}, \mathbf{s}) + \int G^+_0(\mathbf{r}, \mathbf{t}) V(\mathbf{t}) G^+(\mathbf{t}, \mathbf{s}) \, d^4t,
\]
which guarantees uniqueness (see Ref. \([18]\) page 133 or for a detailed proof Ref. \([20]\) page 490 ff).

It is not difficult to check that the unique solution \( G^+ \) of Eqs. \([85]\) and \([86]\), when considered relative to a translated origin of coordinates, satisfies the corresponding equation in the new coordinate system. (Of course, the potential \( V \) will also have a different functional form in the new coordinates.) This uniqueness guarantees that when we find a form for \( G^+ \) in some coordinate system, it will be equal to a translated version of the form arising with another origin.

It is useful to check directly that our general form \([22]\) does indeed satisfy Eqs. \([85]\) and \([86]\). Thus let us assume \( G^+ \) is of the form of Eq. \([22]\) and consider Eq. \([85]\) for example. Then we should have

\[
G^+(\mathbf{r}, \mathbf{s}) = G^+_0(\mathbf{r}, \mathbf{s}) + \int G^+_0(\mathbf{r}, \mathbf{t}) V(\mathbf{t}) G^+(\mathbf{t}, \mathbf{s}) \, d^4t
\]
\[
= \int G^+_0(\mathbf{r}, \mathbf{t}) \left( \nabla_t^2 + E \right) G^+(\mathbf{t}, \mathbf{s}) \, d^4t
\]
\[
= G^+(\mathbf{r}, \mathbf{s}) + \int \left[ G^+_0(\mathbf{r}, \mathbf{t}) \left( \nabla_t^2 + E \right) G^+(\mathbf{t}, \mathbf{s}) - G^+(\mathbf{t}, \mathbf{s}) \left( \nabla_t^2 + E \right) G^+_0(\mathbf{r}, \mathbf{t}) \right] \, d^4t
\]
\[
= G^+(\mathbf{r}, \mathbf{s}) + \lim_{R \to \infty} \int \left\{ G^+_0(\mathbf{r}, \mathbf{t}) \frac{\partial}{\partial t} \left[ G^+(\mathbf{t}, \mathbf{s}) \right] - G^+(\mathbf{t}, \mathbf{s}) \frac{\partial}{\partial t} \left[ G^+_0(\mathbf{r}, \mathbf{t}) \right] \right\} \bigg|_{t=R} R^2 \, d\Omega_t;
\]
where, in the first step we have replaced the $V G^+$ in a similar way to that of Eq. (65) [which is justified because our form for $G^+$ was developed directly from Eq. (14)], in the second we use a similar property of $G^+_0$, and in the third we invoke Green’s theorem for the region within a sphere of radius $R$ (taken to be greater than $r$ and $s$) which we allow to go to infinity. Clearly, for the equation to be true we require that the limit of the integral be zero. Using the appropriate expansions for the Green functions, noting that $t = R > r, s$, we may rewrite this (making use also of spherical-harmonic orthonormality) as the expression

$$Y(\tilde{r})^T p_f(r) \left( M^{-1}_{ij} \right)^T \left[ \lim_{R \to \infty} \left\{ q_f^{(+)}(R)^T q_f^{(+)}(R) - q_f^+(R)^T q_f^+(R) \right\} R^2 \right] M^{-1}_{+} p(s) Y(\hat{s}) .$$

Now, since $q^{(+)}$ was chosen to be asymptotic to the free-particle case $q^{(+)}_f$ (assuming as usual a potential which tends quickly enough to zero), the Wronskian will tend to zero as desired. So, with the foregoing arguments in mind, we may have confidence that the form of $G^+$ that we derive in some local coordinate system is identical to that found in some translated coordinates.

### 1. Re-expansion of free Green functions

Let us now derive the re-expansion formulas for the free Green function $G^+$. These are, of course, well known (and may be found in Ref. [2] whose approach we follow closely). However, it is useful to repeat briefly the derivation, since it allows us to introduce some new notation and express the formulas in a different form than usual. Also it is a model for our later derivations.

First, we recall the atomic centers $\mathbf{R}_i$ (for $i = 1, \ldots, N$) which we introduced earlier. For some general position vector $\mathbf{r}$ let us denote the relative position vector with respect some given atomic center $\mathbf{R}_i$ by

$$\mathbf{r}_i \equiv \mathbf{r} - \mathbf{R}_i .$$

For the purpose of developing the re-expansion formulas we may consider, say, two distinct centers, $\mathbf{R}_i$ and $\mathbf{R}_j$, as being two general points in space. The resulting formulas will then be immediately useful for our multiple-scattering problem.

We consider first the re-expansion of the free radial Schrödinger-equation solutions, $p_f(r) \equiv j(kr)$, and begin by considering a plane wave expressed in terms of coordinates relative to $\mathbf{R}_i$ and $\mathbf{R}_j$ thus:

$$\exp(i \mathbf{k} \cdot \mathbf{r}) = \exp[i \mathbf{k} \cdot (\mathbf{r}_i + \mathbf{R}_i)] = \exp(i \mathbf{k} \cdot \mathbf{r}_i) \exp(i \mathbf{k} \cdot \mathbf{R}_i)$$

and

$$\exp(i \mathbf{k} \cdot \mathbf{r}) = \exp(i \mathbf{k} \cdot \mathbf{r}_j) \exp(i \mathbf{k} \cdot \mathbf{R}_j) .$$

Equating the two expressions and using the plane-wave expansion (35) leads, with some rearrangement, to

$$Y(\tilde{r}_i)^T j(kr_j) \xi Y(\tilde{r}_j) = Y(\tilde{r}_j)^T j(kr_j) \xi Y(\tilde{r}_i) \exp(i \mathbf{k} \cdot \mathbf{R}_{ij}) ,$$

where we have defined the atomic center-to-center vector by

$$\mathbf{R}_{ij} \equiv \mathbf{R}_j - \mathbf{R}_i .$$

If we multiply both sides of our equation on the right by $Y(\hat{k})^T$ and integrate over all $\hat{k}$, then we get

$$Y(\tilde{r}_i)^T j(kr_j) = Y(\tilde{r}_j)^T j(kr_j) D(k; \mathbf{R}_{ij}) ,$$

where we have used spherical-harmonic orthonormality and defined the matrix associated with displacement, for general $\mathbf{R}$, by

$$D(k; \mathbf{R}) \equiv \xi \hat{D}(k; \mathbf{R}) \xi \dagger$$

and

$$\hat{D}(k; \mathbf{R}) \equiv \int Y(\hat{k}) \exp(i \mathbf{k} \cdot \mathbf{R}) Y(\hat{k})^T d\Omega_k .$$
If we now note that the Gaunt coefficients $I_s$ from which one may note that

$$\hat{D}(k; \mathbf{R})$$

is symmetric. The matrix elements of $\hat{D}(k; \mathbf{R})$ are now easily seen to be

$$D_{LL'}(k; \mathbf{R}) = 4\pi \sum_{L''} i^{l''} j^{l'''} (kR) Y_{L'''}(\hat{\mathbf{R}}) I(L, L', L'') ,$$

(93)

from which one may note that $\hat{D}(k; \mathbf{R})$ is symmetric. The matrix elements of $D(k; \mathbf{R})$ are now easily seen to be

$$D_{LL'}(k; \mathbf{R}) = 4\pi \sum_{L''} i^{l'' - l' + l'''} (kR) Y_{L'''}(\hat{\mathbf{R}}) I(L, L', L'') .$$

(94)

If we now note that the Gaunt coefficients $I(L, L', L'')$ are non-zero only when $l + l' + l''$ is an even integer, then we see that $D(k; \mathbf{R})$ is real. Writing out fully the summations in Eq. (90), and using the explicit matrix elements (94), allows us to recover the usual re-expansion formula (2).

Now since the points indexed $i$ and $j$ are arbitrary we may interchange them to obtain another equation like Eq. (90), which we use to eliminate the term $Y(\hat{r}_j)^T j(kr_j)$. On rearrangement we then find

$$Y(\hat{r}_i)^T j(kr_i) \left[ I - D(k; -\mathbf{R}_{ij}) D(k; \mathbf{R}_{ij}) \right] = 0 .$$

Multiplying on the left by $Y(\hat{r}_i)$, integrating over all angles, and invoking spherical-harmonic orthonormality, then leads to

$$j(kr_i) \left[ I - D(k; -\mathbf{R}_{ij}) D(k; \mathbf{R}_{ij}) \right] = 0 .$$

Since the diagonal matrix $j(kr_i)$ consists of the linear independent (regular) solutions of the radial Schrödinger equation, then the expression in square brackets must be the zero matrix. In other words, since $\mathbf{R}_{ij}$ is arbitrary, then we have that, in general,

$$D(k; \mathbf{R})^{-1} = D(k; -\mathbf{R}) .$$

(95)

Furthermore, we have

$$D(k; \mathbf{R})^{-1} = \xi \hat{D}(k; -\mathbf{R}) \xi^\dagger$$

$$= \xi \hat{D}(k; \mathbf{R})^* \xi^\dagger$$

$$= \xi \hat{D}(k; \mathbf{R}) \xi^\dagger$$

$$= D(k; \mathbf{R})^\dagger ,$$

where, in the first step we take the complex conjugate of Eq. (92), and in the second we invoked the symmetry of $\hat{D}(k; \mathbf{R})$. Thus $D(k; \mathbf{R})$ is unitary. Since it is real, then it is orthogonal. It may be also easily seen that

$$\hat{D}(k; \mathbf{R})^{-1} = \hat{D}(k; -\mathbf{R}) = \hat{D}(k; \mathbf{R})^\dagger .$$

(96)

To develop the corresponding formula for the free (outgoing-wave) radial solutions regular at infinity, $q_f^{(+)}(r) = -ih^+(kr)$, we need to use the translation properties of $G_0^{(+)}$. However, since these solutions are singular at the origin, the re-expansion must be approached differently above and below the separation distance, which regions we shall denote as the “far” and “near” regions, respectively.

With reference to the diagram in Fig. 11 let us consider a general point with position vector $s$, on the surface of a sphere centered on $\mathbf{R}_j$, with a radius somewhat greater than $R_{ij}$. Let $r$ represent a general point on a sphere of positive radius centered on $\mathbf{R}_i$, contained entirely within the first sphere. Such a sphere can always be found, since $s_j > R_{ij}$. It may be then seen that in this configuration we shall always have $s_i > r_i$ and $s_j > r_j$. Therefore we may write

$$G_0^{(+)}(r, s) = -\frac{e^{ik|r - s|}}{4\pi |r - s|} = -ik Y(\hat{r}_i)^T j(kr_i) h^+(ks_i) Y(\hat{s}_i) .$$

Translation invariance allows to write also, since $r_i - s_i = r_j - s_j$, that

$$G_0^{(+)}(r, s) = -\frac{e^{ik|r - s|}}{4\pi |r_j - s_j|} = -ik Y(\hat{r}_j)^T j(kr_j) h^+(ks_j) Y(\hat{s}_j) .$$
Equating the two right-hand expressions gives us

$$Y(\mathbf{r}_i)^T j(kr_i) h^+(ks_i) Y(\mathbf{s}_i) = Y(\mathbf{r}_j)^T j(kr_j) h^+(ks_j) Y(\mathbf{s}_j),$$

which may be rewritten, using Eq. (90), as

$$Y(\mathbf{r}_i)^T j(kr_i) \left[ h^+(ks_i) Y(\mathbf{s}_i) - D(k; -\mathbf{R}_{ij}) h^+(ks_j) Y(\mathbf{s}_j) \right] = 0.$$ 

Since the sphere associated with \( \mathbf{r} \) is entirely within that associated with \( \mathbf{s} \), then the last equation is true for all \( \mathbf{r}_i \) and at least a small range of \( r_i \). So we may invoke our previous argument to conclude that the expression in square brackets (which has no dependence on \( r_i \)) is zero. Thus, transposing and using the properties of \( D(k; \mathbf{R}) \), we may write

$$Y(\mathbf{s}_i)^T h^+(ks_i) = Y(\mathbf{s}_j)^T h^+(ks_j) D(k; \mathbf{R}_{ij}) \quad \text{for} \quad s_j > R_{ij},$$

the far-region re-expansion formula. This may be compared with Eq. (99) (indeed the real part corresponds identically).

To obtain the re-expansion formula for the near region we first write out Eq. (97) explicitly, so that we have

$$h^+_t(ks_i) Y_L(\mathbf{s}_i) = 4\pi \sum_{L',L''} d^{l''-l+t} j_{l''}(kR_{ij}) h^+_t(ks_j) Y_{L''}(\mathbf{s}_j) Y_L(\mathbf{r}_i) I(L, L', L'');$$

where \( s_i = s_j + \mathbf{R}_{ij} \) with the restriction \( s_j > R_{ij} \). In the near-region case, where \( s_j < R_{ij} \), we may use the same formula with the variables interchanged, since the vectors are arbitrary apart from the order relation. Therefore, we have

$$h^+_t(ks_i) Y_L(\mathbf{s}_i) = 4\pi \sum_{L',L''} d^{l''-l+t} j_{l''}(kR_{ij}) h^+_t(ks_j) Y_{L''}(\mathbf{s}_j) Y_L(\mathbf{r}_i) I(L, L', L'').$$

This may be written in our notation as

$$Y(\mathbf{s}_i)^T h^+(ks_i) = Y(\mathbf{s}_j)^T h^+(ks_j) F(k; \mathbf{R}_{ij}) \quad \text{for} \quad s_j < R_{ij},$$

where we have defined \( F(k; \mathbf{R}_{ij}) \) by

$$F_{LL'}(k; \mathbf{R}_{ij}) \equiv 4\pi \sum_{L''} d^{l-l'+t} h^+_t(kR_{ij}) Y_{L''}(\mathbf{R}_{ij}) I(L, L', L'').$$

2. Gaunt algebra

Having encountered the Gaunt coefficients yet again in our formulas it seems worthwhile to investigate them in more detail at this point. We shall look briefly at some of their properties, but consider them from a slightly unusual point of view.

Normally the Gaunt coefficients arise in the re-expansion of the product of two spherical harmonics, where

$$Y_L(\mathbf{r}) Y_{L'}(\mathbf{r}) = \sum_{L''} I(L, L', L'') Y_{L''}(\mathbf{r}).$$

Use of spherical-harmonic orthonormality leads immediately to the definition (20) that we presented earlier. In the case of complex spherical harmonics the corresponding versions of the coefficients have a well known expression in terms of Clebsch-Gordan coefficients.

The particular form of the definitions of matrices such as \( w \) of Eq. (100), \( \hat{D}(k; \mathbf{R}) \) of Eq. (102), and \( F(k; \mathbf{R}) \) of Eq. (101), for example, suggests that it may be useful to consider a set of “Gaunt matrices” \( \Gamma^{(L)} \), indexed by \( L \), with matrix elements defined by

$$\Gamma^{(L')}_{LL'} \equiv I(L, L', L''),$$

easily seen to be real and symmetric. We may now reinterpret Eq. (102) as an eigenvalue equation,

$$[Y_L(\mathbf{r})] Y(\mathbf{r}) = \Gamma^{(L)} Y(\mathbf{r}),$$

where
in which, for any \( \mathbf{r} \), the vector \( \mathbf{Y}(\mathbf{r}) \) is an eigenvector of the matrix \( \Gamma^{(L)} \), with eigenvalue \( Y_L(\mathbf{r}) \).

Now the properties of the Gaunt coefficients allow us to say something about the structure of the individual matrices. In particular, we note that the triangle condition on \( L, L', L'' \), and \( l_\ell \) implies that the \( L \)th row (column) of \( \Gamma^{(L')} \) can only have a finite number of nonzero entries, from index \( l' = |L'' - l| \) up to index \( l' = L'' + l \). Furthermore we note that the matrix is banded with respect to \( l \).

Of special note is the fact that the matrix elements of the first row (column) are given by

\[
\Gamma^{(L')}_{(0,0)l'}(0,0) = I((0,0), L', L'') = (4\pi)^{-1/2}\delta_{L',L''},
\]

from which we may deduce that the Gaunt matrices are linearly independent.

For a given vector \( a \) with (in general complex) components \( a_L \), let us define a linear combination of the Gaunt matrices by

\[
\Lambda[a] \equiv \sum_L a_L \Gamma^{(L)}.
\]

There is no need to consider convergence in this definition since each matrix element of \( \Lambda[a] \) only contains contributions from a finite number of the \( a_L \), by virtue of what was said above. Linear independence gives us that

\[
\Lambda[a] = 0 \iff a = 0.
\]

If one is given a \( \Lambda[a] \), one may recover \( a \) by reading off the first row (column) and using Eq. (105), which shows that the correspondence between \( a \) and \( \Lambda[a] \) is one-to-one. It is also not difficult to show that \( \Lambda[a] \) is a linear function of its parameter \( a \), and that, if the products exist and are finite,

\[
\Lambda[a]b = \Lambda[b]a.
\]

Among the cases that we have encountered we may write, for example,

\[
\hat{D}(k; \mathbf{R}) = \Lambda[4\pi\xi(kR)]\mathbf{Y}(\mathbf{R}).
\]

To see some more interesting properties let us consider now the integral of the product of four spherical harmonics,

\[
I_4(L, L', L'', L''') = \int Y_L(\mathbf{R})Y_{L'}(\mathbf{R})Y_{L''}(\mathbf{R})Y_{L'''}(\mathbf{R}) \, d\Omega,
\]

which are manifestly symmetric under all permutations of the indices. We may use Eq. (110) to substitute for pairs of spherical harmonics in this definition, then use orthonormality to obtain three possible equivalent expressions, so that

\[
I_4(L, L', L'', L''') = \sum_{L_1} I(L, L'', L_1)I(L', L'', L_1)
= \sum_{L_1} I(L, L'', L_1)I(L'', L_1)
= \sum_{L_1} I(L, L', L_1)I(L'', L''').
\]

Making a particular choice for the assignment of indices leads to the matrix equations

\[
\Gamma^{(L)}\Gamma^{(L')} = \Gamma^{(L')}\Gamma^{(L)} = \sum_{L_1} I(L, L', L_1)\Gamma^{(L_1)}.
\]

In summary then, the \( \Gamma^{(L)} \) form a set of real, symmetric, linearly independent, mutually commuting matrices, the product of any pair of which may be expressed as a linear combination of some of them (in fact in the same way as the spherical harmonics from which they derive). The fact that they commute with each other is, of course, consistent with their having common eigenvectors.

It is interesting now to consider the \( \Gamma^{(L)} \) as generators of some larger set of matrices. In particular, let us denote by \( A_G \) the set of all linear combinations \( \Lambda[a] \), i.e., the set spanned by the \( \Gamma^{(L)} \). By virtue of the relations (112) we see that this set is closed under matrix multiplication; although, when we consider the product of two elements of \( A_G \),
we must be careful here about convergence. Indeed, we see that the general matrix element of a product of linear combinations may be written

\[ \langle \Lambda | a | \Lambda | b \rangle_{LL'} = \int Y_L(\hat{r}) \left[ \sum_{L''} a_{LL''} Y_{L''}(\hat{t}) \right] \left[ \sum_{L''} b_{L''L} Y_{L''}(\hat{t}) \right] Y_{L'}(\hat{t}) \ d\Omega, \]

which, to be finite, requires that the admissible vectors for \( A_C \) represent convergent spherical harmonic expansions of, say, square-integrable functions of \( \hat{r} \). Clearly \( A_C \) is a commutative algebra of matrices which we shall call the “Gaunt algebra”. (We conjecture also that is possible that the \( l = 1 \) Gaunt matrices generate all the rest.)

It is not difficult to show, using the equations (111), that we have

\[ \Lambda | a | b = \Lambda | a | b. \] (113)

This may be used to show a further property of \( \hat{D}(k; R) \). To see this rewrite the re-expansion formula (90) as

\[ \xi_j(kr_i)Y(\hat{r}_j) = \hat{D}(k; R_{ij}) \xi_j(kr_j)Y(\hat{r}_j). \]

Using Eq. (109) we see straightforwardly that

\[ \hat{D}(k; r_j) = \Lambda[4\pi\xi_j(kr_j)Y(\hat{r}_j)] \]
\[ = \Lambda[\hat{D}(k; R_{ij})4\pi\xi_j(kr_j)Y(\hat{r}_j)] \]
\[ = \hat{D}(k; R_{ij})\Lambda[4\pi\xi_j(kr_j)Y(\hat{r}_j)] \]
\[ = \hat{D}(k; R_{ij})\hat{D}(k; r_j). \]

Now \( r_j = R_{ij} + r_j \) with no restrictions, and the vectors are effectively arbitrary. So we see that, for general vectors \( R \) and \( S \), we have

\[ \hat{D}(k; R + S) = \hat{D}(k; R)\hat{D}(k; S), \] (114)

and it is easy to see that the corresponding relation holds for \( D(k; R) \). We note here that this relation can be proved directly from the definition (12) if one makes use of the angular delta-function property of spherical harmonics,

\[ \sum_L Y_L(\hat{r})Y_L(\hat{s}) = Y(\hat{r})Y(\hat{s}) = \delta(\hat{r} - \hat{s}). \] (115)

This property has been noted before by Natoli et al. in Ref. 23 [see their Appendix A noting that our \( D_{LLL'}(k; R_{ij}) \) corresponds to \( J_{LLL'}^{ij} \) in the notation of their Eq. (A23)].

3. Re-expansion of general regular solutions

We may now derive the re-expansions of the general coupled radial Schrödinger-equation solutions \( p \) and \( q \). For the general regular solutions \( p \) we consider the explicit form (13) of the Lippmann-Schwinger equation and the resulting scattering state \( \chi^{+}(r) \) of Eq. (73), noting that the plane-wave term \( \phi_0(r) \) occurs linearly on the rhs of the former. If we now consider an initial plane wave \( \phi_0(r) \) given by

\[ \phi_0(r) = e^{ikr_i} = e^{ikr_i}e^{-ikR_i} = e^{-ikR_i}\phi_0(r), \] (116)

then we may repeat the derivation of Eq. (73) with respect to a new origin at \( R_i \). This leads to a scattering state

\[ \chi^+_i(r_i) = (4\pi/k)Y(\hat{r}_i)^T p_i(r_i) (M^{-1}_i + \hat{k}) Y(\hat{k}) \], (117)

where the subscript \( i \) on \( p_i, M_i \) (and implicitly \( q_i^{(+)} \)) shows that the coupled radial Schrödinger-equation solutions with respect to the center \( R_i \) will be, in general, different to those of other centers. If we now invoke the linearity with respect to \( \phi_0(r) \) of the rhs of Eq. (119), and the uniqueness of solutions of the Lippmann-Schwinger equation (see for example Ref. 20), then we may conclude that

\[ \chi^+(r) = e^{ikR_i}\chi^+_i(r_i). \]
obtain avoided because of the presence of the inverse of the constant Wronskian matrix solutions centered on different origins whose boundary conditions may be arbitrarily chosen. In fact this problem is required only to be linearly independent, real, and regular at the origin. We do not specify any further boundary conditions or particular form at $r = 0$. From this point we may proceed as in the free Green-function case and find that

It is easy to see that it reduces immediately to the result (90) when then scattering potential vanishes.

We make two observations about our formula (118). First, it may be noted that the radial solution matrices $p_i$ are required only to be linearly independent, real, and regular at the origin. We do not specify any further boundary conditions or particular form at $r = 0$. At first sight this may be thought to pose a problem when we relate solutions centered on different origins whose boundary conditions may be arbitrarily chosen. In fact this problem is avoided because of the presence of the inverse of the constant Wronskian matrix $M$ for each center, which serves to “standardize” the regular solutions by reference, through the $q^{(+)}$, to the common boundary conditions at infinity.

Second, we note for the free radial functions that the re-expansion formula has a certain symmetry because both the functions themselves and the displacement operator $D$ involve the spherical Bessel functions. In fact this symmetry underlies the product formula (114). As a consequence the expressions on both sides of the formula may be easily seen to satisfy the free Schrödinger equation when considered as functions of $r_i$, $r_j$, or $R_{ij}$. If one wishes to investigate the analogous properties of our latest expression, then one must take into account the “hidden” dependence of $p_i$ on $R_i$.

4. Re-expansion of general irregular solutions in the far region

With the result of the previous section we may proceed quickly to obtain the re-expansion formula for general irregular solutions in the far region. To see this we consider again Fig. 11 where the position vector $s$ is such that $s_j > R_{ij}$, and we have $s_i > r_i$ and $s_j > r_j$. Expressing the general Green function in terms of vectors relative to the centers $R_i$ and $R_j$ in turn, using Eq. (22), leads to

$$G^+(r, s) = \mathcal{Y} (\hat{r}_i)^T p_i (r_i) (M^{-1}_{i+})^T q_i^{(+)}(s_i)^T \mathcal{Y} (\hat{s}_i) = \mathcal{Y} (\hat{r}_j)^T p_j (r_j) (M^{-1}_{j+})^T q_j^{(+)}(s_j)^T \mathcal{Y} (\hat{s}_j).$$

(119)

Making use of the previous section’s results leads immediately to

$$\mathcal{Y} (\hat{r}_i)^T p_i (r_i) (M^{-1}_{i+})^T \left[ q_i^{(+)}(s_i)^T \mathcal{Y} (\hat{s}_i) - D(k; -R_{ij})q_j^{(+)}(s_j)^T \mathcal{Y} (\hat{s}_j) \right] = 0 .$$

By similar reasoning to that which led to Eq. (97), we see that the expression inside the square brackets in the last equation must be zero, and we may then write (on transposing)

$$\mathcal{Y} (\hat{s}_i)^T q_i^{(+)}(s_i) = \mathcal{Y} (\hat{s}_j)^T q_j^{(+)}(s_j)D(k; R_{ij}) \text{ for } s_j > R_{ij} ,$$

(120)

the general far-region re-expansion formula. It is also easily seen to reduce to the free result when the potential vanishes. Taking the complex conjugate of (120), noting the reality of the spherical harmonics and the $D(k; R_{ij})$, leads to the corresponding formula for the incoming-wave solutions:

$$\mathcal{Y} (\hat{s}_i)^T q_i^{(-)}(s_i) = \mathcal{Y} (\hat{s}_j)^T q_j^{(-)}(s_j)D(k; R_{ij}) \text{ for } s_j > R_{ij} .$$

(121)
5. Translation of the single-scattering amplitude

Our re-expansion formulas for the general irregular solutions in the far region allow us to take the development of the single-scattering problem further. In particular we may now elucidate the behavior of the scattering amplitude as seen with respect to different origins. Intuitively, since the scattering is calculated from the asymptotic behavior of the solutions, one expects that a finite displacement should have no real effect. This is not quite the case as we shall see.

First, however, we must use the formula (64) to rewrite the general Green function (22) in terms of only the irregular solutions. With some algebra we find, noting (75) and (60), that

\[
G(r, s) = \frac{ik}{2}Y(\mathbf{r})^T \left[ q^{(+)}(r) \hat{A} q^{(+)}(s)^T - q^{(-)}(r) q^{(+)}(s)^T \theta(s - r) - q^{(+)}(r) q^{(-)}(s)^T \theta(r - s) \right] Y(\mathbf{s}) .
\]

We now consider this form expressed relative to the centers \(R_i\) and \(R_j\) in turn, as before, to give us two equivalent forms for \(G(r, s)\). Let us then take the general vectors \(r\) and \(s\) to be such that \(r_j > R_{ij}\) and \(s_j > R_{ij}\), and use the re-expansion formulas (120) and (121) to replace the \(q_{ij}^{(+)}\) and \(q_{ij}^{(-)}\) terms in the first of these equations. We should also choose \(r\) and \(s\) to be on spheres centered on \(R_j\) such that, say, \(r_j < s_j\) by a margin large enough so that \(r_i < s_i\) as well. This ensures that the theta functions correspond. Equating the right-hand sides, canceling the theta-function terms, and rearranging, we find that

\[
Y(\mathbf{r}_j)^T q_{ij}^{(+)}(r_j) \left[ \mathbf{D}(k; R_{ij}) \hat{A}_i \mathbf{D}(k; -R_{ij}) - \hat{A}_j \right] q_{ij}^{(+)}(s_j)^T Y(\mathbf{s}_j) = 0 .
\]

For large enough \(r_j\) and \(s_j\), their order relations above are true for all values of the angular variables, so we can conclude that the expression in square brackets is zero. Using our earlier definitions we then find that

\[
\hat{D}(k; R_{ij}) \hat{A}_i \hat{D}(k; -R_{ij}) = A_j .
\]

We have seen in Eq. (109) that \(\hat{D}(k; R_{ij})\) is a linear combination of Gaunt matrices and as such shares the common eigenvectors \(Y(\mathbf{r})\) for arbitrary \(\mathbf{r}\). It is not difficult to see that the associated eigenvalue is \(\exp(i k \mathbf{r} \cdot \mathbf{R}_{ij})\), and so

\[
Y(\mathbf{k}')^T A_j Y(\mathbf{k}) = Y(\mathbf{k}')^T \hat{D}(k; R_{ij}) A_i \hat{D}(k; -R_{ij}) Y(\mathbf{k})
= \exp[i (k' - k) \cdot R_{ij}] Y(\mathbf{k}')^T A_i Y(\mathbf{k})
\]

If we now consider the term from Eq. (80) for the scattering amplitude, involving the identity matrix, we see that it is precisely of the form of Eq. (115), i.e., a delta function of the angular variables. Therefore it is unchanged if we multiply by \(\exp[i (k' - k) \cdot R_{ij}]\), since this is a function of the difference of the same variables and is unity when they coincide. So finally we may write

\[
f_j(k', k) = \exp[i (k' - k) \cdot R_{ij}] f_i(k', k) .
\]

We see from this that the cross section is unchanged, but there is a phase shift when the scattering amplitude is calculated with respect to a different origin. The first is entirely in accord with our expectations, while the second is what gives rise to interference effects if we had several disjoint scattering potentials.

6. Re-expansion of general irregular solutions in the near region

In the case of the near-region re-expansion formula, we do not yet have a generally applicable method leading to a closed formula similar to those of the immediately preceding sections. The argument leading to the re-expansion formula (100) for the free Green function is not available to us in the case of a general potential, since it makes use of the fact that the free radial solutions are independent of which center they are referred to.

Let us therefore look for an alternative approach by considering the situation in Fig. [2] returning to the free Green function in the first instance. Thus we choose an arbitrary general point \(s\) on some sphere centered on \(R_j\) with, now, \(s_j < R_{ij}\); and an arbitrary \(r\) on a sphere centered on \(R_i\), entirely outside the first sphere. Since here we shall always have \(s_i > r_i\) and \(s_j < r_j\), an argument similar to that preceding Eq. (97) leads instead to

\[
Y(\mathbf{r}_i)^T j(kr_i) h^+(ks_i) Y(\mathbf{s}_i) = Y(\mathbf{r}_j)^T h^+(kr_j) j(ks_j) Y(\mathbf{s}_j) .
\]
One sees here already, since \( r \) and \( s \) are independent and arbitrary, the likely proportionality between \( h^+(ks_j)Y(\bar{s}_i) \) and \( j(ks_j)Y(\bar{s}_j) \). To see this explicitly we first multiply on the left by \( Y(\bar{r}_i) \), integrate over the angular variables \( \bar{r}_i \), and use orthonormality of spherical harmonics to get
\[
j(ks_j)h^+(ks_j)Y(\bar{s}_i) = \left[ \int Y(\bar{r}_i)Y(\bar{r}_j)^T h^+(kr_j) \ d\Omega_{\bar{r}_i} \right] j(ks_j)Y(\bar{s}_j) \tag{127}\]
To eliminate the \( j(ks_j) \) term, and thus the dependence on \( r_i \) on the left-hand side (lhs), we use the famous Wronskian formula \( 58 \) for spherical Bessel functions in the form
\[
h^+(kr) \frac{\partial}{\partial r} \left[ j(ks_j)Y(\bar{s}_j) \right] = -\frac{i}{kr^2} j(ks_j)Y(\bar{s}_j) \tag{128}\]
Thus, if we multiply our main equation on the left by the derivative with respect to \( \text{(wrt)} \) \( r_i \) of \( h^+(kr_i) \), and the same derivative of our main equation by \( h^+(kr_i) \), and take the difference, we obtain, after some rearrangement,
\[
h^+(ks_j)Y(\bar{s}_i) = i k K^{ji}_f T j(ks_j)Y(\bar{s}_j) \quad \text{for} \quad s_j < R_{ij}; \tag{129}\]
where we have defined the important matrix
\[
K^{ji}_f T \equiv \tau^2_i \int \left\{ h^+(kr_i)Y(\bar{r}_i) \frac{\partial}{\partial r_i} \left[ Y(\bar{r}_j)^T h^+(kr_j) \right] - \frac{\partial}{\partial r_i} \left[ h^+(kr_i) \right] Y(\bar{r}_j)Y(\bar{r}_j)^T h^+(kr_j) \right\} \ d\Omega_{\bar{r}_i}. \tag{130}\]
If we introduce some notation from Ref. 23 for vectors of free radial solutions, denoted \( J(kr) \), \( N(kr) \), and \( H^\pm(kr) \), with elements given by
\[
J_L(kr) \equiv j_i(kr)Y_L(\bar{r}), \tag{131}\]
\[
N_L(kr) \equiv n_i(kr)Y_L(\bar{r}), \tag{132}\]
and
\[
H^\pm_L(kr) \equiv h^\pm_i(kr)Y_L(\bar{r}) \tag{133}\]
then we may write
\[
K^{ji}_f = \tau^2_i \int \left\{ \frac{\partial}{\partial r_i} \left[ H^+(kr_j) \right] H^+(kr_i) - H^+(kr_i) \frac{\partial}{\partial r_i} \left[ H^+(kr_j)^T \right] \right\} \ d\Omega_{\bar{r}_i}, \tag{134}\]
where the volume \( \tau_i(r_i) \) is a sphere of radius \( r_i \) centered on \( \bar{R}_i \).

Now Eq. (129) is clearly another form of the near-region re-expansion formula (100) for the free irregular solutions, and comparison with this latter shows, using also Eq. (129), that
\[
K^{ji}_f = -(i/k)\mathcal{F}(k; R_{ij}) = -(i/k)\xi A[4\pi\xi H^+(kR_{ij})] \xi^\dagger. \tag{135}\]
It should also be clear that \( K^{ji}_f \) is constant, even though the definition (130) and alternative forms (134) appear to depend on \( r_i \). We may show this directly by using Green’s theorem to transform the second form in Eq. (134) into a volume integral. First, however, we note that the gradient operator in the integrand of this latter form may be taken to be wrt \( r \), since \( r_i \) is just a translation of this by a constant vector. One then sees that this integrand is anti-symmetric under the simultaneous exchange of the indices \( i \) and \( j \) and matrix transposition. Second, from Fig. 2 we see that the constraints on our geometric configuration imply that \( r_i < R_{ij} = R_{ji} \) and we can therefore use our preceding results (129) to write
\[
h^+(kr_j)Y(\bar{r}_j) = ik K^j_i T j(ks_j)Y(\bar{s}_j). \tag{136}\]
We may now use this and Eq. (129) to eliminate the irregular solutions altogether from Eq. (126) and find, on rearranging, that
\[
Y(\bar{r}_i)^T j(ks_j) \left[ ik K^j_i - ik K^j_i T \right] j(ks_j)Y(\bar{s}_j) = 0, \tag{137}\]
from which we deduce that

$$\mathcal{K}_f^{ij} = \mathcal{K}_f^{ji \ T} \qquad \text{(137)}$$

Now the integrand of Eq. (134) is singular at \( r = R_i \) and \( r = R_j \). Using Green’s theorem (30) we find that

$$\mathcal{K}_f^{ij} = \int_{\Sigma_{\tau_i(r)}} \left\{ (\nabla^2 + E)\mathcal{H}(kr_j) \right\} \mathcal{H}^+(kr_i)T - \mathcal{H}^+(kr_j) \left[ (\nabla^2 + E)\mathcal{H}^+(kr_i)T \right] \ d^3r .$$

Since the vectors \( \mathcal{H}^+(kr_i) \) and \( \mathcal{H}^+(kr_j) \) are solutions of the free Schrödinger equation, the integrand is identically zero away from the singularities. Thus the only finite contribution to the integral comes from the singularities themselves. It is then clear that the surface integral expression for \( \mathcal{K}_f^{ij} \) may be taken over any surface which encloses only the singularity at \( r = R_i \). In particular, the integral is independent of \( r_i \). The possibility then arises that the closed form of Eq. (134) may be obtained by evaluating the integral as \( r_j \rightarrow 0 \). This is not so interesting in the free-electron case, but might be applicable to our general irregular solutions which we consider below.

It is not difficult to show that the contribution to such an integral from the singularity at \( r = R_j \) would be equal and opposite to that at \( r = R_i \). This may be seen by evaluating the second form in Eq. (134) over the surface \( \partial \Sigma_{\tau_j(r_j)} \), using the anti-symmetry of the integrand to show that the result is \(-\mathcal{K}_f^{ij \ T}\), and noting Eq. (137). Alternatively we might consider an integral over a surface which encloses both singularities and show that the result is zero. One simple possibility is a spherical surface of radius \( R > R_{ij} \) centered on \( r = R_i \), so that we can use the far-region re-expansion formula (197) to replace the term \( \mathcal{H}^+(kr_j) \). Thus we would have, say,

$$\mathcal{X}^{ij} = \int_{\partial \Sigma_{\tau_i(R)}} \left\{ \nabla \left[ \mathcal{H}^+(kr_j) \right] \right\} \mathcal{H}^+(kr_i)T - \mathcal{H}^+(kr_j) \nabla \left[ \mathcal{H}^+(kr_i)T \right] \cdot \hat{n} \ d\sigma$$

$$= D(k; R_{ij}) \int_{\partial \Sigma_{\tau_i(R)}} \left\{ \nabla \left[ \mathcal{H}^+(kr_i) \right] \right\} \mathcal{H}^+(kr_i)T - \mathcal{H}^+(kr_i) \nabla \left[ \mathcal{H}^+(kr_i)T \right] \cdot \hat{n} \ d\sigma$$

$$= 0 ,$$

where the last step is justified by noting that the integrand is anti-symmetric and, when the integration over angles is done, the result is diagonal.

With the foregoing development in mind we may proceed to consider in a similar way the near-region re-expansion of the general irregular solutions. Noting again the situation in Fig. 2 and the order relations, the expressions for the general Green function relative to the two centers, \( R_i \) and \( R_j \), lead to

$$\mathcal{Y}(\hat{r}_i)^T p_i(r_i) \left( M_{i+}^{-1} \right)^T q_i^{(+) \ T}(s_i)^T \mathcal{Y}(\hat{s}_i) = \mathcal{Y}(\hat{r}_j)^T q_j^{(+) \ T}(r_j) \left( M_{j+}^{-1} \right)^T p_j(s_j)^T \mathcal{Y}(\hat{s}_j) .$$

As before we have then

$$p_i(r_i) \left( M_{i+}^{-1} \right)^T q_i^{(+) \ T}(s_i)^T \mathcal{Y}(\hat{s}_i) = \left[ \int \mathcal{Y}(\hat{r}_i)\mathcal{Y}(\hat{r}_j)^T q_j^{(+) \ T}(r_j) \ d\Omega_{\hat{r}_j} \right] \left( M_{j+}^{-1} \right)^T p_j(s_j)^T \mathcal{Y}(\hat{s}_j) .$$

Using now Eq. (25) we obtain

$$q_i^{(+) \ T}(s_i)^T \mathcal{Y}(\hat{s}_i) = \mathcal{K}_{ji \ T} \left( M_{j+}^{-1} \right)^T p_j(s_j)^T \mathcal{Y}(\hat{s}_j) \ \text{for} \ s_j < R_{ij} ;$$

with the definition

$$\mathcal{K}_{ji \ T} = -r_i^2 \int \left\{ q_j^{(+) \ T}(r_i) \mathcal{Y}(\hat{r}_i)\mathcal{Y}(\hat{r}_j)^T \partial_{r_i} \left[ q_j^{(+) \ T}(r_j) \right] - \partial_{r_j} \left[ q_j^{(+) \ T}(r_i) \right] \mathcal{Y}(\hat{r}_j)\mathcal{Y}(\hat{r}_j)^T q_j^{(+) \ T}(r_j) \right\} \ d\Omega_{\hat{r}_i} .\quad (140)$$

One may easily check the correspondence with our earlier formula in the limit of zero potential. Again we may consider the re-expansion from center \( i \) to center \( j \) and obtain

$$q_j^{(+) \ T}(r_j) \mathcal{Y}(\hat{r}_j) = \mathcal{K}^{ij \ T} \left( M_{i+}^{-1} \right)^T p_i(r_i)^T \mathcal{Y}(\hat{r}_i) \ \text{for} \ r_i < R_{ij} ;$$

using the two re-expansion formulas to prove the symmetry

$$\mathcal{K}^{ij} = \mathcal{K}^{ji \ T} . \quad (142)$$
Let us define vectors of general solutions by
\[ P(r) \equiv p(r)^T Y(\mathbf{r}) , \]
and
\[ Q^{(\pm)}(r) \equiv q^{(\pm)}(r)^T Y(\mathbf{r}) . \]

We may write
\[ K^{ji} = -r_i^2 \int_{\partial \tau, (r_i)} \left\{ \nabla \left[ Q^{(+)\dagger}(r_j) \right] Q^{(+)\dagger}(r_i)^T - Q^{(+)\dagger}(r_j) \nabla \left[ Q^{(+)\dagger}(r_i)^T \right] \right\} \cdot \mathbf{n} \, d\sigma , \]
and show, as above, the independence wrt \( r_i \). Precisely the same comments as before about surface and volume integrals, apply in this case, except that, in using Green’s theorem it should be noted that the terms like \((\nabla^2 + E)Q^{(+\dagger)}(r_j)\) are not zero, but \( V_j(r_j)Q^{(+\dagger)}(r_j)\), and they will cancel each other out in the integrand of the volume integral (since \( V_i(r_i) = V_j(r_j) = V(r) \) by definition), so that this is again zero away from the singularities.

In the absence of a closed formula for the \( K^{ij} \) we must evaluate them numerically via Eq. (145). The freedom in choice of surface may be invoked to use the atomic-sphere surfaces of radius \( b_i \) that we introduced earlier. The possibility that a closed form might be obtained by taking the limit as \( r_i \to 0 \) remains to be investigated.

### E. Multiple-scattered-wave method

Having developed the necessary new mathematical machinery we may now return to consideration of the multiple-scattering problem. Here we follow the general approach of Ref. [3], but with several important differences. It will be clear that the foregoing development of re-expansion for formulas for general solutions of Schrödinger’s equation is intended for the distorting potential \( V_I(r) \). Thus it is assumed that we have available, for each atomic center with position vector \( \mathbf{R}_i \) (for \( i = 1, \cdots , N \)), the exact solution matrices \( p_i \) and \( q_i^{(+\dagger)} \), regular at \( r_i = 0 \) and \( \infty \), respectively, in this potential. Finding these solutions is thus, of course, a large part of the computational burden in our approach to the multiple-scattering problem. For each center we evaluate the constant Wronskian matrix \( M_{i+} \) from these solutions, via Eq. (23), at some suitable radius \( r_i = b_i \), say.

We are interested in finding the scattering solution \( \psi^+(r) \) of the Schrödinger equation for our multicenter potential \( V(r) \), which develops from an incoming plane wave \( \phi_0(r) \). It is assumed that we have solved the scattering problem for our potential \( V_I(r) \) in terms of the \( p_i \), \( q_i^{(+\dagger)} \), and \( M_{i+} \) just mentioned, and thus have expressions for the Green function \( G_I(r,s) \), of the form of Eq. (22), with respect to any atomic center \( i \). In particular, we have an explicit expression for the distorted wave \( \chi^+(r) \) given by Eq. (122).

Following our earlier discussion it is then clear that to find \( \psi^+(r) \) we must solve the Lippmann-Schwinger equation (11) with the Green function \( G_I(r,s) \) and the singular part \( V_A(r) \) of our multicenter potential, together with the distorted wave as inhomogeneous part, i.e.,
\[ \psi^+(r) = \chi^+(r) + \int G_I^+(r,s)V_A(s)\psi^+(s) \, d^3s . \]

As usual the first step is to split the volume integral in this equation according to the molecular partition. Therefore we write
\[ \psi^+(r) = \chi^+(r) + \sum_{i=1}^N \int_{\tau_i} G_I^+(r,s)V_A(s)\psi^+(s) \, d^3s + \int_I G_I^+(r,s)V_A(s)\psi^+(s) \, d^3s , \]
where we have denoted the interstitial volume by \( I \), so that
\[ I \equiv \bigcup_{i=1}^N \tau_i . \]

Now, by construction, the singular part of the potential is zero in the interstitial region, so the last term in our equation vanishes, and we therefore have
\[ \psi^+(r) = \chi^+(r) + \sum_{i=1}^N \int_{\tau_i} G_I^+(r,s)V_A(s)\psi^+(s) \, d^3s . \]
Now $\psi^+(r)$ is a solution of the Schrödinger equation (1) for the full potential, and because of Eq. (6) we have

$$V_A(r)\psi^+(r) = [\nabla^2 + E - V_I(r)] \psi^+(r).$$

(148)

Using this we can eliminate $V_A(r)$ and obtain

$$\psi^+(r) = \chi^+(r) + \sum_{i=1}^{N} \int_{\tau_i} G^+_I(r,s) \left[ (\nabla^2 + E) \psi^+(s) - V_I(s) \psi^+(s) \right] d^3s$$

$$= \chi^+(r) + \sum_{i=1}^{N} \int_{\tau_i} \left\{ [G^+_I(r,s) (\nabla^2 + E) \psi^+(s) - \psi^+(s) (\nabla^2 + E) G^+_I(r,s)] + \delta^3(r-s) \psi^+(s) \right\} d^3s,$$

(149)

where in the last step we have used the basic property (14) of the Green function, noting the symmetry (52). Because of the delta-function term we see that there are two distinct cases to be considered. Invoking first Green’s theorem, we find that

$$\psi^+(r) = \chi^+(r) + \sum_{i=1}^{N} \int_{\partial \tau_i} \left[ G^+_I(r,s) \nabla_s \psi^+(s) - \psi^+(s) \nabla_s G^+_I(r,s) \right] \cdot \hat{n}_i \, d\sigma_i$$

if $r \notin \bigcup_{i=1}^{N} \tau_i$, 

(150)

and

$$0 = \chi^+(r) + \sum_{i=1}^{N} \int_{\partial \tau_i} \left[ G^+_I(r,s) \nabla_s \psi^+(s) - \psi^+(s) \nabla_s G^+_I(r,s) \right] \cdot \hat{n}_i \, d\sigma_i$$

if $r \in \bigcup_{i=1}^{N} \tau_i$.

(151)

We may now rewrite these equations in terms of radial Schrödinger-equation solutions at each atomic center. We have already discussed the Green function at considerable length, and the associated radial functions may be taken as known. We require also expressions for the wavefunction $\psi^+(r)$ inside each atomic sphere $\tau_i$. Here we follow the development of Natoli, Benfatto, and Doniach who show that we may write, for $r \in \tau_i$,

$$\psi^+(r) = \sum_{LL'} C^i_{LL'} R^i_{LL'}(r) Y_L(\hat{r}_i),$$

(152)

where the $C^i_{LL}$ are constants, and the $R^i_{LL'}(r_i)$ constitute a set, indexed by $L'$, of linearly independent solutions to the radial Schrödinger equations at center $i$,

$$\left[ \frac{1}{r_i^2} \left( \frac{\partial}{\partial r_i} \left( r_i^2 \frac{\partial}{\partial r_i} \right) \right) - \frac{l(l+1)}{r_i^2} + E \right] R^i_{LL'}(r_i) - \sum_{L''} v^i_{LL',L''}(r_i) R^i_{L''L'}(r_i) = 0,$$

(153)

which are regular at the origin. The potential matrix is given by

$$v^i_{LL',L''}(r_i) \equiv \sum_{L''} I(L, L', L'') V^i_L(r_i),$$

(154)

where $V^i_L(r_i)$ comes from the partial-wave expansion of the full molecular potential $V(r)$ at center $i$, i.e.,

$$V(r) \equiv \sum_{L} V^i_L(r_i) Y_L(\hat{r}_i).$$

(155)

In our matrix notation we may write the atomic solution as

$$\psi^+(r) = Y(\hat{r}_i)^T R^i(r_i) C^i.$$

(156)

If we now consider the case where our general vector $r$ is inside one of the atomic spheres and return to the second of our main equations, Eq. (151), then we see that there are two possibilities: either the integration variable is on the
surface of the same sphere, or another one. For the first of these possibilities we have \( s_i > r_i \) and we can therefore write the Green function as

\[
G^+_f(r, s) = Y(\vec{r}_i)^T p_i(r_i) \left( M^{-1}_{i+} \right)^T q_i^{(+)}(s_i) Y(\vec{s}_i) .
\]

The surface integral may be then evaluated as follows:

\[
\int_{\partial\Sigma_i} \left[ G^+_f(r, s) \nabla_s \psi^+(s) - \psi^+(s) \nabla_s G^+_f(r, s) \right] \cdot \hat{n}_i \, d\sigma_i
\]

\[
= Y(\vec{r}_i)^T p_i(r_i) \left( M^{-1}_{i+} \right)^T \int_{\partial\Sigma_i} \left[ q_i^{(+)}(s_i) Y(\vec{s}_i) Y(\vec{s}_i)^T R'(s_i) C^i - q_i^{(+)}(s_i) Y(\vec{s}_i) Y(\vec{s}_i)^T R'(s_i) C^i \right] \, d\sigma_i
\]

\[
= b_i^2 Y(\vec{r}_i)^T p_i(r_i) \left( M^{-1}_{i+} \right)^T \left[ q_i^{(+)}(b_i)^T R'(b_i) - q_i^{(+)}(b_i)^T R'(b_i) \right] C^i .
\]

For the second possibility, with \( j \neq i \), we have \( r_j > s_j \), and the Green function is given by

\[
G^+_f(r, s) = Y(\vec{r}_j)^T q_j^{(+)}(r_j) \left( M^{-1}_{j+} \right) p_j(s_j)^T Y(\vec{s}_j) ,
\]

which becomes, noting that \( r_i < R_{ij} \) and using the re-expansion formula \( 139 \),

\[
G^+_f(r, s) = Y(\vec{r}_i)^T p_i(r_i) \left( M^{-1}_{i+} \right)^T K^{ij} \left( M^{-1}_{j+} \right) p_j(s_j)^T Y(\vec{s}_j) .
\]

We then have

\[
\int_{\partial\Sigma_j} \left[ G^+_f(r, s) \nabla_s \psi^+(s) - \psi^+(s) \nabla_s G^+_f(r, s) \right] \cdot \hat{n}_j \, d\sigma_j
\]

\[
= b_j^2 Y(\vec{r}_i)^T p_i(r_i) \left( M^{-1}_{i+} \right)^T K^{ij} \left( M^{-1}_{j+} \right) \left[ p_j(b_j)^T R'(b_j) - p_j'(b_j)^T R'(b_j) \right] C^j .
\]

If we define the Wronskian of two matrix functions \( a(r) \) and \( b(r) \), say, by

\[
W[a, b](r) \equiv a(r)b'(r) - a'(r)b(r) ,
\]

then our results may be written

\[
0 = \chi^+(r) + Y(\vec{r}_i)^T p_i(r_i) \left( M^{-1}_{i+} \right)^T \left\{ b_i^2 W[q_i^{(+)}(b_i)^T R'(b_i)] C^i + \sum_{j \neq i} b_j^2 K^{ij} \left( M^{-1}_{j+} \right) W[p_j^T, R'](b_j) C^j \right\} .
\]

Let us now define

\[
B^i \equiv b_i^2 \left( M^{-1}_{i+} \right) W[p_i^T, R'](b_i) C^i ,
\]

which we may presumably invert to recover

\[
C^i = b_i^{-2} W[p_i^T, R'](b_i)^{-1} M_{i+} B^i .
\]

Define also, for each atomic site, the matrices

\[
T^{-1}_{a} \equiv W[q_i^{(+)}T, R'](b_i) W[p_i^T, R'](b_i)^{-1} M_{i+} .
\]

We now note that the inhomogeneous term may be written, using Eqs. \( 73 \) and \( 118 \) (noting that the re-expansion we wish to effect is from the origin of coordinates to center \( i \)), as

\[
\chi^+(r) = (4\pi/k) Y(\vec{r}_i)^T p_i(r_i) \left( M^{-1}_{i+} \right)^T D(k; R_i) \xi Y(\vec{k}) .
\]
We may now write our results

\[ 0 = Y(\mathbf{r}_i) T_i(p_i) (M_{i+}^{-1}) T_i (4\pi/k) D(k; \mathbf{r}_i) \xi Y(\mathbf{k}) + T_{a}^{-1} B^i + \sum_{j \neq i} K^{ij} B^j \]  

(164)

for which it is necessary that

\[ T_{a}^{-1} B^i + \sum_{j \neq i} K^{ij} B^j = -(4\pi/k) D(k; \mathbf{r}_i) \xi Y(\mathbf{k}) . \]

(165)

There will be one of these equations for each \( i \), and together they constitute the multiple-scattering equations for the case of an incoming plane wave of direction \( \mathbf{k} \). Clearly they form a linear system which may be solved for the unknown vectors \( B^i \) by inversion of the secular matrix whose elements are defined by

\[ S_{LL}^{ij} = T_{a}^{-1} \delta_{ij} + (1 - \delta_{ij}) K_{LL}^{ij} . \]

(166)

More generally, following Ref. [7], we replace the exciting amplitude \( 4\pi i Y_L(\mathbf{k}) \) by \( \delta_{LL''} \) and find a solution vector \( B^i_L(L'') \) for each partial-wave channel \( L'' \). The results may be then applied to more general situations.

With the solution vector \( B^i \) we may find the wavefunction inside the atomic spheres by using Eq. (161) to determine the coefficients \( C^i \), then inserting them into Eq. (162). For the interstitial-region wavefunction we must return to perform the surface integrals in Eq. (150). In this case, for \( r \) in the interstitial region and \( s \) on the surface of atomic sphere \( i \), we have \( r_i > s_i \), so that

\[ G_i^+(r, s) = Y(\mathbf{r}_i)^T q_i^{(+)}(r_i) (M_{i+}^{-1}) p_i(s_i)^T Y(\mathbf{s}_i) . \]

We obtain then

\[ \psi^+(r) = \chi^+(r) + \sum_{i=1}^{N} b_i^2 Y(\mathbf{r}_i)^T q_i^{(+)}(r_i) (M_{i+}^{-1}) \left[ p_i(b_i)^T R_i^{'}(b_i) - p_i(b_i)^T R_i(b_i) \right] C^i \]

\[ = \chi^+(r) + \sum_{i=1}^{N} Y(\mathbf{r}_i)^T q_i^{(+)}(r_i) B^i . \]

(167)

This completes the solution of the multiple-scattering problem.

1. Symmetry of the secular matrix

We see from Eq. (162) that the second term in the secular matrix (166) is symmetric. The question then arises as to whether the first term \( T_{a}^{-1} \) has any symmetry. There appears to be none manifest in its definition (162). However, the author has treated (in Ref. [15]) a similar problem for the bound-state version of the method of Natoli, Benfatto, and Doniach [5]. In fact, a proof of the symmetry of \( T_{a}^{-1} \) may also be developed in our present case.

To see this we first define the matrices \( d \) and \( t \) by

\[ d \equiv W[p^T, R(b)^{-1} M_{+} , \]

and

\[ t \equiv (d^{-1})^T T_{a}^{-1} (d^{-1}) , \]

suppressing for the moment the atomic index \( i \). We may recover our original matrix via

\[ T_{a}^{-1} = d^T t d . \]

It is clear from the definitions that the symmetry of \( t \) is equivalent to that of \( T_{a}^{-1} \).

Expanding \( t \) we have (suppressing dependence on the radius \( b \))

\[ t = W[p^T, R^T (M_{+}^{-1})^T W[q^{(+)}]^T, R] \]

\[ = \left\{ R'^T \left[ p (M_{+}^{-1})^T q^{(+)} \right]^T R \right\} + \left\{ R^T \left[ p' (M_{+}^{-1})^T q^{(+)}^T \right] R \right\} - f , \]

(168)
where we have defined

\[ f \equiv R^T \left[ p \left( M^{-1}_+ \right)^T q^{(+)} \right] R + R^T \left[ p' \left( M^{-1}_+ \right)^T q^{(+)} \right] R' \quad (169) \]

It may be seen now that the two expressions collected between braces in Eq. (168) are each individually symmetric; the first by virtue of Eq. (26) and the second from Eq. (59). So the symmetry of \( f \) is equivalent to that of \( t \). Substituting from Eq. (27) in the second term of Eq. (169) leads to

\[ f = \left\{ R^T \left[ p \left( M^{-1}_+ \right)^T q^{(+)} \right] R + R^T \left[ q^{(+)}' \left( M^{-1}_+ \right) p' \right] R' \right\} - \frac{1}{b^2} R^T R'. \]

The term in braces here is now manifestly symmetric and we are left with the term in \( R^T R' \). However this last is also symmetric for similar reasons to the comparable term in \( p \) of Eq. (24), i.e., since \( R \) is the matrix solution, regular at the origin, of the coupled radial Schrödinger equations for a real potential. The proof may be seen in Ref. [1]. Thus our result is shown.

2. Bound States

As mentioned above our new MSW method is readily adapted to bound states. In their exposition of a non-MT MSW method, Natoli, Benfatto, and Doniach [5] do not treat this case explicitly (this is done in Ref. [15]), but observe that it is achieved by dropping the inhomogeneous term in the Lippmann-Schwinger equation; making the analytic continuation \( k \to ik \), \( E \to -E \) where necessary; using the appropriate re-expansion formulas for modified spherical Bessel, Neumann, and Hankel functions; and imposing decaying-wave boundary conditions in the asymptotic region. In our case we expect that similar comments should apply.

Although again we shall not develop the bound-state case explicitly, it is necessary to address briefly several issues which arise in our present approach. Firstly, we note that dropping the inhomogeneous term in the Lippmann-Schwinger equation (166) leads to

\[ \psi(r) = \int G_j^+(r, s)V_A(s)\psi(s) \, d^3s \quad (170) \]

as the main equation to be satisfied by a bound state \( \psi(r) \) at some energy \( E < 0 \). It is not difficult to show directly that such a \( \psi(r) \) will satisfy Schrödinger’s equation for the full potential \( V(r) \), even though the two-stage picture of the distorted-wave formalism is lost.

A more substantial problem arises when we come to derive the re-expansion formulas. In particular, since there is no inhomogeneous term in Eq. (170), the argument leading to the re-expansion formula (118) for the general regular solutions is no longer available to us. In principle, following the comments above, we may analytically continue Eq. (118) to obtain a similar equation:

\[ Y(\vec{r}_i)^T p_i(r_i) \left( M^{-1}_- \right)^T = Y(\vec{r}_j)^T p_j(r_j) \left( M^{-1}_- \right)^T D^{(-)}(\kappa; R_{ij}); \quad (171) \]

where \( \kappa \) is such that \( \kappa > 0 \) and \( \kappa^2 = -E \), and \( D^{(-)}(\kappa; R_{ij}) \) is obtained from \( D(k; R_{ij}) \) by the substitution \( k \to i\kappa \), therefore having components

\[ D^{(\kappa)}_{LL'}(\kappa; R) = 4\pi \sum_{L''} i^{L''-L'}(\kappa R)Y_{L''}^*(\vec{R})I(L, L', L''). \quad (172) \]

The \( p_i(r_i) \) and \( q_i(r_i) \), etc., are solution matrices at our negative energy \( E \), and the \( q_f(r_i) \) are asymptotic to the decaying-wave free solutions \( q_f(r_i) \), given by

\[ q_f(r) = i\xi k^+ (kr), \quad (173) \]

rather than those of Eq. (15), since this is the analytic continuation of the free positive-energy solutions (28). Such a procedure, however, should really be more rigorously mathematically justified.

An alternative derivation may be developed via an argument more in line with our earlier approach. We first note that, taking \( p_f \) from Eq. (111) and \( q_f \) from Eq. (173), we find the inverse transpose of the constant matrix \( M_f \) to be

\[ \left( M^{-1}_f \right)^T = i\kappa \xi . \quad (174) \]
The re-expansion formulas for the free solutions at negative energies are well known (see Eqs. II.25 and II.23 of Ref. [2] for example). They may be also obtained by the substitution $k \rightarrow ik$ in our earlier Eqs. (90) and (97). It is not difficult to check that they can be written in our present notation as

$$Y(\hat{r}_i)^T \rho_f(r_i) \left( M_i^{-1} \right)^T = Y(\hat{r}_j)^T \rho_f(r_j) \left( M_j^{-1} \right)^T D^{(-)}(\kappa; R_{ij})$$

(175)

and

$$Y(\hat{r}_i)^T q_f(r_i) = Y(\hat{r}_j)^T q_f(r_j) D^{(-)}(\kappa; R_{ij}) \text{ for } r_j > R_{ij} \, .$$

(176)

If we now consider a situation such as that of Fig. 1, with no restriction on $r_i$ other than that we maintain the order relations $s_j > R_{ij}$, $s_i > r_i$, and $s_j > r_j$; then we may use the general Green-function formula to write, similarly to Eq. (119),

$$Y(\hat{r}_i)^T \rho_i(r_i) \left( M_i^{-1} \right)^T q_i(s_i) Y(\hat{s}_i) = Y(\hat{r}_j)^T \rho_j(r_j) \left( M_j^{-1} \right)^T q_j(s_j) Y(\hat{s}_j) \, .$$

(177)

If, for the moment, we assume that the potential is identically zero beyond some large radius $R$, and if we take the sphere of possible vectors $s$, large enough to be entirely outside this radius, then $q_i(s_j)$ and $q_j(s_i)$ may be taken to be identically $q_f(s_j)$ and $q_f(s_i)$ respectively in this region. We may therefore use the transpose of Eq. (176) to substitute on the lhs of Eq. (177), rearranging then to obtain

$$\left[ Y(\hat{r}_i)^T \rho_i(r_i) \left( M_i^{-1} \right)^T D^{(-)}(\kappa; R_{ij})^T - Y(\hat{r}_j)^T \rho_j(r_j) \left( M_j^{-1} \right)^T \right] q_f(s_j)^T Y(\hat{s}_j) = 0 \, ,$$

and we may conclude that the expression in square brackets here is identically zero. Now by an argument similar to that leading to Eq. (93) we may show that

$$D^{(-)}(\kappa; R)^{-1} = D^{(-)}(\kappa; -R) \, .$$

(178)

Furthermore it is easily seen from the explicit formula (172) that

$$D^{(-)}(\kappa; -R) = D^{(-)}(\kappa; R)^* = D^{(-)}(\kappa; R)^T$$

(179)

(showing incidentally that $D^{(-)}(\kappa; R)$ is hermitian), and we may therefore deduce that the re-expansion formula (177) for the general regular solutions at negative energies is indeed correct. Presumably we may use this result to obtain, in a similar way to the derivation of Eq. (120), the corresponding general far-region irregular-solution re-expansion formula

$$Y(\hat{s}_i)^T q_i(s_i) = Y(\hat{s}_j)^T q_j(s_j) D^{(-)}(\kappa; R_{ij}) \text{ for } s_j > R_{ij} \, .$$

(180)

Our derivation here is less general than we should like because of the assumption that the potential is zero beyond some large radius. If, however, we note the fact that the regular solutions $\rho_i(r_i)$ are determined by the choice of boundary conditions at $r_i = 0$, and that the $D^{(-)}(\kappa; R)$ are completely given quantities, then the effect of the potential cutoff will only be felt by the $q_i(r_i)$ and consequently the $M_i$. Thus, since we may keep $r_i$ and $r_j$ fixed in Eq. (177), only $M_i$ and $M_j$ will vary as a function of the potential cutoff, and we may plausibly invoke a limiting argument to justify the formula as the cutoff tends to infinitely large distance, i.e., no cutoff.

A further issue arises when we consider the potential $V_I(r)$. It is possible (indeed likely for large molecules) that $V_I(r)$ itself may support bound states. This would appear to cause problems when our energy passes through that of such a state. In the bound-state multiple-scattering case the secular equation is constructed in a similar way to that for the continuum case [16], except that there is no inhomogeneous part. The condition for a bound state is that the secular matrix becomes singular, allowing a non-zero solution vector from which the corresponding wavefunction may be constructed. As shown in Ref. [1] a bound state of $V_I(r)$ leads to the constant matrices $M_i$, involved in the construction of the secular matrix, becoming themselves singular, and would give rise to problems when the inverses of these matrices are required. Conceivably it may be possible to factor out such a singularity, or deal with the problem in another way. This issue remains to be investigated in more detail.

A systematic way of bypassing this problem is suggested by a comment of Natoli, Benfatto, and Doniach in the context of their non-MT MSW method [3]. In particular, we combine their subtraction of a constant value from the interstitial-region potential (useful in their case to obtain a convergent Born expansion for the interstitial-region scattering $T$ matrix) with the use of an outer sphere (as we describe in the next section) to obtain a $V_I(r)$ which does not bind.
A final issue is that of normalization of the wavefunction. Since the wavefunction is constructed from the coefficients $B_i$ in the solution vector of the homogeneous bound-state secular equation, the normalization is not known. One must integrate the square of the resulting function over all space to determine the multiplying coefficient which leads to unit norm. In practice one may evaluate this numerically (although there are analytic methods that may be adapted to our present approach [2]) and we shall leave further consideration of this issue outside the scope of the present work.

3. Outer Sphere

As in previous versions of the MSW method it is sometimes useful to add to the partition of space the outer sphere $\tau_0$, containing all the atomic spheres, that we have defined in an earlier section. In the region $\tau_0^-$ outside the outer sphere the potential is expanded as a multipole expansion relative to the sphere center $R_0$ and the coupled radial Schrödinger equations are solved, similarly to the atomic centers, leading, for $r \in \tau_0^-$, to

$$
\psi(r) = Y(\mathbf{r}_0)^T R^0(r_0) C^0,
$$

for some unknown coefficients $C^0$, with the difference being that the $R^0(r_0)$ are integrated inwards from suitable boundary conditions at infinity.

The use of an outer sphere leads to a modified secular equation. We shall not reproduce the algebra here since it is a relatively straightforward adaptation of the method of Ref. [5], using the formulas and approach we have developed above.

The utility of the outer sphere is that it enables one to impose boundary conditions directly on the solution of the Schrödinger equation, important in the case of, for example, long-range Coulomb potentials. It is also useful to reduce the size of the interstitial region, which is important in the MT version of the MSW method, and in the non-MT version of Ref. [5], it helps to reduce the effect of the interstitial $T$ matrix. For our present approach maximizing the size of the atomic spheres (and minimizing the size of the outer sphere) would tend to produce smaller potential gradients at the sphere surfaces and hence a more gently varying distorting potential $V_I$ (if the atomic parts of $V_I$ were chosen to be smooth continuations of the true interstitial potential).

As mentioned in the previous section, the use of an outer sphere is a way of avoiding the possibility that $V_I$ has bound states of its own. This may be done by choosing the extra-molecular part of $V_I$ to be asymptotic to some constant potential sufficiently less than zero that no bound states arise in the resulting new $V_I$. Since the old $V_I$ must be bounded from below, one obvious choice would be the minimum of this potential, although it may not be, in general, necessary to set the new asymptotic value as low as this. For particular cases some experimentation may be required. The smooth continuation of the new $V_I$ into the extra-molecular region may be then set identical to the chosen asymptotic value beyond some large radius, so that the resulting $q_i$ would be identical to the diagonal modified spherical Hankel function forms for all larger values of the radius.

One consequence of this new effective zero for the $V_I$ is that between this value and the true energy zero of $V$ we must use the standing-wave Green function related to $V_I$, in a manner similar to the original version [2] of the MSW method. This is, however, expected to be a straightforward modification of the usual positive-energy formulas [22], with the $q_i(r_i)$ now asymptotic to $n(k' r_i)$ and $k'$ calculated relative to the new asymptote of $V_I$.

III. NUMERICAL IMPLEMENTATION

The main computational task for the solution of the multizone scattering problem is the setting up of the secular matrix which is then inverted to solve the secular equation. The essential ingredients for this are the radial solution matrices $p_i$, $q_i^{(+)}$, and $R_i$ for each atomic center. For these we require the multipole components at each center of $V_I$ from $r_i = 0$ to $\infty$, and of $V$ from $r_i = 0$ to $b_i$. These, however, need only be calculated once. The radial solutions must be calculated for each energy required. With these solutions we can evaluate the constant Wronskian matrices $M_{ij}$ at $r_i = b_i$, which are then inverted; and the matrices $K_{ij}$ for which the surface integrals may also be evaluated at the same radius. From these requirements we see that $p_i$, and $R_i$ are needed over the range $r_i = 0$ to $b_i$, and $q_i^{(+)}$ from $r_i = b_i$ to $\infty$. (Infinity here may be taken to be a suitably large radius.)

The solution of coupled radial Schrödinger equations for various types of potential has received considerable attention over many years and has a sizeable literature (see for example Ref. [24]), and, for our immediate purposes, we may consider currently available numerical methods adequate. Although it is known that there are situations where problems may arise, for the types of potential we consider they appear not to occur. Our own experience with the
matrix Numerov method, for example, in the form given in Ref. [5], has thrown up no obvious difficulties; and, for calculations where an independent check is available, gives quite acceptable results.

The key to an accurate implementation of our present approach is the choice of distorting potential $V_f(r)$. It is important that this potential be well behaved, avoiding discontinuities and wide variations. Since it is constrained to coincide with the true interstitial potential in that region, the only freedom we have is in the choice of values inside the atomic volumes. Here we should replace the true singular atomic potential with a smooth continuation of the interstitial potential which is finite everywhere. This may be done in a variety of ways. One possibility, which has been used in a slightly different context by the author, is to replace, for $r_i < b_i$, each multipole component of the true potential $V$ by a polynomial, in $r_i$, of minimal degree, which matches the true multipole component at $r_i = b_i$, and (perhaps) some of its derivatives.

IV. DISCUSSION

Our new approach to non-MT MSW theory results in formulas similar in overall form to those of some previous versions, and indeed should be thought of as a direct development of them. Although the derivation of the new secular equation in particular owes much to the approach of Ref. [5], the final form of the result is more reminiscent of the original MT-based version of Slater and Johnson [2]. This may be understood if one notes that our distorting potential corresponds to the constant potential of their method. Thus where one sees free-electron waves (expressed in terms of spherical Bessel, Neumann, and Hankel functions) in their formulas, one sees the distorted waves $p_i$ and $q_i$ in ours. (In fact, the MT version of the method should result from our present algebra when $V_f$ is replaced by the constant average interstitial potential.) We treat directly the multiple scattering in terms of waves which are already being scattered in the distorting potential. By contrast, and very loosely speaking, the method of Ref. [5] adds as an extra step (via the interstitial $T$ matrix) the effect of the interstitial region potential on the waves scattering from the atomic centers.

To enable development of the non-MT MSW theory in the direction we have taken it requires, however, elaboration of the formal machinery that makes up the bulk of this present work. It seems likely that some of the results derived here are new and should prove useful beyond our immediate subject. Firstly, the explicit general Green-function expansions of Ref. [1] are necessary to implement the distorted-wave Lippmann-Schwinger formalism, leading, in particular, to an explicit form [3] for the distorted wave itself. Further direct development of the material of Ref. [1] was required, leading to some useful formulas, notably the important relation [50] between regular and irregular matrix solutions of the coupled radial Schrödinger equations [18]. We then saw how one can use these results to develop a complete (if skeletal) solution to the single-scattering problem for a general noncentral potential, whose most important result is the formula [74] for the matrix $A$ in the expression for the scattering amplitude. Indeed, having been presented with such a solution one might reasonably ask why it could not be applied directly to the scattering problem of the multicenter potential $V$. As is well known, the singularities of $V$ have only slowly convergent spherical-harmonic expansions relative to a single center. To have an accurate treatment of scattering in such a potential requires an approach which is capable of combining individual accurate solutions in the regions of the singularities. This, of course, is the essential utility of the multiple-scattering approach to the solution of Schrödinger’s equation for multicenter potentials.

As mentioned in Ref. [1] certain mathematical issues relating to the derivation and manipulation of our Green-function expansions have been glossed over, and thus must be counted among the assumptions of our approach. The use of vectors and matrices of infinite dimension and questions of convergence should be considered in more depth. Such issues are frequently bypassed in the literature, it being noted that for practical purposes such vectors and matrices are truncated at finite dimension in real calculations. Of more physical interest is the asymptotic behavior of the general irregular radial solutions $q_i$. The derivation of the Green-function expansions in Ref. [1] assumes that it is possible to choose these solutions asymptotic to a diagonal form. Indeed we assume here that this diagonal form is the free solution appropriate to outgoing waves of Eq. [28]. In the absence of finite charge moments the potential will typically decay exponentially and this would almost certainly be the case. It may easily be shown that the potential multipole expansion is dominated by the monopole component at infinity, even in the presence of a finite dipole or higher moment. Thus the potential matrix of Eq. [19] will be diagonally dominant. The nature of the limiting behavior necessary may in fact be seen from the expression [71] in the derivation of the explicit form for the scattered wave in a given potential, and in the algebra [at Eq. [81] which verifies the defining equation for the general Green function.

It is possible to bypass the issue of the asymptotic behavior of the irregular solutions by using the outer-sphere option. Here one may set the distorting potential to a constant value beyond some finite radius. In this region, as we mentioned above, the general irregular solutions may be chosen identical to the free ones, although once inside the finite radius they will, in general, deviate from them. This can be the case even if the true potential in the
The extra-molecular region contains charge monopole, dipole or higher components.

The second important set of results which enables our version of the non-MT MSW theory is that related to the re-expansion of general regular and irregular solutions of the coupled radial Schrödinger equations. This is central to our approach and we have devoted a significant fraction of this present work to a careful presentation of the derivations, returning more than once to particular points, and including alternative derivations of some formulas. As mentioned in the section on bound states, and illustrated in Eq. (71), the particular form of the matrix $D(k; R_{ij})$ associated with translations is dependent on the asymptotic form of $q$. It is interesting that this matrix, which has been encountered before in MSW theory, has a more general function than previously appreciated.

V. CONCLUSIONS

We have presented here a new approach to multiple-scattering theory for general potentials, based on the distorted-wave (two-potential) Lippmann-Schwinger formalism. (We propose to refer to it therefore as the “DW-MS” method.)

Our method makes use of the familiar partition of space into non-overlapping atomic spheres and a remaining interstitial region; splits the multicenter molecular potential into a well behaved background distorting potential and a singular atomic part; and uses some newly developed Green-function expressions and re-expansion formulas to derive the new secular equations.

The central improvement offered by this approach is to avoid any volume integrals, which will have significant benefits for the scaling behavior of calculations, the most complicated parts of which are now the surface integrals associated with the matrices $K_i^0$. In fact, the possibility arises, perhaps by taking the limit of the integrals as $r_i \to 0$, that even these may be reduced to one-dimensional integrations. Calculation of the effects of the varying interstitial potential appears implicitly via the irregular solutions $q_{ij}^{(+)}$ of the coupled radial Schrödinger equations for the distorting potential $V_I(r)$. Another attractive feature of the approach is that the above calculational tasks require only numerical methods that are already well tried and tested in related approaches.

It may be noted that, in a formal sense at least, the separation between geometry and scattering has been recovered. In reality of course this is not quite true since there is a connection between the distorting potential and the scattering centers. However, it may be possible to exploit this in an approximate way to reduce the computational burden in the context of geometry searches and total energy minimization.

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FIG. 1: Diagram of vectors and sphere surfaces in the derivation of the re-expansion of the irregular radial solutions in the far region.
FIG. 2: Diagram of vectors and sphere surfaces in the derivation of the re-expansion of the irregular radial solutions in the near region.