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Partial-wave Green-function expansions for general potentials

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We present a derivation of the partial-wave expansions of the exact, time-independent, single-particle Green function for an arbitrary potential taken from a wide class typical of atomic and molecular systems, whose expansion in spherical harmonics about some point is given. The Green-function expansions are expressed in terms of matrix solutions, one regular at the origin and one at infinity, of the coupled radial Schrödinger equations related to that potential, and a constant, Wronskian-type matrix constructed from them. Expansions are developed for both positive energies, relevant to scattering states, and negative energies, where we elucidate the mathematical condition for bound states.

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I. INTRODUCTION

Over the past two or three decades, there has been a steady accumulation of theoretical developments aimed at extending multiple-scattering methods to systems of non-spherically-symmetric scatterers. Since about 1990, there have followed computational implementations, of varying degrees of generality and applicability, which lead one to hope that reliable methods of treating such systems may be routinely included in standard computational packages in the near future.

We are speaking primarily of real-space, non-basis-set methods deriving from or related to the well-known theory of Korringa, Kohn, and Rostoker [1,2]. This KKR method has been widely used over many years with considerable success for calculations of various properties of solid-state and molecular systems [where the adaptation of the method to molecules and clusters is generally associated with Johnson and Slater and their co-workers (see, for example, Ref. [3]), but has suffered from its restriction to potentials of the so-called "muffin-tin" (MT) type, i.e., with spherically symmetric scattering centers, separated by an interstitial region in which the potential is constant. Consequently, those requiring computational methods which take into account more realistic potentials have had to rely on other, nonscattering techniques, with, in general, their own limitations.

In recent years there has been something of a renewal of interest in the real-space KKR methodology, with successful applications to, for example, photonic band-gap materials (see Ref. [4] and further references therein) and acoustic (or phononic) band-gap systems [5,6]. In these new fields of application, there has also arisen the need to be able to treat nonspherical scattering centers, emphasizing further the importance of the development of widely available and computationally reliable extensions to multiple-scattering methods to do this.

At present, the development of non-MT [or "full potential" (FP)] extensions to the real-space KKR methodology appears to have progressed in two main directions: that which follows the approach of Williams and Morgan [7], and later variants, mainly for periodic systems, with typical application to the band structure of crystalline solids; and a molecular (or cluster) approach, mainly represented by the theoretical developments of Natoli and co-workers [8,9], implemented by the present author and colleagues [10,11], with typical application to x-ray-absorption spectroscopy [12]. Despite the considerable progress made in this field, however, it seems likely (at least to the present author) that further theoretical developments are required before they become widely and routinely used.

With the motivation for this article therefore oriented towards the improvement of multiple-scattering methods, in the context we have described, we do not consider them further in detail except to note a common general feature. In particular, the derivation of the central equations of each method typically begins with the Lippmann-Schwinger equation for scattering states $\psi(\mathbf{r})$ in a multicenter potential $V(\mathbf{r})$,

$$\psi(\mathbf{r}) = \phi_0(\mathbf{r}) + \int G_0^+(\mathbf{r},\mathbf{s})V(\mathbf{s})\psi(\mathbf{s})d^3s, \qquad (1)$$

where $\phi_0(\mathbf{r})$ is a plane wave, the integral is over all space, and $G_0^+(\mathbf{r},\mathbf{s})$ is the time-independent free Green function with outgoing wave boundary conditions, whose one- and two-center spherical harmonic (partial-wave) expansions are well known in terms of spherical Bessel and related functions.

One may question the suitability of the free Green function in the case of non-MT potentials and consider instead starting from a different Lippmann-Schwinger equation, using the exact Green function for a background potential more adapted to the scattering situation than the free-electron one. This is undoubtedly not a new idea, but the apparent lack in the available literature of general formulas for the expansion of Green functions of arbitrary noncentral potentials would seem a major obstacle to carrying it out. It is just this lack that the present work is intended to redress.

In the following section, we derive partial-wave expansions of the exact Green functions for an arbitrary potential expanded in spherical harmonics. Although motivated by the needs of the multiple-scattering methods we have mentioned, the results should be of general interest to all those making use of scattering techniques in quantum mechanics, as well as areas where the governing equations are similar, such as the propagation of electromagnetic waves in media with varying refractive index or acoustic waves in inhomogeneous media.

II. THEORY

Our starting point is the Schrödinger equation,

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

associated with the potential $V(\mathbf{r})$. [To simplify the algebra, we use the so-called "Rydberg atomic units" in which Planck's (reduced) constant, the electron mass, the positron charge, and the Bohr radius all have unit magnitude; and, to remove a factor of one-half from Schrödinger's equation, energies are expressed in Rydbergs.]

We assume that the potential $V(\mathbf{r})$ has a well-behaved, convergent expansion in spherical harmonics about some point which we take as the origin of coordinates, so that

$$V(\mathbf{r}) \equiv \sum_L v_L(r) Y_L(\hat{\mathbf{r}}), \tag{3}$$

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

$$\sum_L \equiv \sum_{l=0}^{\infty} \sum_{m=-l}^{l}. \tag{4}$$

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.

If we now consider a solution of Schrödinger's equation as a spherical harmonic expansion,

$$\psi(\mathbf{r}) \equiv \sum_L \phi_L(r) Y_L(\hat{\mathbf{r}}), \tag{5}$$

then, as is also well known, one is led to the coupled radial equations

$$\left\{\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)\right] - \frac{l(l+1)}{r^2} + E\right\}\phi_L(r) - \sum_{L'} w_{LL'}(r)\phi_{L'}(r) = 0, \tag{6}$$

where we have used spherical harmonic orthonormality and defined the potential matrix elements

$$w_{LL'}(r) \equiv \sum_{L''} I(L,L',L'') v_{L''}(r) \tag{7}$$

[with the Gaunt coefficients for real spherical harmonics given by

$$I(L,L',L'') \equiv \int Y_L(\hat{\mathbf{t}}) Y_{L'}(\hat{\mathbf{t}}) Y_{L''}(\hat{\mathbf{t}}) d\Omega_{\mathbf{t}}$$

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.

We are interested in spherical harmonic expansions of the full Green function of the Schrödinger equation (2), for potentials with nontrivial higher multipole components, which will be expressed in terms of solutions of the coupled radial equations (6) with different boundary conditions. In general, it is known that a solution of the coupled radial equations may pose problems for certain classes of potentials. (See, for example, the exchange between Ziegler [13,14] and Newton [15].) Therefore, we will restrict our attention to spin-independent, real potentials which are no more singular than r^{-2} at the origin and which go to zero at infinity, typical of a large class of real, molecular systems.

Ziegler [14] points out that, to avoid problems in the solution of the coupled radial equations, the off-diagonal matrix elements of $w_{LL'}(r)$ in Eq. (6) should go to zero at the origin, and thus should not contain any contribution from $v_{0,0}(r)$, since this component will contain the Coulomb singularity if the potential is centered on an atomic nucleus, or, at best, tend to some nonzero value. That this will always be the case may be seen by considering the Gaunt coefficients and the summation over L'' in Eq. (7). In particular, in the definition of $w_{LL'}(r)$, $v_{0,0}(r)$ only appears multiplied by $I(L,L',(0,0))$, but because of spherical harmonic orthonormality, this is proportional to $\delta_{LL'}$. Thus $v_{0,0}(r)$ appears only on the diagonal of $w_{LL'}(r)$.

A. Derivation of the Green-function partial-wave expansion

We consider first an energy $E<0$ and seek the time-independent Green function $G(\mathbf{r},\mathbf{s})$ corresponding to this energy, which satisfies

$$\left[\nabla_{\mathbf{r}}{}^2 + E - V(\mathbf{r})\right]G(\mathbf{r},\mathbf{s}) = \delta^3(\mathbf{r}-\mathbf{s}), \tag{8}$$

together with the appropriate boundary conditions. We are interested in a solution of Eq. (8) in partial waves and approach the problem directly. Let us assume that G may be expanded in spherical harmonics as

$$G(\mathbf{r},\mathbf{s}) \equiv \sum_L \sum_{L'} g_{LL'}(r,s) Y_L(\hat{\mathbf{r}}) Y_{L'}(\hat{\mathbf{s}}), \tag{9}$$

for some as yet undetermined $g_{LL'}(r,s)$. We consider first, however, the expansion of G in partial waves in the variable $\mathbf{r}$ only, so that

$$G(\mathbf{r},\mathbf{s}) = \sum_L \Gamma_L(\mathbf{s};r) Y_L(\hat{\mathbf{r}}), \tag{10}$$

where

$$\Gamma_L(\mathbf{s};r) \equiv \sum_{L'} g_{LL'}(r,s) Y_{L'}(\hat{\mathbf{s}}). \tag{11}$$

If we now concentrate on operations with respect to $\mathbf{r}$, holding $\mathbf{s}$ constant for the moment, then we may use the spherical harmonic expansion (see, for example, Ref. [16], p. 32) for the δ function,

$$\delta^3(\mathbf{r}-\mathbf{s}) = \sum_L \sum_{L'} \frac{\delta(r-s)}{rs}\,\delta_{LL'}\,Y_L(\hat{\mathbf{r}})\,Y_{L'}(\hat{\mathbf{s}}),$$

together with definition (10) in Eq. (8) to obtain

$$\left\{\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)\right] - \frac{l(l+1)}{r^2} + E\right\}\Gamma_L(\mathbf{s};r) - \sum_{L'} w_{LL'}(r)\,\Gamma_{L'}(\mathbf{s};r) = \frac{\delta(r-s)}{rs}\,Y_L(\hat{\mathbf{s}}). \tag{12}$$

Because of the δ function on the right-hand side (rhs) of Eq. (12), we consider solutions of the homogeneous equation in the two regions, $r<s$ and $r>s$, separately. It has been shown elsewhere (see, for example, the discussion in Ref. [8]) that the most general solution $\phi_L(r)$ of the homogeneous version of the coupled radial equations (12) may be written

$$\phi_L(r) = \sum_{L'} C_{L'}\,R_{LL'}(r), \tag{13}$$

where the $R_{LL'}(r)$ constitute a set of linearly independent vector solutions indexed by L'. We can find a set of such solutions, $p_{LL'}(r)$, regular at the origin, which we use for the region $r<s$; and a set, $q_{LL'}(r)$, regular at infinity and which go to zero as $r\to\infty$ (since we are dealing with negative energies), which we use for the region $r>s$. Thus, by analogy with Eq. (13), we may write

$$\Gamma_L(\mathbf{s};r) = \sum_{L'}\left[C_{L'}(\mathbf{s})\,p_{LL'}(r)\,\theta(s-r) + D_{L'}(\mathbf{s})\,q_{LL'}(r)\,\theta(r-s)\right], \tag{14}$$

where C_L and D_L will now depend on $\mathbf{s}$, and we have used the Heaviside unit step function

$$\theta(x) \equiv \begin{cases} 0 & \text{if } x<0,\\ 1/2 & \text{if } x=0,\\ 1 & \text{if } x>0. \end{cases}$$

If we now assume that $C_L(\mathbf{s})$ and $D_L(\mathbf{s})$ may be expanded in spherical harmonics,

$$C_L(\mathbf{s}) \equiv \sum_{L'} c_{L'L}(s)\,Y_{L'}(\hat{\mathbf{s}}),$$

$$D_L(\mathbf{s}) \equiv \sum_{L'} d_{L'L}(s)\,Y_{L'}(\hat{\mathbf{s}}), \tag{15}$$

then we may use Eqs. (11) and (14) and the orthonormality of spherical harmonics to obtain

$$g_{LL'}(r,s) = \sum_{L''}\left[c_{L'L''}(s)\,p_{LL''}(r)\,\theta(s-r) + d_{L'L''}(s)\,q_{LL''}(r)\,\theta(r-s)\right], \tag{16}$$

which may also be written in an obvious matrix form as

$$\mathsf{g}(r,s) = \mathsf{p}(r)\mathsf{c}(s)^T\theta(s-r) + \mathsf{q}(r)\mathsf{d}(s)^T\theta(r-s), \tag{17}$$

where T indicates the matrix transpose.

Our task now is to find expressions for $\mathsf{c}(s)$ and $\mathsf{d}(s)$. This may be accomplished as follows: We substitute Eq. (16) into the coupled radial Schrödinger equations, and make use of the fact that the derivative of the Heaviside unit step function is, in the generalized function sense, the Dirac δ function, i.e.,

$$\theta'(x) = \delta(x).$$

Using the fact that $\mathsf{p}(r)$ and $\mathsf{q}(r)$ satisfy the homogeneous equations, and s is held constant, this leads to

$$\left\{-2\left[\mathsf{p}'(r) + \frac{1}{r}\mathsf{p}(r)\right]\mathsf{c}(s)^T\delta(s-r) + \mathsf{p}(r)\mathsf{c}(s)^T\delta'(s-r)\right\} + \left\{2\left[\mathsf{q}'(r) + \frac{1}{r}\mathsf{q}(r)\right]\mathsf{d}(s)^T\delta(r-s) + \mathsf{q}(r)\mathsf{d}(s)^T\delta'(r-s)\right\} = \frac{\delta(r-s)}{rs}\mathsf{I},$$

where I is the matrix identity with elements $\delta_{LL'}$.If we gather together terms in δ and δ', using the symmetry of the former and the antisymmetry of the latter, we obtain

$$\left\{2\left[\mathsf{p}'(r) + \frac{1}{r}\mathsf{p}(r)\right]\mathsf{c}(s)^T - 2\left[\mathsf{q}'(r) + \frac{1}{r}\mathsf{q}(r)\right]\mathsf{d}(s)^T + \frac{1}{rs}\mathsf{I}\right\}\delta(r-s) + \left\{\mathsf{p}(r)\mathsf{c}(s)^T - \mathsf{q}(r)\mathsf{d}(s)^T\right\}\delta'(r-s) = 0. \tag{18}$$

We may now use some basic properties of the δ function and its derivatives (see p. 29 of Ref. [17]) for general, sufficiently smooth $f(r)$ and constant s, i.e.,

$$f(r)\,\delta(r-s) = f(s)\,\delta(r-s)$$

and

$$f(r)\,\delta'(r-s) = -f'(s)\,\delta(r-s) + f(s)\,\delta'(r-s),$$

to remove r from Eq. (18), and obtain, after some cancellations,

$$\left\{\left[\mathsf{p}'(s) + \frac{2}{s}\mathsf{p}(s)\right]\mathsf{c}(s)^T - \left[\mathsf{q}'(s) + \frac{2}{s}\mathsf{q}(s)\right]\mathsf{d}(s)^T + \frac{1}{s^2}\mathsf{I}\right\}\delta(r-s) + \left\{\mathsf{p}(s)\mathsf{c}(s)^T - \mathsf{q}(s)\mathsf{d}(s)^T\right\}\delta'(r-s) = 0. \tag{19}$$

It is now possible to invoke a general result concerning finite linear combinations of the δ function and its derivatives (see p. 56 of Ref. [17]) to show that Eq. (19) implies that the coefficients of the δ function and its first derivative are both zero. Therefore, we have

$$\left[s^2\mathsf{q}'(s) + 2s\mathsf{q}(s)\right]\mathsf{d}(s)^T - \left[s^2\mathsf{p}'(s) + 2s\mathsf{p}(s)\right]\mathsf{c}(s)^T = \mathsf{I} \tag{20}$$

and

$$\mathsf{p}(s)\mathsf{c}(s)^T = \mathsf{q}(s)\mathsf{d}(s)^T. \tag{21}$$

We can add $2s$ times Eq. (21) to Eq. (20) to effect some further cancellations and obtain

$$s^2\left[\mathsf{q}'(s)\mathsf{d}(s)^T - \mathsf{p}'(s)\mathsf{c}(s)^T\right] = \mathsf{I}. \tag{22}$$

Finally, Eqs. (21) and (22) are simultaneous equations for $\mathsf{c}(s)^T$ and $\mathsf{d}(s)^T$ and may be expressed in supermatrix form as

$$\begin{pmatrix} \mathsf{p}(s) & -\mathsf{q}(s) \\ -\mathsf{p}'(s) & \mathsf{q}'(s) \end{pmatrix} \begin{pmatrix} \mathsf{c}(s)^T \\ \mathsf{d}(s)^T \end{pmatrix} = \frac{1}{s^2} \begin{pmatrix} 0 \\ \mathsf{I} \end{pmatrix}. \tag{23}$$

If we operate on this from the left with the supermatrix

$$\mathcal{S} \equiv \begin{pmatrix} \mathsf{q}'(s)^T & \mathsf{q}(s)^T \\ \mathsf{p}'(s)^T & \mathsf{p}(s)^T \end{pmatrix}, \tag{24}$$

then we obtain

$$\begin{pmatrix} [\mathsf{q}'(s)^T\mathsf{p}(s) - \mathsf{q}(s)^T\mathsf{p}'(s)] & -[\mathsf{q}'(s)^T\mathsf{q}(s) - \mathsf{q}(s)^T\mathsf{q}'(s)] \\ [\mathsf{p}'(s)^T\mathsf{p}(s) - \mathsf{p}(s)^T\mathsf{p}'(s)] & -[\mathsf{p}'(s)^T\mathsf{q}(s) - \mathsf{p}(s)^T\mathsf{q}'(s)] \end{pmatrix} \times \begin{pmatrix} \mathsf{c}(s)^T \\ \mathsf{d}(s)^T \end{pmatrix} = \frac{1}{s^2} \begin{pmatrix} \mathsf{q}(s)^T \\ \mathsf{p}(s)^T \end{pmatrix}. \tag{25}$$

To evaluate the matrix elements on the lhs of Eq. (25), we begin by using an argument from, for example, Appendix B of Ref. [9]. First, we define

$$u_{LL'}(r) \equiv w_{LL'}(r) + \frac{l(l+1)}{r^2}\delta_{LL'} - E\delta_{LL'}, \tag{26}$$

which is real and symmetric. Since p and q are solutions of the homogeneous coupled radial Schrödinger equations, then we have

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \mathsf{u}(r)\right]\mathsf{p}(r) = 0 \tag{27}$$

and

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \mathsf{u}(r)\right]\mathsf{q}(r) = 0. \tag{28}$$

If we now multiply Eq. (27) on the left by $\mathsf{q}(r)^T$, and Eq. (28) on the left by $\mathsf{p}(r)^T$, and subtract the latter from the transpose of the former, then, noting that $\mathsf{u}(r)$ is symmetric, we get

$$\begin{aligned} 0 &= \left[\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)\mathsf{p}(r)^T\right]\mathsf{q}(r) - \mathsf{p}(r)^T\left[\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)\mathsf{q}(r)\right] \\ &= \left(\frac{d}{dr} + \frac{2}{r}\right)[\mathsf{p}'(r)^T\mathsf{q}(r) - \mathsf{p}(r)^T\mathsf{q}'(r)], \end{aligned}$$

which may be easily rearranged to give

$$\frac{d}{dr}\{r^2[\mathsf{p}'(r)^T\mathsf{q}(r) - \mathsf{p}(r)^T\mathsf{q}'(r)]\} = 0,$$

which has the obvious solution

$$\mathsf{p}'(r)^T\mathsf{q}(r) - \mathsf{p}(r)^T\mathsf{q}'(r) = -\frac{1}{r^2}\mathsf{M}, \tag{29}$$

where M is a constant matrix (with elements $M_{LL'}$) and the minus sign has been introduced for later convenience. [Note that the lhs of Eq. (29) is in the form of a matrix Wronskian.]

In a similar way, we may show that

$$\mathsf{p}'(r)^T\mathsf{p}(r) - \mathsf{p}(r)^T\mathsf{p}'(r) = -\frac{1}{r^2}\mathsf{N} \tag{30}$$

for constant N. In the case of a spherically symmetric potential, both p and p' would be diagonal for all r, so that N would be zero. In our more general case, we may still show that $\mathsf{N}=0$ by an argument used in Ref. [10].

Let us define $\mathsf{y}(r) \equiv r\mathsf{p}(r)$, so that the homogeneous radial equations (27) become

$$\mathsf{y}''(r) - \mathsf{u}(r)\mathsf{y}(r) = 0. \tag{31}$$

From the definition of $\mathsf{y}(r)$, one may easily show that

$$\mathsf{y}(r)^T\mathsf{y}'(r) = r\mathsf{p}(r)^T\mathsf{p}(r) + r^2\mathsf{p}(r)^T\mathsf{p}'(r), \tag{32}$$

which implies that the symmetry of the matrix product $\mathsf{p}(r)^T\mathsf{p}'(r)$ is equivalent to that of the term $\mathsf{y}(r)^T\mathsf{y}'(r)$. If we now take the derivative of the latter, we have

$$\begin{aligned} \frac{d}{dr}[\mathsf{y}(r)^T\mathsf{y}'(r)] &= \mathsf{y}'(r)^T\mathsf{y}'(r) + \mathsf{y}(r)^T\mathsf{y}''(r) = \mathsf{y}'(r)^T\mathsf{y}'(r) \\ &\quad + \mathsf{y}(r)^T\mathsf{u}(r)\mathsf{y}(r), \end{aligned}$$

where we have used Eq. (31) in the last step to replace $\mathsf{y}''(r)$. Invoking again the symmetry of $\mathsf{u}(r)$, we see that the derivative of $\mathsf{y}(r)^T\mathsf{y}'(r)$ is symmetric for all r, and likewise all the higher derivatives. To show that $\mathsf{y}(r)^T\mathsf{y}'(r)$ itself is symmetric for all r, we must now show it to be symmetric for a particular value of r. Noting that $\mathsf{p}(r)$ is, by definition, the set of vector solutions regular at $r=0$, we see from Eq. (32) that by virtue of the factors r and r^2, the lhs is the zero matrix for $r=0$, which is trivially symmetric. So $\mathsf{y}(r)^T\mathsf{y}'(r)$ is symmetric for all r. So, from the definition of $\mathsf{y}(r)$, $\mathsf{p}(r)^T\mathsf{p}'(r)$ is symmetric for all $r>0$, and by appealing to the regularity of $\mathsf{p}(r)$ we may continue this to $r=0$. More explicitly, we have therefore

$$\mathsf{p}(r)^T\mathsf{p}'(r) = [\mathsf{p}(r)^T\mathsf{p}'(r)]^T = \mathsf{p}'(r)^T\mathsf{p}(r), \tag{33}$$

which, on referring to Eq. (30), shows that $\mathsf{N}=0$.

We may use a similar argument for $\mathsf{q}(r)$, defining now $\mathsf{y}(r) \equiv r\mathsf{q}(r)$, and showing again that the derivative of $\mathsf{y}(r)^T\mathsf{y}'(r)$ is symmetric for all r. In this case, however, when we come to show symmetry at a particular r, we must proceed differently, since $\mathsf{q}(r)$ may be singular at $r=0$. Instead, we must consider the behavior at large r, where our assumption that the potential is dominated by the monopole component means that we can choose $\mathsf{q}(r)$ and its derivative to be diagonal so that the combination $\mathsf{q}(r)^T\mathsf{q}'(r)$ is trivially symmetric and our desired result follows.

We note at this point that nothing has been assumed about the reality or otherwise of p or q. Since u is real, we may choose solutions p and q to be entirely real; for negative energies and bound states, this is the appropriate choice. For positive energies and a Green function relevant to scattering states, we must consider complex q. We shall return to this point later.

We may now return to Eq. (25) for our unknown functions and rewrite it in the light of the foregoing argument as

$$\begin{pmatrix} \mathsf{M}^T & 0 \\ 0 & \mathsf{M} \end{pmatrix} \begin{pmatrix} \mathsf{c}(s)^T \\ \mathsf{d}(s)^T \end{pmatrix} = \begin{pmatrix} \mathsf{q}(s)^T \\ \mathsf{p}(s)^T \end{pmatrix}. \tag{34}$$

If we assume the invertibility of M, then this leads straightforwardly to

$$\mathsf{c}(s)^T = (\mathsf{M}^T)^{-1}\mathsf{q}(s)^T \quad \text{and} \quad \mathsf{d}(s)^T = \mathsf{M}^{-1}\mathsf{p}(s)^T. \qquad (35)$$

Substitution of this into Eq. (17) [observing that $(\mathsf{M}^T)^{-1} = (\mathsf{M}^{-1})^T$] leads to our main result,

$$\mathsf{g}(r,s) = \mathsf{p}(r)(\mathsf{M}^{-1})^T\mathsf{q}(s)^T\theta(s-r) + \mathsf{q}(r)\mathsf{M}^{-1}\mathsf{p}(s)^T\theta(r-s). \qquad (36)$$

It is easy to see from this that we have the symmetry

$$\mathsf{g}(r,s) = \mathsf{g}(s,r)^T.$$

We may also back-substitute the results (35) into Eqs. (21) and (22) to obtain

$$\mathsf{p}(r)(\mathsf{M}^{-1})^T\mathsf{q}(r)^T = \mathsf{q}(r)\mathsf{M}^{-1}\mathsf{p}(r)^T,$$

showing that $\mathsf{g}(r,s)$ is continuous at $r=s$; and

$$\mathsf{q}'(r)\mathsf{M}^{-1}\mathsf{p}(r)^T - \mathsf{p}'(r)(\mathsf{M}^{-1})^T\mathsf{q}(r)^T = \frac{1}{r^2}\mathsf{I}.$$

B. Negative energies and bound states

For negative energies, there is always the possibility that the potential will support bound states. At such energies the Green function is, of course, singular, and it is useful to see how this comes about in our main expression (36). To work this out, we follow the argument of Gordon [18].

Consider, therefore, a bound state with wave function $\psi(\mathbf{r})$ expanded in spherical harmonics,

$$\psi(\mathbf{r}) = \sum_L \phi_L(r)Y_L(\hat{\mathbf{r}}),$$

where the $\phi_L(r)$ satisfy the coupled homogeneous radial Schrödinger equations and are regular at the origin and infinity. In particular, as in Eq. (13), there must exist coefficients P_L and Q_L such that both

$$\phi_L(r) = \sum_{L'} P_{L'}p_{LL'}(r)$$

and

$$\phi_L(r) = \sum_{L'} Q_{L'}q_{LL'}(r)$$

hold for all r. Therefore, since $p_{LL'}(r)$ and $q_{LL'}(r)$ satisfy the radial equations, these equations will be true for all r, if the expressions on the rhs and their first derivatives are equal for a particular r. Now denoting the infinite coefficient vectors with components P_L and Q_L by P and Q, respectively, we may write these two conditions in supermatrix form as

$$\begin{pmatrix} \mathsf{p}(r) & -\mathsf{q}(r) \\ -\mathsf{p}'(r) & \mathsf{q}'(r) \end{pmatrix}\begin{pmatrix} \mathsf{P} \\ \mathsf{Q} \end{pmatrix} = 0,$$

which has a nonzero vector solution if the matrix is singular. If, as before, we operate on this from the left with the super matrix $\mathcal{S}$ from Eq. (24), and use our results for the matrix Wronskians, then we obtain

$$\begin{pmatrix} \mathsf{M}^T & 0 \\ 0 & \mathsf{M} \end{pmatrix}\begin{pmatrix} \mathsf{P} \\ \mathsf{Q} \end{pmatrix} = 0,$$

from which one may see that the condition for a bound state is the singularity of the matrix M. If the state is degenerate, then the degeneracy may presumably be inferred from the dimension of the null space of M.

C. Positive energies and scattering

For energies greater than zero ($E>0$ and $k>0$ defined such that $E=k^2$), the boundary conditions at infinity are different. For a real potential, we now have two acceptable independent sets of real radial functions, regular at infinity, which we may arrange to be the real and imaginary parts of a complex-conjugate pair. As usual, these will correspond to outgoing and incoming wave boundary conditions and lead to the advanced and retarded Green functions, respectively. Thus we have $\mathsf{q}^{(+)}(r)$ and $\mathsf{q}^{(-)}(r)$ with

$$\mathsf{q}^{(-)}(r) = \mathsf{q}^{(+)}(r)^*.$$

We define therefore $q^{(+)}_{LL'}(r)$ as the solution which approaches asymptotically, as $r\to\infty$, the standard diagonal form

$$q^{(+)}_{\infty LL'}(r) \equiv -ih_l^+(kr)\delta_{LL'}. \qquad (37)$$

We note here that we may, without loss of generality, multiply each diagonal element of Eq. (37) by an arbitrary nonzero factor, since it is canceled by the presence of M^{-1} [which contains q by Eq. (29)] in the final result. On the other hand, if the potential $V(\mathbf{r})$ contains a nonzero Coulomb monopole component, then it is well known [19] that the radial solutions cannot be asymptotic to the form (37). In this case, the diagonal asymptotic form should be constructed from the appropriate Coulomb radial functions, the important point here being that one still has two sets of functions regular at infinity.

In any case one is again led to the result (36) except that the matrix M that results from Eq. (29) will now be, in general, complex and also different for the advanced and retarded Green functions, i.e., M_+ and M_-, respectively, with

$$\mathsf{M}_+ = \mathsf{M}_-^*.$$

It is interesting to check that $\mathsf{q}^{(\pm)}(r)$ have the required properties. Thus, let $\mathsf{q}(r)$ be one of them and construct a state

$$\psi(\mathbf{r}) \equiv \sum_{LL'} Q_{L'}q_{LL'}(r)Y_L(\hat{\mathbf{r}})$$

for some arbitrary coefficients Q_L. In our atomic units, the flux density is given by

$$\mathbf{j}(\mathbf{r}) \equiv (1/2i)[\psi(\mathbf{r})^*\nabla\psi(\mathbf{r}) - \nabla\psi(\mathbf{r})^*\psi(\mathbf{r})].$$

Let us consider the total radial particle flux associated with ψ at some radius r [integrating the radial component of $\mathbf{j}(\mathbf{r})$ over the spherical surface of constant r] to get

$$
\begin{aligned}
J_r &\equiv \frac{r^2}{2i}\int\left\{\left[\sum_{LL'} Q^*_{L'} q_{LL'}(r)^* Y_L(\hat{\mathbf{r}})\right]\left[\sum_{L_0L''} Q_{L''} q'_{L_0L''}(r) Y_{L_0}(\hat{\mathbf{r}})\right]\right.\\
&\qquad \left. - \text{c.c.}\right\} d\Omega\\
&= \frac{r^2}{2i}\sum_{L'L''}\{Q^*_{L'}Q_{L''}\left[\sum_L q_{LL'}(r)^* q'_{LL''}(r)\right]\\
&\qquad - Q_{L'}Q^*_{L''}\left[\sum_L q_{LL'}(r) q'_{LL''}(r)^*\right]\}\\
&= \frac{r^2}{2i}\sum_{L'L''} Q^*_{L'}Q_{L''}\left\{\sum_L \left[q_{LL'}(r)^* q'_{LL''}(r) - q_{LL''}(r) q'_{LL'}(r)^*\right]\right\}\\
&= \frac{r^2}{2i}\mathsf{Q}^\dagger\left[\mathsf{q}(r)^\dagger\mathsf{q}'(r) - \mathsf{q}'(r)^\dagger\mathsf{q}(r)\right]\mathsf{Q}, \qquad (38)
\end{aligned}
$$

where, in the penultimate step, we have swapped dummy indices in the second term. Now the Hermitian conjugate Wronskian in the last expression may be evaluated by first writing q explicitly in terms of its real and imaginary parts, $\mathsf{q} \equiv \mathsf{q}_R + i\mathsf{q}_I$, and then using our earlier results. Thus we find

$$\mathsf{q}(r)^\dagger\mathsf{q}'(r) - \mathsf{q}'(r)^\dagger\mathsf{q}(r) = i(\mathsf{K} + \mathsf{K}^T)/r^2,$$

where the constant matrix K is given by

$$\mathsf{q}'_R(r)^T\mathsf{q}_I(r) - \mathsf{q}_R(r)^T\mathsf{q}'_I(r) = -\frac{1}{r^2}\mathsf{K}.$$

[Note that K will always be a diagonal matrix, since q_R and q_I are diagonal at the same limit, by contrast with M of Eq. (29).] If we had chosen q to be $\mathsf{q}^{(+)}$, then K could be evaluated from the asymptotic limit, using the well-known formula [20] for spherical Bessel and Neumann functions,

$$j'_l(x)n_l(x) - j_l(x)n'_l(x) = -\frac{1}{x^2}.$$

This leads to

$$\mathsf{K} = \frac{1}{k}\mathsf{I},$$

and we then have

$$J_r^+ = \frac{1}{k}\mathsf{Q}^\dagger\mathsf{Q}, \qquad (39)$$

which is positive as expected for an outgoing wave. If we had used $\mathsf{q}^{(-)}$, then it may have been seen directly from the expression for the flux density (replacing ψ by its complex conjugate) that the resulting total flux would be exactly the negative of J_r^+.

It may be surprising to see k appearing as an inverse in Eq. (39) for the total flux, since one expects from the classical physics point of view that the particle flux is proportional to the particle velocity (momentum). To see, at least in an approximate way, why this is not a problem here, we must consider in more detail the nature of the product $\mathsf{Q}^\dagger\mathsf{Q}$. Let us therefore consider the probability density associated with ψ, averaged over the sphere at radius r. We find in a manner similar to the algebra leading to Eq. (38) that this average probability density $\langle\rho\rangle_r$ is given by

$$\langle\rho\rangle_r = (4\pi)^{-1}\mathsf{Q}^\dagger\left[\mathsf{q}^{(+)}(r)^\dagger\mathsf{q}^{(+)}(r)\right]\mathsf{Q}.$$

If we now consider the asymptotic form (37) of $\mathsf{q}^{(+)}$, together with the asymptotic form of the spherical Hankel function [19], i.e.,

$$h_l^+(x) \rightarrow \frac{1}{x}e^{i[x-(1/2)(l+1)\pi]} \quad \text{as } r \rightarrow \infty, \qquad (40)$$

then we find, for large enough r, that

$$\langle\rho\rangle_r \sim \frac{\mathsf{Q}^\dagger\mathsf{Q}}{4\pi(kr)^2}.$$

Noting that the average outward flux density at radius r may be seen from Eq. (39) to be

$$\langle\mathbf{j}\cdot\hat{\mathbf{r}}\rangle_r \equiv \frac{J_r^+}{4\pi r^2} = \frac{\mathsf{Q}^\dagger\mathsf{Q}}{(4\pi r^2)k},$$

we then have

$$\langle\mathbf{j}\cdot\hat{\mathbf{r}}\rangle_r \sim k\langle\rho\rangle_r,$$

which is more in accord with our intuition.

With reference now to the complete expressions for the Green function, one may readily check that the advanced and retarded versions show the usual symmetry (see [19], p. 305 ff) under complex conjugation [stemming from the reality of $V(\mathbf{r})$], i.e.,

$$G^+(\mathbf{r},\mathbf{s}) = G^-(\mathbf{s},\mathbf{r})^*. \qquad (41)$$

D. Free-electron case

Let us now check that the formulas we have developed reduce to the standard results for the case of the free electron. First, we have, for $E<0$ and $\kappa^2=-E$ with $\kappa>0$ (and noting that the zero potential is of course spherically symmetric), that a suitable set of vector solutions regular at the origin could be given by

$$p_{LL'}(r) = i_l(\kappa r)\,\delta_{LL'},$$

where i_l is the usual modified spherical Bessel function of order l. Similarly, a set regular at infinity and tending to zero at this limit could be

$$q_{LL'}(r) = k_l^+(\kappa r)\,\delta_{LL'},$$

where k_l^+ is the modified spherical Hankel function of the first kind of order l. With these solutions, the Wronskian constant matrix is given by

$$M_{LL'} = -(-1)^l(1/\kappa)\,\delta_{LL'},$$

whose inverse is obvious. Therefore, the free Green function for negative energies may now be readily evaluated from Eq. (36) to be

$$G_0(\mathbf{r},\mathbf{s}) = -\kappa\sum_L (-1)^l[i_l(\kappa r)k_l^+(\kappa s)\theta(s-r) + k_l^+(\kappa r)i_l(\kappa s)\theta(r-s)]Y_L(\hat{\mathbf{r}})Y_L(\hat{\mathbf{s}}), \qquad (42)$$

which may be expressed in the more familiar form

$$G_0(\mathbf{r},\mathbf{s}) = -\kappa\sum_L (-1)^l i_l(\kappa r_<)k_l^+(\kappa r_>)Y_L(\hat{\mathbf{r}})Y_L(\hat{\mathbf{s}}),$$

where $r_< \equiv \min\{r,s\}$ and $r_> \equiv \max\{r,s\}$. Similarly for the positive-energy advanced Green function (for $E>0$ and $k^2=E$ with $k>0$), we may choose

$$p_{LL'}(r) = j_l(kr)\delta_{LL'}$$

and

$$q_{LL'}^{(+)}(r) = -ih_l^+(kr)\delta_{LL'},$$

and we find that

$$(M_+)_{LL'} = (1/k)\delta_{LL'}.$$

Therefore, we obtain

$$G_0^+(\mathbf{r},\mathbf{s}) = -ik\sum_L [j_l(kr)h_l^+(ks)\theta(s-r) + h_l^+(kr)j_l(ks)\theta(r-s)]Y_L(\hat{\mathbf{r}})Y_L(\hat{\mathbf{s}}). \qquad (43)$$

III. DISCUSSION

It may be noted that the above derivation is effectively a direct adaptation of the standard textbook one to the case of noncentral potentials. Because of the higher multipole components in the potential, we have to deal with coupled radial equations and hence manipulate matrices. Unsurprisingly, the main obstacle to carrying through the derivation in the standard way is essentially an issue of matrix commutativity, which is then dealt with in the argument leading to the matrix Wronskians between sets of coupled radial solutions and the constant matrix M [in particular Eqs. (29), (33), and (34)]. This is the central novelty of our present approach.

The use of some basic δ-function properties, while perhaps slightly unfamiliar, serves to unify and make more compact the derivation. It also avoids the usual cumbersome manipulations required to match solutions of the homogeneous equations across $r=s$. Further justification may be found in the fact that the defining equation (8) of the Green function already obliges us to deal with δ functions. We note in passing that this approach is readily adaptable to the more compact derivation of Green functions of some other equations.

One should note that the matrices that we deal with in the derivation are, strictly speaking, infinite-dimensional, and we have neglected some of the finer mathematical issues of convergence, existence of inverses, etc., for the sake of clarity and to avoid somewhat deeper mathematical waters. Consequently, that such issues do not lead to problems must be counted among the assumptions underlying our present derivation. It is partly with this in mind that we consider only potentials of the form mentioned in the previous section (although the class of such potentials is large enough to include very many situations of practical interest).

In practical implementations these problems do not arise, since both the partial wave expansions of the potential and the wave function will be truncated at some maximum (but not necessarily equivalent) l value. Thus one has only to deal with finite matrices, and there has been considerable research into numerical methods for the solution of such coupled systems. (Reference [21], for example, has a useful comparison of various methods of this type.) Given that, in practical problems, the potential multipole expansion will most likely be specified in numerical form, it is envisaged that the principal utility of our main result will be to provide a computational means of generating the Green function in numerical form also. The computational burden for a particular problem will then consist mainly of finding the coupled radial solutions, p and q, starting their numerical integration at the origin and infinity, respectively, with the appropriate boundary conditions, and evaluating the matrix M from them at some suitable intermediate radius.

IV. CONCLUSIONS

In summary, we have derived the partial-wave expansions for the exact, time-independent Green functions, at positive and negative energies, for an arbitrary single-particle potential (within the limitations discussed above). The results may be written out in full as follows:

$$G(\mathbf{r},\mathbf{s}) = \mathsf{Y}(\hat{\mathbf{r}})^T\left[\mathsf{p}(r)(\mathsf{M}^{-1})^T\mathsf{q}(s)^T\theta(s-r) + \mathsf{q}(r)\mathsf{M}^{-1}\mathsf{p}(s)^T\theta(r-s)\right]\mathsf{Y}(\hat{\mathbf{s}}), \qquad (44)$$

where $\mathsf{Y}(\hat{\mathbf{r}})$ is a column vector with elements $Y_L(\hat{\mathbf{r}})$, p is a set of vector solutions to the radial Schrödinger equations regular at $r=0$, and q is a set regular at infinity, which tends to zero at that limit in the case of negative energies, or tends asymptotically to the diagonal form (37) (or its complex conjugate) for the advanced (or retarded) Green function in the case of positive energies. Although algebraically simple in form, it appears not to exist in the literature.

There are several directions in which our results might be generalized. Since only the basic properties of spherical harmonics are used, it would appear then possible to extend them to hyperspherical harmonic expansions, so that Green functions of several particles may be treated. Whether this is feasible will presumably depend on the form of the potential as a function of the coordinates, bearing in mind our earlier comments on this matter. This leads to another generalization worthy of investigation, namely the possibility of extending the results to a wider class of potential, including, for example, spin-dependent potentials or those not tending to zero at infinity.

It is worth noting finally that our main result is a single-center expansion in two variables. As we mentioned in the Introduction, the free Green function is used in typical multiple-scattering theories. Part of its mathematical utility (as distinct from its physical association with free-particle propagation between scattering events) is that both one- and two-center expansions (the latter also called "reexpansion theorems") are known explicitly (see, for example, the Appendix in Ref. [3]). It would be very useful from the point of view of multiple-scattering theory if the two-center form of our partial-wave Green-function expansions were also available. How such expansions might be used in a multiple-scattering scheme is the subject of work that the author hopes to present in the near future.

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