Determination of the scattering matrix by use of the Sturmian representation of the wave function

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(Received 14 October 1986)

We derive an expansion of the scattering matrix for any reasonable atomic potential $V(r)$ by using the Sturmian expansion of the Coulomb Green's function. We demonstrate the method for the case where $V(r)$ is a Coulomb potential plus a Yukawa potential.

The purpose of this paper is to describe a simple method for calculating, in a discrete basis set, the irregular solution $u_{kl}(r)$ to the radial Schrödinger equation for a long-range potential $V(r)$. From this solution we may calculate the scattering matrix for $V(r)$ on both the physical and unphysical sheets. While results were previously obtained[1] for potentials that decrease as $1/r^3$ and $1/r^4$ at large distances, to our knowledge we give the first demonstration that a convergent expansion of the scattering matrix can be obtained, using a discrete basis set, for potentials that are Coulombic at large distances. We do not invoke complex coordinate techniques,[2] nor do we require our basis functions (Sturmian functions) to be square integrable in the usual sense.

Using atomic units throughout, we assume that

$$V(r)=-\frac{Z}{r}+W(r)\ , \tag{1}$$

where $W(r)$ is a short-range potential, that is, $rW(r)$ vanishes for $r\sim\infty$. We also assume that $W(r)$ has a uniformly convergent expansion in powers of r:

$$W(r)=\sum_{m=-1}^{\infty} W_m r^m\ . \tag{2}$$

Note that any reasonable potential in atomic physics has the above form. The irregular function $u_{kl}(r)$ satisfies the radial Schrödinger equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}-\frac{Z}{r}+W(r)-E\right]u_{kl}(r)=0\ , \tag{3}$$

subject to the boundary conditions

$$u_{kl}(r)=NW_{i\gamma,l+1/2}(-2ikr)e^{i\delta_l(k)},\quad r\sim\infty \tag{4}$$

where $W_{a,b}(z)$ is the irregular Whittaker function and N is a normalization constant. Here $k=\sqrt{2E}$; we draw a branch cut along the positive real E axis and take the branch of k which is positive when E is on the upper edge of the cut. This defines the physical energy sheet. In Eq. (4) we introduced the quantity $\gamma=Z/k$, and the additional phase shift $\delta_l(k)$ due to the potential $W(r)$.

To determine the form of $u_{kl}(r)$ in the region near the origin, we expand in powers of r beginning with r^{-l}. We cannot expand beyond r^l owing to the presence of a logarithmic term. Thus for $r\sim 0$ we have $u_{kl}(r)\approx\psi_{kl}(r)$ where

$$\psi_{kl}(r)=e^{ikr}\sum_{n=-l}^{l} u_n r^n\ , \tag{5}$$

where the coefficients u_n are determined by substituting the above expansion into Eq. (3) and equating similar powers of r using Eq. (2). This yields the recurrence relation

$$\tfrac{1}{2}[l(l+1)-n(n+1)]u_{n+1}-(Z+ink)u_n+\sum_{m=-1}^{n+l-1} W_m u_{n-m-1}=0\ , \tag{6}$$

with $u_n=0$ if $|n|>l$. We start this recurrence relation by fixing the value of u_{-l}; the value we choose is linearly related to the boundary conditions, and so we may take $u_{-l}=1$ if we later adjust u_{-l} to satisfy Eq. (4).

We now convert Eq. (3) to the integral equation

$$u_{kl}(r)=W_{i\gamma,l+1/2}(-2ikr)+\int_0^\infty dr' g_{kl}(r,r')W(r')u_{kl}(r')\ , \tag{7}$$

where $g_{kl}(r,r')$ is the Coulomb radial Green's function appropriate to the boundary conditions satisfied by $u_{kl}(r)$. We have[3,4]

$$g_{kl}(r,r')=\sum_{n=l+1}^{\infty}\frac{S_{nl}^k(r)S_{nl}^k(r')}{Z+ink}\ , \tag{8}$$

where the Sturmian functions $S_{nl}^k(r)$ are defined as

$$S_{nl}^k(r)=A_{nl}(-ikr)^{l+1}\times e^{ikr}{}_1F_1(l+1-n,2l+2,-2ikr)\ , \tag{9a}$$

$$A_{nl}=\frac{2^{l+1}}{(2l+1)!}\left[\frac{(n+l)!}{(n-l-1)!}\right]^{1/2}\ , \tag{9b}$$

with the normalization

$$\int_0^\infty dr\, S_{n'l}^k(r)(1/r)S_{nl}^k(r)=\delta_{n'n}\ . \tag{9c}$$

Note that for E real and positive, the $S_{nl}^k(r)$ are undamped outgoing waves, and are not square integrable in the usual sense. If $E=|E|e^{i(\pi-2\phi)}$, where $-\pi/2\langle\phi\leq\pi/2$, the integral $\int_0^\infty dr' g_{kl}(r,r')f(r')$ has a convergent Sturmian expansion if[4,5] the function $f_\phi(r)=f(re^{i\phi})$ is such that $f_\phi(r)/r^l$ is bounded for $r\sim 0$ and the integral $\int_0^\infty r\,dr\,f_\phi^2(r)$ is finite. We must therefore subtract from $u_{kl}(r)$ the irregular part $\psi_{kl}(r)$, and so we introduce a new wave function

$$\bar{u}_{kl}(r)=u_{kl}(r)-\psi_{kl}(r)\ , \qquad (10)$$

which vanishes more rapidly than r^l for $r\sim 0$. It is convenient to decompose $W(r)\psi_{kl}(r)$ into irregular and regular parts, $A_{kl}(r)$ and $B_{kl}(r)$, respectively,

$$W(r)\psi_{kl}(r)=A_{kl}(r)+B_{kl}(r)\ , \qquad (11a)$$

$$A_{kl}(r)=e^{ikr}\sum_{m=-l-1}^{l-1}A_m r^m\ , \qquad (11b)$$

$$A_m=\sum_{n=-l}^{m+1}W_{m-n}u_n\ , \qquad (11c)$$

$$B_{kl}(r)=e^{ikr}\sum_{n=-l}^{l}u_n r^n\left[W(r)-\sum_{m=-1}^{l-n-1}W_m r^m\right]$$
$$=0(r^l)\ . \qquad (11d)$$

We showed previously[5] that

$$\int_0^\infty dr' g_{kl}(r,r')A_{kl}(r')=\alpha_{kl}W_{i\gamma,l+1/2}(-2ikr)+e^{ikr}\sum_{m=-l}^{l}f_m r^m\ , \qquad (12a)$$

where the f_m satisfy the recurrence relation

$$\tfrac{1}{2}[m(m+1)-l(l+1)]f_{m+1}+(Z+imk)f_m=A_{m-1}\ , \qquad (12b)$$

with $f_m=0$ if $|m|>l$. Putting $m=l$ in Eq. (12b) we immediately obtain

$$(Z+ilk)f_l=A_{l-1}\ , \qquad (12c)$$

and hence the f_m are uniquely defined by the A_m and are linearly related to u_{-l}. The coefficient α_{kl} is given as[5]

$$\alpha_{kl}=-f_{-l}/d_{-l}\ , \qquad (12d)$$

where the coefficients d_m are defined by Eq. (14) below. It follows from Eqs. (7), (10), (11a), and (12a) that

$$\bar{u}_{kl}(r)=(1+\alpha_{kl})W_{i\gamma,l+1/2}(-2ikr)+e^{ikr}\sum_{m=-l}^{l}f_m r^m-\psi_{kl}(r)+\int_0^\infty dr' g_{kl}(r,r')[B_{kl}(r')+W(r')\bar{u}_{kl}(r')]\ . \qquad (13)$$

Equation (13) is an integral equation for the regular part $\bar{u}_{kl}(r)$ of $u_{kl}(r)$. Since $e^{-ikr}\bar{u}_{kl}(r)$ vanishes more rapidly than r^l for $r\sim 0$, the terms in $r^n e^{ikr}$, $|n|\le l$, must cancel in the inhomogeneous part of this equation. We can, therefore, write the inhomogeneous part as

$$(1+\alpha_{kl})\left[W_{i\gamma,l+1/2}(-2ikr)-e^{ikr}\sum_{m=-l}^{l}d_m r^m\right]\ ,$$

where, with $(a)_m$ the Pochhammer symbol,

$$d_m=(-1)^{m+l}\frac{(-2ik)^m}{\Gamma(l+1-i\gamma)}\frac{(l-m)!}{(l+m)!}(-l-i\gamma)_{m+l}\ . \qquad (14)$$

However, the condition for this cancellation to occur fixes the appropriate value of u_{-l}. Considering the cancellation of the r^{-l} term, we should have $(1+\alpha_{kl})d_{-l}+f_{-l}-u_{-l}=0$. Since α_{kl} and f_{-l} are each proportional to u_{-l}, we require

$$u_{-l}=d_{-l}\ . \qquad (15)$$

To determine $\bar{u}_{kl}(r)$ we write

$$\bar{u}_{kl}(r)=\sum_{n=l+1}^{\infty}a_n S_{nl}^k(r)\ , \qquad (16)$$

and substitute this expansion into Eq. (13). Using Eq. (8) and the orthonormality relation expressed by Eq. (9c) we find that the a_n are given by the matrix equation

$$\sum_{n'}C_{nn'}a_{n'}=b_n\ , \qquad (17a)$$

where

$$b_n=\int_0^\infty dr(1/r)S_{nl}^k(r)\left[(1+\alpha_{kl})W_{i\gamma,l+1/2}(-2ikr)-(1+\alpha_{kl})e^{ikr}\sum_{m=-l}^{l}d_m r^m+(Z+ink)^{-1}rB_{kl}(r)\right]\ , \qquad (17b)$$

$$C_{nn'}=\delta_{nn'}-(Z+ink)^{-1}\int_0^\infty dr\, S_{n'l}^k(r)W(r)S_{n'l}^k(r)\ . \qquad (17c)$$

All of the above integrals can be expressed very simply in closed form. Note that while the coefficients a_n tend to zero as n increases, they do so slowly. The expansion of Eq. (16) is deficient in that it cannot incorporate the logarithmic branch-point singularity of $\bar{u}_{kl}(r)$ at the origin. Recall that $\bar{u}_{kl}(r)$ behaves as $r^{l+1}\ln(r)$ for $r\sim 0$. Moreover, $W(r)\bar{u}_{kl}(r)/r^l$ is not bounded at $r=0$ if $W_{-1}\ne 0$; it diverges as $W_{-1}\ln(r)$, and consequently the replacement of $g_{kl}(r,r')$ by its Sturmian expansion on the right of Eq. (13) is not completely justified. This difficulty would not occur if $V(r)$ were an analytic potential (that is, expandable in powers of r^2) for then $\bar{u}_{kl}(r)$ would not have a logarithmic singularity.

If we write $g_{kl}(r,r')$ as

$$g_{kl}(r,r')=-\frac{i}{k}\frac{\Gamma(l+1-i\gamma)}{(2l+1)!}M_{i\gamma,l+1/2}(-2ikr_<)\times W_{i\gamma,l+1/2}(-2ikr_>)\ , \qquad (18)$$

where $M_{a,b}(z)$ is the regular Whittaker function, it follows immediately from Eq. (7) that

$$u_{kl}(r)=(1+D_{kl})W_{i\gamma,l+1/2}(-2ikr),\quad r\sim\infty \qquad (19a)$$

$$D_{kl}=-\frac{i}{k}\frac{\Gamma(l+1-i\gamma)}{(2l+1)!}\times\int_0^\infty dr\, M_{i\gamma,l+1/2}(-2ikr)W(r)u_{kl}(r)\ . \qquad (19b)$$

Comparison of Eq. (17a) with Eq. (4) reveals that

$$Ne^{i\delta_l(k)}=1+D_{kl}\ . \qquad (20)$$

However, we do not know N, nor its phase, and so we cannot yet determine $\delta_l(k)$. Indeed, we cannot determine $\delta_l(k)$ from a consideration of the outgoing wave solution $u_{kl}(r)$ alone, since the phase shift is defined through the

TABLE I. Diagonal $[N,N]$ Padé approximates to the s-wave phase shift $\delta_0(k)$, with k in a.u.

N	$\delta_0(k)$ $k=0.50$	$k=1.0$
1	−0.552	1.12
2	−0.363	1.12
3	−0.437	−0.647
4	−1.54	−0.668
5	1.53	−0.824
6	1.27	0.195
7	1.44	1.40
8	1.35	1.41
9	1.35	1.33
10	1.34	1.33
11	1.35	1.36

TABLE II. Diagonal $[N,N]$ Padé approximates to the p-wave phase shift $\delta_1(k)$.

N	$\delta_1(k)$ $k=0.50$	$k=1.0$
1	−1.04	1.14
2	−0.682	−0.478
3	−0.325	−0.666
4	−0.396	−0.651
5	−0.379	−0.670
6	−0.636	−0.617
7	−0.574	−0.594
8	−0.573	−0.645
9	−0.557	−0.546
10	−0.557	−0.567
11	−0.566	−0.571

interference of ingoing and outgoing waves. We now introduce the regular standing wave $\phi_{kl}(r)$, which satisfies the boundary condition $\phi_{kl}(r)/\phi^c_{kl}(r)\rightarrow A$ as $r\rightarrow 0$, where A is any *real* number and ϕ^c_{kl} is the pure Coulomb standing wave. Hereafter we assume that k is real and positive. We may analytically continue to complex k; in particular, we can analytically continue onto the unphysical energy sheet, because all integrals can be reduced to analytic expressions. Since $u_{kl}(r)$ and $[u_{kl}(r)]^*$ are independent solutions of Eq. (3), we can write

$$\phi_{kl}(r)=pu_{kl}(r)+q[u_{kl}(r)]^* \ . \tag{21}$$

Now $\phi_{kl}(r)$ is regular at the origin and, therefore,

$$p\psi_{kl}(r)+q[\psi_{kl}(r)]^*=0 \ . \tag{22}$$

Considering just the r^{-l} term we have $pu_{-l}+qu^*_{-l}=0$. It follows that

$$\phi_{kl}(r)=p\{\bar{u}_{kl}(r)-\exp(2i\xi_{kl})[\bar{u}_{kl}(r)]^*\} \ , \tag{23}$$

where $\xi_{kl}=\arg(u_{-l})$. From Eqs. (14) and (15) we have $\xi_{kl}=l\pi/2-\eta_l(k)$ where $\eta_l(k)=\arg[\Gamma(l+1-i\gamma)]$ is the Coulomb phase shift. Since $\phi^c_{kl}(r)$ and $\phi_{kl}(r)$ both satisfy real boundary conditions, they are both real (for real k) and we have

$$\phi_{kl}(r)=B\sin[kr-\tfrac{1}{2}l\pi+\gamma\ln(2kr)+\eta_l(k)+\delta_l(k)] \ , \quad r\sim\infty \tag{24}$$

where B is a real amplitude. Now since $\phi_{kl}(r)$ is real we must have, up to an overall sign,

$$\phi_{kl}(r)=|p|[\bar{u}_{kl}(r)e^{i\eta_l(k)-i(l+1)\pi/2}+\text{c.c.}] \ , \tag{25}$$

where c.c. means complex conjugate. Inserting the asymptotic form of $u_{kl}(r)$ from Eq. (4) into Eq. (25), using Eq. (22), and the asymptotic form of the Whittaker function, we obtain Eq. (24) provided that the phase of N is unity. It follows that $\delta_l(k)=\arg(1+D_{kl})$.

To evaluate D_{kl} we insert the expansion of $u_{kl}(r)$ into the integrand on the right of Eq. (19b), and interchange sum and integral. The integrals are straightforward to evaluate. However, since the expansion of $u_{kl}(r)$ is not uniformly convergent, owing to the logarithmic singularity, the resulting sum may diverge. Nevertheless, because $F(r)=M_{i\gamma,l+1/2}(-2ikr)W(r)$ is an integrable function, the sum can be made to converge either by expanding $F(r)$ in terms of a finite number of damped outgoing waves[4] or by using Padé summation.[1] We chose the latter technique because it yields more rapid convergence, though it may be less economical since Eq. (17a) must be repeatedly solved to generate the Padé sequence.

We have tested our method for the potential $W(r)=\beta e^{-\lambda r}/r$, where $\beta=4.0$, $\lambda=2.0$, and $Z=2$. Results are shown in Tables I and II for the s- and p-wave phase shifts at two energies. Convergence to within a few percent is fairly rapid, though very high accuracy is difficult to achieve. We hope to present results of a more thorough investigation in the future, but we note for now that convergence is slow when $k\ll l+\frac{1}{2}$ (near threshold) or $k\ll Z$ (near the accumulation of bound states) or $k\gg\lambda$ [$F(r)$ highly oscillatory], though in the latter case the distorted-wave Born approximation can be used to compute $\delta_k(k)$.

Note that in the method of Johnson and Reinhardt,[1] Padé summation was used to convert an originally diverging series into a converging one. In the method of Rescigno and McCurdy,[1] Padé summation is not required. The latter authors diagonalize the Green's function, which has outgoing wave character, in a complex basis consisting of both outgoing and ingoing waves; in our method $g_{kl}(r,r')$ is expanded in terms of outgoing waves, while $\phi_{kl}(r)$ is a linear combination of ingoing and outgoing waves.

We thank Professor Tu-nan Chang for independently checking our results. This work was supported by the National Science Foundation, Grant No. PHY-8512495.

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[5]R. Shakeshaft, Phys. Rev. A **34**, 5119 (1986). Note that Eqs. (12) break down in the limit $Z \rightarrow 0$. In this limit $\alpha_{kl} \rightarrow \infty$ and the right side of Eq. (12a) must be replaced by a term in $kr \ln(kr) j_l(kr)$ plus an infinite power series in r, beginning with the term r^{-l}.