Distorted-wave reaction theory with long-range multipole potentials

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(Received 11 September 2000; published 13 February 2001)

A distorted-wave theory is developed in which the effect of long-range multipole potentials, having off-diagonal elements in channel space, is accounted for in the construction of asymptotic states. The theory may be applied to the scattering of an electron by a polarizable atomic system carrying a net positive charge and a permanent quadrupole moment. The current treatment is confined to such a system, though greater generality is possible. Asymptotic states are introduced in the form of a superposition of Coulomb wave functions with expansion coefficients determined by means of a modified perturbation theory. Analytic properties of the basis functions are preserved in this expansion and this allows, in the spirit of effective-range theory, for the determination of the energy dependence of the scattering matrix in the neighborhood of reaction thresholds. In particular, the Rydberg series of resonances that appears just below the energy for the opening of a new channel, well described by standard quantum-defect theory, is exhibited for the extended model scattering system considered here.

DOI: 10.1103/PhysRevA.63.032714 PACS number(s): 34.80.Kw, 03.65.Nk, 34.80.−i

I. INTRODUCTION

In one of the early versions of quantum-defect theory, Gailitis [1] considered the scattering of an electron by a hydrogenic ion at an energy near the threshold for target excitation. Owing to the angular momentum degeneracy of the excited levels, a long-range dipole interaction is present in the effective potential. Distorted incoming and outgoing waves that account for this additional inverse-square potential were constructed rather simply with the introduction of an appropriate shift in the orbital quantum number. The known analytic properties of such basis states were used in the formulation of a modified effective-range theory; this allowed, in particular, for the analytic continuation of the scattering matrix from an energy just above the excitation threshold to the resonance region just below the threshold. A generalization of this analysis is developed here, one that allows for the presence of a superposition of long-range multipole potentials forming a matrix in channel space. Asymptotic states are introduced in the form of a sum of Coulombic basis states with shifted orbital quantum numbers; this follows a method first presented by Cavagnero [2] and developed further in subsequent papers [3,4]. The method, based on a modified form of perturbation theory, differs from that used in standard quantum-defect theory [5,6] in that the basis functions are defined only in a region $r>r_0$, where the effective potential may be considered to have taken on its long-range power-law form. This procedure has certain limitations; the asymptotic solutions are obtained in an approximate form, showing slow convergence for the lowest partial waves in the presence of the Coulomb potential [7]. On the positive side, the perturbation approach serves a useful formal role in establishing the general structure and analyticity properties of the asymptotic solutions, thus providing the basis for an effective-range formulation. Since the treatment of a general class of multipole potentials within the context of the standard quantum-defect theory has presented some difficulties [8], the procedure outlined here should provide a useful alternative.

A description of the perturbation theory for the construction of the asymptotic states is taken up in Sec. II. Only the lowest two orders are examined in detail. This will suffice to illustrate those features of the method not encountered in earlier treatments in which the target was taken to be neutral [3] or charged but spherically symmetric [4]. A distorted-wave scattering formalism is developed in Sec. III. The pure Coulomb asymptotic waves may be thought of as being modified by a unitary wave operator that accounts for the effect of the inverse-cube and inverse fourth-power potentials present in the model scattering system. The unitarity property, not readily verified in finite orders of perturbation theory, is arrived at formally and used as the basis for establishing the symmetry of the reaction matrix and for setting up a variational principle for its approximate evaluation. In Sec. IV a representation of the scattering matrix is obtained, providing for an effective-range analysis in which the energy dependence of scattering parameters just above the reaction threshold and just below the resonance region are exhibited. For ease of reference, an Appendix is included summarizing properties of Coulomb solutions that are used in the text.

II. CONSTRUCTION OF ASYMPTOTIC STATES

The radial Schrödinger equation considered here takes the matrix form $L\Psi=0$, representing coupled equations with (in atomic units)

$$L_{ji}=-\frac{1}{2}\left[\frac{d^3}{dr^2}+k_j^2-\frac{l_j(l_j+1)}{r^2}+\frac{2Z}{r}\right]\delta_{ji}+V_{ji}. \quad (2.1)$$

where only a finite number of channels are accounted for. Our attention is focused on scattering energies near the highest reaction threshold, taken to correspond to two coupled degenerate channels labeled 1 and 2, with $k_1=k_2\equiv k$ and orbital quantum numbers l_1 and $l_2=l_1+2$. In the external region $r>r_0$ the non-Coulombic contribution to the effective potential takes the form $V=V^L$, with

$$V^L=-\frac{1}{2}\begin{pmatrix} r^{-4}\beta_4^{(1)^2} & r^{-3}\beta_3+r^{-4}\beta_4'^2 \\ r^{-3}\beta_3+r^{-4}\beta_4'^2 & r^{-4}\beta_4^{(2)^2}\end{pmatrix}. \quad (2.2)$$

We look for a pair of linearly independent 2×2 matrix solutions of the wave equation in the region $r>r_0$ in the form $C_i(\pi z/2)^{1/2}m_{ji}(z)$, with $z=kr$ and C_i a normalization factor to be determined, as described below. In terms of the operator

$$L(l_j)=z^2\frac{d^2}{dz^2}+z\frac{d}{dz}+z^2-2\eta z-(l_j+\tfrac{1}{2})^2, \quad (2.3)$$

with $\eta=-Z/k$, the equation to be solved is

$$L(l_j)m_{ji}(z)=-\left(\frac{\Delta_3}{z}+\frac{\Delta_4}{z^2}\right)m_{\bar{j}i}(z)-\frac{D_j}{z^2}m_{ji}(z). \quad (2.4)$$

We have defined the dimensionless parameters $\Delta_3=\beta_3 k$, $\Delta_4=(\beta_4' k)^2$, and $D_j=(\beta_4^{(j)}k)^2$, and we have let the symbol $\bar{j}$ take on the values 2 for $j=1$ and 1 for $j=2$. We seek an approximate solution of Eq. (2.4) in the form of an expansion

$$m_{ji}=\sum_{s=0}^{\infty} m_{ji}^{(s)}, \quad (2.5)$$

with Δ_3 treated as a parameter of first order and Δ_4 and D_j as quantities of second order. The successive approximation procedure employed here differs from the usual perturbation approach in that the addition of a new term to an existing sum is accompanied by an updating of terms previously introduced in a manner explained below. [Note that in the transformation to the form (2.3) the term containing the orbital quantum number has had its radial dependence removed, thus allowing for this term to play the role of an eigenvalue.]

Solutions of the unperturbed Coulomb wave equation with nonintegral orbital quantum numbers γ, behaving at great distances as outgoing or incoming traveling waves of unit amplitude, are well known [5,9]; we denote them here, in an abbreviated notation, as $O(\gamma)$ and $I(\gamma)$, respectively. The outgoing wave has the asymptotic form

$$O(\gamma)\sim \exp i[kr-\gamma\pi/2-\eta\ln 2kr+\sigma_\gamma], \quad (2.6)$$

with $\sigma_\gamma=\arg\Gamma(1+\gamma+i\eta)$ and $I_\gamma=O_\gamma^*$. Then $H(\gamma)\equiv(\pi z/2)^{-1/2}O(\gamma)$ satisfies $L(\gamma)H(\gamma)=0$. The lowest-order term in the expansion (2.5) is taken to be $m_{ji}^{(0)}=a_{ji}H(\gamma_{ji})$, where we have anticipated [3] the appearance of a solution with a shifted orbital quantum number $\gamma_{ji}=l_j-(2/\pi)\delta_i$, with the phase δ_i and the matrix a_{ji} to be determined [10]. From the relation

$$L(l_j)m_{ji}^{(0)}=[(\gamma_{ji}+\tfrac{1}{2})^2-(l_j+\tfrac{1}{2})^2]a_{ji}H(\gamma_{ji}), \quad (2.7)$$

we see that in lowest order $\delta_i=0$ and that a_{ji} may be taken to be δ_{ji}. The structure of the higher-order terms is determined by the recursion relations

$$\begin{aligned}\frac{1}{z}H(\gamma)&=\sum_{p=-1}^{1} d_p^{(1)}(\gamma)H(\gamma+p),\\ \frac{1}{z^2}H(\gamma)&=\sum_{p=-2}^{2} d_p^{(2)}(\gamma)H(\gamma+p);\end{aligned} \quad (2.8)$$

the coefficients appearing in these sums are listed in the Appendix. One sees that a general term $m_{ji}^{(s)}$ in the expansion (2.5) will take the form of a sum of functions $H(\gamma_{ji}+p)$ with coefficients $\alpha_{ji;p}^{(s)}$. These may be determined at any finite stage by inserting the form of the approximate solution into Eq. (2.4) and requiring that the coefficient of each function $H(\gamma_{ji}+p)$ must vanish. Setting the coefficient of $H(\gamma_{ji})$ equal to zero, we arrive at a relation of the form

$$[(\gamma_{ji}+\tfrac{1}{2})^2-(l_j+\tfrac{1}{2})^2]a_{ji}+\sum_{j'=1}^{2}\Gamma_{jj'}a_{j'i}=0, \quad j=1,2, \quad (2.9)$$

with the functions $\Gamma_{jj'}$, free of near singularities, determined from the solution obtained in lower orders. One then searches for values of the two phase parameters δ_1 and δ_2 allowing for a solution of Eq. (2.9) and providing values for the ratios a_{2i}/a_{1i}. The matrix a_{ji} is then fixed by imposing the normalization condition $a_{1i}^2+a_{2i}^2=1$. [The constant C_i introduced earlier, below Eq. (2.2), remains available to fix the overall normalization of the asymptotic solution.] Numerical methods are required in general to determine the phases, though approximate analytical procedures can be used if the phases are small compared to unity. Both approaches have been illustrated in earlier treatments of simpler models [3,4], providing solutions with smooth energy dependence near threshold, a property assumed to hold in the more general case studied here.

For the purpose of illustration we summarize results obtained in first and second orders. With second-order terms ignored, the differential equation takes the form

$$\begin{aligned}&[(\gamma_{ji}+\tfrac{1}{2})^2-(l_j+\tfrac{1}{2})^2]a_{ji}H(\gamma_{ji})+L(l_j)m_{ji}^{(1)}\\ &\quad=-\Delta_3 a_{\bar{j}i}\sum_{p=-1}^{1} d_p^{(1)}(\gamma_{\bar{j}i})H(\gamma_{\bar{j}i}+p).\end{aligned} \quad (2.10)$$

This suggests that we set $m_{ji}^{(1)}=\Sigma_{p=-1}^{1}\alpha_{ji;p}^{(1)}H(\gamma_{\bar{j}i}+p)$. Anticipating that the coefficients will have second-order corrections, we write $\alpha_{ji;p}^{(1)}\cong\alpha_{ji;p}^{(1,1)}+\alpha_{ji;p}^{(1,2)}$ and find from Eq. (2.10) that the first-order contribution is

$$\alpha_{ji;p}^{(1,1)}=a_{\bar{j}i}\Delta_3[(l_j+\tfrac{1}{2})^2-(\gamma_{\bar{j}i}+\tfrac{1}{2}+p)^2]^{-1}d_p^{(1)}(\gamma_{\bar{j}i}). \quad (2.11)$$

To this order, the Γ matrix vanishes, leaving the phases δ_1 and δ_2 and matrix a_{ji} unchanged from their lowest order values. At the next level of approximation we set $m_{ji}\cong m_{ji}^{(0)}+m_{ji}^{(1)}+m_{ji}^{(2)}$ and retain only terms of first and second order on the right-hand side of Eq. (2.4). By examining the coefficient of $a_{ji}H(\gamma_{ji})$ in the resultant equation, we find that in second order

$$\Gamma_{jj}=D_j d_0^{(2)}(\gamma_{ji})+\Delta_3^2\sum_{p=-1}^{1} d_p^{(1)}(\gamma_{ji}-p)[(l_j+\tfrac{1}{2})^2 - (\gamma_{ji}+\tfrac{1}{2}+p)^2]^{-1} d_p^{(1)}(\bar{\gamma}_{ji}), \tag{2.12}$$

and from the form of the coefficient of $a_{ji}H(\bar{\gamma}_{ji})$ we find that

$$\Gamma_{21}=\Delta_4 d_2^{(2)}(\gamma_{1i}), \quad \Gamma_{12}=\Delta_4 d_{-2}^{(2)}(\gamma_{2i}). \tag{2.13}$$

We now record the second-order contribution to $\alpha_{ji;p}^{(1)}$; to reduce notational complexity we specify that $j=2$ and write $\alpha_{2i;p}^{(1,2)}=[(l_2+\frac{1}{2})^2-(\gamma_{1i}+\frac{1}{2}+p)^2]^{-1}\beta_{2i;p}^{(1,2)}$. The relation $H(\gamma_{2i}-1)=H(\gamma_{1i}+1)$, which follows from $l_2=l_1+2$, is used to obtain

$$\beta_{2i;1}^{(1,2)}=\Delta_3[\alpha_{1i;0}^{(1,1)}d_{-1}^{(1)}(\gamma_{2i})+\alpha_{1i;-1}^{(1,1)}d_0^{(1)}(\gamma_{2i}-1)] + \Delta_4 a_{1i} d_1^{(2)}(\gamma_{1i})+D_2 a_{2i} d_{-1}^{(2)}(\gamma_{2i}). \tag{2.14a}$$

In addition, it is found that

$$\beta_{2i;0}^{(1,2)}=\Delta_3\alpha_{1i;-1}^{(1,1)}d_{-1}^{(1)}(\gamma_{2i})+\Delta_4 a_{1i} d_0^{(2)}(\gamma_{1i}), \tag{2.14b}$$

and $\beta_{2i;-1}^{(1,2)}=0$. Using these results we may identify the surviving terms to be canceled by suitable choice of $m_{2i}^{(2)}$. Accordingly, we set $j=2$ and $m_{2i}^{(2)}=\Sigma_p \alpha_{2i;p}^{(2)}H(\gamma_{2i}+p)$ with

$$\alpha_{2i;p}^{(2)}=[(l_2+\tfrac{1}{2})^2-(\gamma_{2i}+\tfrac{1}{2}+p)^2]^{-1}\beta_{2i;p}^{(2)}.$$

The nonvanishing contributions corresponding to $p=-4$, -2, 1, and 2 are determined as

$$\beta_{2i;2}^{(2)}=\Delta_3\alpha_{1i;1}^{(1,1)}d_1^{(1)}(\gamma_{2i}+1)+D_2 a_{2i} d_2^{(2)}(\gamma_{2i}), \tag{2.15a}$$

$$\beta_{2i;1}^{(2)}=\Delta_3\alpha_{1i;0}^{(1,1)}d_1^{(1)}(\gamma_{2i})+\Delta_3\alpha_{1i;1}^{(1,1)}d_0^{(1)}(\gamma_{2i}+1) + D_2 a_{2i} d_1^{(2)}(\gamma_{2i}), \tag{2.15b}$$

$$\beta_{2i;-2}^{(2)}=D_2 a_{2i} d_{-2}^{(2)}(\gamma_{2i}), \tag{2.15c}$$

$$\beta_{2i;-4}^{(2)}=\Delta_4 a_{1i} d_{-2}^{(2)}(\gamma_{1i}). \tag{2.15d}$$

Results for $j=1$ are found in a similar way. We remark that (as described in Ref. [3] for the special case of a neutral target) a systematic, graphical treatment of this procedure may be formulated; the introduction of partial summations of the perturbation series leads to level-shift corrections to the denominators that appear in the expansion coefficients.

III. DISTORTED-WAVE FORMALISM

The procedure described above may be used to construct asymptotic solutions of the Schrödinger equation in the form of outgoing or incoming waves, denoted, respectively, as $\bar{O}_{ji}$ and $\bar{I}_{ji}$. From these, standing-wave solutions are obtained in the form $\bar{F}_{ji}=(\bar{O}_{ji}-\bar{I}_{ji})/2i$ and $\bar{G}_{ji}=-(\bar{O}_{ji}+\bar{I}_{ji})/2$. In the limit $r\to\infty$, these functions behave as

$$\bar{F}_{ji}\sim c_{ji}\sin\theta_{ji}+d_{ji}\cos\theta_{ji}, \tag{3.1a}$$

$$\bar{G}_{ji}\sim -c_{ji}\cos\theta_{ji}+d_{ji}\sin\theta_{ji}, \tag{3.1b}$$

with $\theta_{ji}=kr-\eta\ln 2kr-\gamma_{ji}\pi/2+\sigma_{l_j}$. Actually, it is the phase $\theta_{ji}+\sigma_{\gamma_{ji}}-\sigma_{l_j}$ that first appears but for our later purposes we find it convenient, using the appropriate trigonometric identities, accompanied by a redefinition of the expansion coefficients by means of a simple linear transformation, to express the result in the equivalent form shown above.

A reaction matrix may be defined by expressing the standing-wave solution of the scattering problem in the region $r>r_0$, where the potential has taken on its long-range form, as

$$U_{ji}=(2/k)^{1/2}\left[\bar{F}_{ji}-\sum_{j'}\bar{G}_{jj'}K_{j'i}\right]. \tag{3.2}$$

(The sum runs over all channels; but with the assumption that only the two degenerate channels 1 and 2 experience the effect of the long-range potential for energies close to their threshold, we focus our attention on those.) We suppose that a trial function $U_{ji,t}$ has been formed, regular at the origin as is U_{ji}, and taking the form (3.2) for $r>r_0$ but with the exact reaction matrix replaced by a trial matrix $K_{ji,t}$. A variational identity for K_{ji} may be derived by consideration of the integral expression

$$R_{i'i}=\sum_{j,j'}\int_0^{r_0}[U_{j'i'}(L_{j'j}U_{ji,t})-(L_{jj'}U_{j'i'})U_{ji,t}]dr. \tag{3.3}$$

Since LU vanishes we have

$$R_{i'i}=\sum_{j,j'}\int_0^{r_0}[U_{j'i'}(L_{j'j}U_{ji,t})dr. \tag{3.4}$$

Alternatively, integration by parts and use of the boundary conditions lead to the relation

$$R_{i'i}=\tfrac{1}{2}\sum_j (U'_{ji'}U_{ji,t}-U_{ji'}U'_{ji,t})|_{r=r_0}, \tag{3.5}$$

with the prime on the wave function denoting differentiation with respect to r.

Wronskian relations satisfied by the asymptotic states are required for the evaluation of this surface term. Since closed analytic forms for these states are not available, we resort to a somewhat indirect argument. We introduce the notation

$$W[a,b]_{i'i}=\sum_j (a'_{ji'}b_{ji}-a_{ji'}b'_{ji}).$$

The fact that $W[\bar{F},\bar{F}]_{i'i}$ is independent of r for $r>r_0$ is verified directly by repeating the discussion leading from Eq. (3.3) to Eq. (3.5) but with the true and trial wave functions U and U_t each being replaced by $\bar{F}$ and the integration running from r_0 to r. Similarly, the Wronskians of $\bar{F}$ with $\bar{G}$ and $\bar{G}$

with itself are seen to be independent of r for $r>r_0$. Accordingly, they may each be evaluated in the limit $r\to\infty$ as will be done below.

To derive the expected relation $W[\overline{F},\overline{F}]_{i'i}=0$ we set $U_t=U$ and observe that the condition $R_{ii'}=0$ is equivalent to $W[U,U]_{i'i}|_{r=r_0}=0$. With U replaced by the form shown in Eq. (3.2) we obtain a sum of terms, each a multiple of one of the Wronskians, adding to zero. One term is $W[\overline{F},\overline{F}]_{i'i}$, the only one not involving a coefficient containing the reaction matrix K. Since this term is independent of K it cannot cancel against the remaining terms and therefore must vanish. When evaluated for large r with the aid of Eq. (3.1a) the relation

$$\sum_j \{(c_{ji'}c_{ji}+d_{ji'}d_{ji})\sin(\delta_i-\delta_{i'}) + (c_{ji'}d_{ji}-d_{ji'}c_{ji})\cos(\delta_i-\delta_{i'})\}=0 \quad (3.6)$$

is obtained. If this is to be satisfied in general, independently of the particular values of the polarization phases δ_i, the coefficient of the cosine function must vanish, that is,

$$\sum_j (c_{ji'}d_{ji}-d_{ji'}c_{ji})=0, \quad (3.7a)$$

and the coefficient of the sine function must vanish for $i'\neq i$. Its value for $i'=i$ may be adjusted, by suitable choice of the overall normalization constant (denoted as C_i in Sec. II), to give

$$\sum_j (c_{ji'}c_{ji}+d_{ji'}d_{ji})=\delta_{i'i}. \quad (3.7b)$$

It may now be verified with the aid of Eqs. (3.1b) and (3.7) that $W[\overline{G},\overline{G}]_{i'i}$ vanishes. In a similar way one finds that $W[\overline{G},\overline{F}]_{i'i}=k\delta_{i'i}$. With these results in hand, the relation $W[U,U]_{i'i}|_{r=r_0}=0$ is seen to reduce to the symmetry statement $K_{ii'}-K_{i'i}=0$. As a final step in this analysis we may combine Eqs. (3.4) and (3.5), along with the symmetry property just obtained, to arrive at the identity

$$K_{i'i}=K_{i'i,t}-\sum_{j,j'}\int_0^{r_0}U_{j'i'}L_{j'j}U_{ji,t}dr. \quad (3.8)$$

A variational approximation for the K matrix is obtained by replacing the exact solution on the right by a trial function.

A scattering matrix is introduced by writing the wave function in the region $r>r_0$, expressed in terms of distorted incoming and outgoing waves, as

$$\Psi_{ji}=\overline{I}_{ji}-\sum_{j'=1}^{2}\overline{O}_{jj'}S_{j'i}. \quad (3.9)$$

With the T matrix defined by the relation $S=1+2iT$, we have

$$(i/2)\Psi_{ji}=\overline{F}_{ji}+\sum_{j'}\overline{O}_{jj'}T_{j'i}, \quad r>r_0. \quad (3.10)$$

Comparison of the two forms (3.2) and (3.10) leads to the connection $T^{-1}=K^{-1}-i$ and from this, along with the symmetry of the K matrix, the unitarity property of T follows. Returning to Eq. (3.9), we may take the limit $r\to\infty$ and make use of Eqs. (3.1) to find that, with the superscript T denoting matrix transpose,

$$\Psi_{ji}\sim e^{-i\omega_j}B^{\dagger}{}_{ji}-e^{i\omega_j}(B^{\mathrm{T}}S)_{ji}. \quad (3.11)$$

Here we define $\omega_j=kr-\eta\ln 2kr-l_j\pi/2+\sigma_{l_j}$, and

$$(B^{\mathrm{T}})_{ji}=(c_{ji}+id_{ji})e^{i\delta_i}. \quad (3.12)$$

Using Eqs. (3.7) we verify that $c+id$ is a unitary matrix and hence $BB^{\dagger}=1$; assuming that B has an inverse we also have $B^{\dagger}B=1$. Then the wave function Ψ^0, defined in terms of undistorted incoming and outgoing waves, satisfies

$$\Psi^0_{ji}\sim e^{-i\omega_j}\delta_{ji}-e^{i\omega_j}S^0_{ji}, \quad r\to\infty, \quad (3.13)$$

with $\Psi^0=\Psi B$ and $S^0=B^TSB$. From the last relation and the unitarity properties of the matrices B and S it follows that S^0 is unitary.

IV. THRESHOLD BEHAVIOR

The identification of those scattering parameters with smooth energy dependence near a reaction threshold requires an analysis of the analytic properties of the asymptotic wave functions. For a purely Coulombic long-range potential this analysis is well known; a brief review, reproducing in a somewhat different manner some results obtained in Ref. [1], will be included here in preparation for generalizations to a wider class of multipole potentials.

Two Coulomb wave functions that are analytic in energy and sinusoidal at great distances have been identified [9]. They are denoted here as $J(\gamma)$ and $Q(\gamma)$, the first regular and the second irregular at the origin, each corresponding to nonintegral orbital quantum number γ. (In the absence of channel-changing asymptotic interactions each of these functions may be considered as an element of a diagonal matrix in channel space.) The outgoing-wave solution $O(\gamma)$ introduced earlier may be represented (the argument γ is suppressed temporarily) as the linear combination

$$O=(c_3+c_4G)J+c_4Q. \quad (4.1)$$

The functions c_3, c_4, and G are defined in the Appendix. One writes $J=AF$, where the diagonal elements of the matrix function F have the asymptotic behavior $F\sim\sin[kr-\gamma\pi/2-\eta\ln 2kr+\sigma_\gamma]$; the coefficient A is defined in the Appendix as is the matrix function $f=-(c_4A)^{-1}$.

In the region $r>r_0$ the effective potential is (as we have temporarily assumed) purely Coulombic and the wave function may be expressed in the matrix form $\Psi=F+OT$. By means of a straightforward transformation a renormalized wave function is arrived at, behaving for $r>r_0$ as

$$u = JM - Q. \tag{4.2}$$

The analyticity of the matrix M in the energy variable may be shown to follow from the analytic properties of the wave functions J and Q [1]. The matrices M and T are related by

$$T = f^{1/2}[M - (h + if)]^{-1} f^{1/2}, \tag{4.3}$$

where the functions h and f are the real and imaginary parts, respectively, of $-(c_4^{-1}c_3 + G)$. From the relation $T^{-1} = K^{-1} - i$ one finds that the real, symmetric matrices M and K are related by

$$M = f^{1/2}K^{-1}f^{1/2} + h, \tag{4.4}$$

a relation that may be taken as the basis for effective-range theory.

We now consider the extension of the preceding results to allow for distortion effects arising from the inclusion of the long-range potential V^L. Distorted versions, $\overline{O}$ and $\overline{I}$, of the purely Coulombic outgoing and incoming waves are obtained directly from the modified perturbation procedure described above in Sec. II along with the normalization prescription defined in Sec. III. In a somewhat schematic form, omitting channel subscripts, we have, for example, the expansion

$$\overline{O}(\gamma) = \sum_p a_p O(\gamma + p). \tag{4.5}$$

The standing wave $\overline{F} \equiv (\overline{O} - \overline{I})/2i$ is then defined as well and is constructed in the form

$$\overline{F}(\gamma) = \sum_p a_p F(\gamma + p). \tag{4.6}$$

We seek a distorted version of the function J that retains its analytic property. The simplest candidate is the form $\overline{J}(\gamma) = A(\gamma)\overline{F}(\gamma)$. The analyticity of this solution, rewritten as

$$\overline{J}(\gamma) = \sum_p a_p \frac{A(\gamma)}{A(\gamma + p)} J(\gamma + p), \tag{4.7}$$

may be examined in perturbation theory. The ratio $A(\gamma)/A(\gamma + p)$, evaluated in the Appendix, contains branch-point singularities on the negative k^2 axis but is analytic in the neighborhood of the threshold. The expansion coefficients a_p in Eq. (4.7) are formed from the coefficients $\alpha^{(s)}_{ji:p}$ generated in the perturbation procedure (so designed as to be free of singularities); these coefficients are analytic as well near $k^2 = 0$; this is seen explicitly in the first- and second-order calculations of Sec. II. Thus the perturbation series provides a function $\overline{J}(\gamma) = A(\gamma)\overline{F}(\gamma)$ with smooth energy dependence near the threshold. As shown in the Appendix, the irregular Coulomb solution $Q(\gamma)$, analytic in k^2, may be expressed as a linear combination of $J(\gamma)$ and $J(-\gamma - 1)$. It then follows that a distorted version $\overline{Q}(\gamma)$ that preserves this analytic property may be defined by replacing $J(\gamma)$ and $J(-\gamma - 1)$ by their distorted versions in Eq. (A6). The derivation of Eq. (4.3) may now be repeated, with wave functions J and Q in Eq. (4.2) being replaced by $\overline{J}$ and $\overline{Q}$, respectively, and with the matrices T and M now modified by the distorting potential.

The fact that the M matrix has no singularity below the threshold for channels 1 and 2 may be used to study the form of the T matrix, for scattering in channels that are open below threshold, at energies just below threshold. In the notation of Ref. [1], the initial and final states of these ''old'' channels are denoted as i and f, respectively, while the pair of channels 1 and 2 that open at the threshold are referred to as ''new,'' and are denoted collectively by the symbol t. We assume that close to the threshold the values M^a and M^b of the M matrix, evaluated just above and just below threshold, may be taken to be approximately equal. Then, defining $X^{-1} = f^{1/2}T^{-1}f^{1/2}$ and $\tau = h + if$, we have

$$M^b - \tau^b \cong M^a - \tau^b = (X^{-1})^a + \tau^a - \tau^b. \tag{4.8}$$

The matrix equation $X^b = X^a - X^a Y X^b$, with $Y \equiv \tau^a - \tau^b$, is derived from the preceding relations. The solution of this equation is simplified by the assumption that elements of the matrix Y corresponding to ''old'' channels are small enough to be neglected; only ''new'' channels contribute by virtue of the discontinuity of τ at threshold. The solution, reexpressed in terms of the T matrix, provides us with the representation

$$T^b_{fi} = T^a_{fi} - \sum_{t,t'} T^a_{ft}[(\hat{T} - Y^{-1})^{-1}]_{t,t'} T^a_{t'i}, \tag{4.9}$$

where $\hat{T}$ contains matrix elements of T^a connecting new channels only. We approximate τ^a by its near-threshold value i (obtained from the limiting behavior $f \to 1$ and $h \to 0$) and evaluate $\tau^b = -(c_4^{-1}c_3 + G)$ using Eqs. (A2) to determine the ratio $c_4^{-1}c_3$ and to verify that G vanishes as the energy approaches the threshold value from below. We then have $\tau^b = -\cot \pi(Z/\kappa - \gamma)$, where we have replaced k by $i\kappa$, with κ real. Then $Y = i + \cot \pi(Z/\kappa - \gamma)$ and Eq. (4.9) becomes, when written in terms of the matrix $S = 1 + 2iT$,

$$S^b_{fi} = S^a_{fi} - \sum_{t,t'} S^a_{ft} \left[\frac{1}{\hat{S} - \exp\{2\pi i(\gamma - Z/\kappa)\}} \right]_{tt'} S^a_{t'i}. \tag{4.10}$$

The rapid energy dependence of the scattering matrix just below threshold, corresponding to a Rydberg series of resonances, is described in this representation. The result is of the standard form [5], here modified by the renormalization of the orbital quantum number, and involving matrix elements for scattering in the presence of both the monopole and multipole long-range potentials.

V. SUMMARY

The analytic continuation of the S matrix below an excitation threshold, in the form shown in Eq. (4.10), represents an extension of a result obtained in Ref. [1] and in later developments of quantum-defect theory [5,6] as well, in that it allows a wider class of long-range potentials, including

those that are nondiagonal in channel space. A key element in the present analysis is the development, in Sec. II, of a modified perturbation procedure for determining the asymptotic states; exact analytic solutions are unavailable for potentials of this type. There are indications from earlier calculations [4] that the rate of convergence of this procedure may in many cases be unsatisfactory for the lowest partial waves; it may then be necessary to supplement the method with a more direct numerical approach. In any event the perturbation method provides guidance regarding the structure and analytic properties of the asymptotic solutions. An integral identity for the reaction matrix was derived in Sec. III—this was done formally, independent of any specific results of the perturbation calculation—that can be useful in developing variational approximations of the K matrix. Unitarity properties of the scattering matrix were established in the course of this discussion. The analysis of threshold behavior given in Sec. IV was based on the representation, in the distorted-wave version of Eq. (4.3), of the T matrix in terms of a matrix M that has a smooth energy dependence in the neighborhood of the threshold for the opening of one or more new channels. Such a representation may be used as the basis for a modified effective-range theory, starting with the replacement of the M matrix by the first two terms in an expansion in powers of the energy above (or below) a reaction threshold. While the representation (4.10) for the S matrix is restricted to the immediate neighborhood of the threshold, that energy range is of considerable interest since it includes the accumulation point of a Rydberg series of resonances.

As remarked in Ref. [2], alternative methods, based on asymptotic expansions, for solving close-coupled radial equations in the presence of long-range multipole potentials were proposed some time ago [11,12] and improved versions [13] are now widely used in accurate variational R-matrix calculations. The close relationship between those alternative methods and the modified perturbation theory introduced by Cavagnero was discussed briefly in Ref. [2]. Similar comments may be made in the context of the present extension of the modified perturbation theory. Specifically, the introduction of a modified orbital quantum number in Ref. [12] has its counterpart here, accompanied by a clear criterion for its choice, namely, the avoidance of spurious singularities. This modification has the effect of building into the asymptotic solution the phase shifts that accumulate in the long-range field. In more general terms, the distinctive feature of the method lies in the directness of its description of long-range effects in near-threshold reactions using a relatively simple and algebraically generated perturbation expansion. This should lead to benefits in numerical applications at energies near thresholds though no extensive computations based on this method have yet been performed.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation under Grant No. PHY-0070525.

APPENDIX

Here we record some of the properties of Coulomb wave functions that entered into the discussion in the text. The recursion relations shown in Eq. (2.8) involve the coefficients

$$d_1^{(1)}(\gamma)=\frac{[(\gamma+1)^2+\eta^2]^{1/2}}{(2\gamma+1)(\gamma+1)},\quad d_{-1}^{(1)}(\gamma)=d_1^{(1)}(-\gamma-1),$$

$$d_0^{(1)}(\gamma)=-\frac{\eta}{\gamma(\gamma+1)},$$

$$d_0^{(2)}(\gamma)=d_1^{(1)}(\gamma)d_{-1}^{(1)}(\gamma+1)+d_{-1}^{(1)}(\gamma)d_1^{(1)}(\gamma-1)+d_0^{(1)}(\gamma)^2,$$

$$d_1^{(2)}(\gamma)=d_1^{(1)}(\gamma)[d_0^{(1)}(\gamma+1)+d_0^{(1)}(\gamma)],$$

$$d_{-1}^{(2)}(\gamma)=d_{-1}^{(1)}(\gamma)[d_0^{(1)}(\gamma)+d_0^{(1)}(\gamma-1)],$$

$$d_2^{(2)}(\gamma)=d_1^{(1)}(\gamma)d_1^{(1)}(\gamma+1),$$

$$d_{-2}^{2}(\gamma)=d_{-1}^{(1)}(\gamma)d_{-1}^{(1)}(\gamma-1). \tag{A1}$$

The coefficients appearing in Eq. (4.1) are defined, with $n=-i\eta=iZ/k$, as

$$c_3(\gamma)=\exp[(\eta-i\gamma)\pi/2+i\sigma_\gamma]\Gamma(\gamma+1+n)n^{-(\gamma+1)}\times\cos\pi(-\gamma-1+n),$$

$$c_4(\gamma)=\exp[(\eta-i\gamma)\pi/2+i\sigma_\gamma]\Gamma(n-\gamma)n^{\gamma}\times\sin\pi(-\gamma-1+n). \tag{A2}$$

The analytic solution $Q(\gamma)$ in Eq. (4.1) is defined as

$$Q(\gamma)=N(\gamma)-G(\gamma)J(\gamma). \tag{A3}$$

where

$$N(\gamma)=\frac{\Gamma(\gamma+1+n)}{n^{(2\gamma+1)}\Gamma(n-\gamma)}\cot\pi(2\gamma+1)J(\gamma)-\frac{1}{\sin\pi(2\gamma+1)}J(-\gamma-1) \tag{A4}$$

and

$$G(\gamma)=\left[\frac{\Gamma(\gamma+1+n)}{n^{(2\gamma+1)}\Gamma(n-\gamma)}-\sum_{p=0}^{l}\frac{b_p(\gamma)}{n^{2p}}\right]\cot\pi(2\gamma+1). \tag{A5}$$

Here $b_p(\gamma)$ are polynomials in γ with $b_0(\gamma)=1$; the procedure for calculation of these parameters is given by Ham [9]. The integer l is the orbital quantum number of interest in the limit $V^L=0$. By combining Eqs. (A3)–(A5) we obtain the form, more convenient for our present purposes,

$$Q(\gamma)=\left[\sum_{p=0}^{l}\frac{b_p(\gamma)}{n^{2p}}\cot\pi(2\gamma+1)\right]J(\gamma)-\frac{1}{\sin\pi(2\gamma+1)}J(-\gamma-1). \quad \text{(A6)}$$

The function $A(\gamma)$, first appearing just below Eq. (4.1), is defined as

$$A(\gamma)=\frac{2|\eta|^{\gamma+1}e^{\eta\pi/2}}{|\Gamma(\gamma+1+n)|}. \quad \text{(A7)}$$

We note that the function $f=-(c_4A)^{-1}$ is evaluated as

$$f(\gamma)=(2\pi)^{-1}e^{-\eta\pi}|\Gamma(\gamma+1+i\eta)|^2|\eta^{-(2\gamma+1)}|, \quad \text{(A8)}$$

which may be identified as the imaginary part of $-(c_4^{-1}c_3+G)$, its real part being

$$h=-\mathrm{Re}\,G(\gamma)+fe^{2\pi\eta}\sin 2\pi\gamma. \quad \text{(A9)}$$

From Eq. (A7) we find that the ratio $A(\gamma)/A(\gamma+p)$, entering into the discussion in Sec. IV, is evaluated for $p>0$ as

$$A(\gamma)/A(\gamma+p)=[(\gamma+1+p-1)^2(k/Z)^2+1]^{1/2}\times[(\gamma+1+p-2)^2(k/Z)^2+1]^{1/2}\cdots\times[(\gamma+1)^2(k/Z)^2+1]^{1/2}, \quad \text{(A10)}$$

while for $p<0$

$$A(\gamma)/A(\gamma+p)=[\gamma^2(k/Z)^2+1]^{-1/2}[(\gamma-1)^2(k/Z)^2+1]^{-1/2}\cdots[(\gamma+1+p)^2(k/Z)^2+1]^{-1/2}. \quad \text{(A11)}$$

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