Electron scattering by nonspherically symmetric atoms: Zero-energy limit

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A modified perturbation theory, previously introduced for the construction of asymptotic states accounting for a general class of long-range angle-dependent multipole potentials is developed in further detail. The threshold behavior of these states is presented in explicit form and these results are used, with the aid of a modified effective-range formulation, to determine the threshold energy dependence of the multichannel transition matrix. Unitarity properties are established formally and verified in the low-energy limit. A variational procedure for determining the parameters appearing in the modified effective-range expansion is described. The same procedure accounts for the presence of zero-energy bound states leading to resonant behavior that alters the threshold energy dependence.

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I. INTRODUCTION

Interest in the threshold properties of transition amplitudes, starting with Wigner's early work in the context of nuclear reaction theory [1], and then extended in modified form to account for long-range atomic interactions [2], has persisted and intensified in parallel with experimental efforts involving collisions at the lowest energies [3]. Stimulated by these efforts, particular attention has been paid to systems with angle-dependent effective scattering potentials having long-range, inverse-cube and higher-order multipole components [4,5]. A much earlier study, of the amplitude for low-energy electron scattering by an atom with a permanent quadrupole moment [6], was based on a generalization of the asymptotic expansion approach of Levy and Keller [7]. In a later effective-range analysis of low-energy electron scattering by nonpolar molecules [8], the problem was formulated in terms of coupled radial equations and the threshold behavior of partial-wave amplitudes for such systems was studied. Methods, based on asymptotic expansions, for solving close-coupling radial equations in the presence of long-range multipole potentials, proposed some time ago [9,10], are widely used in accurate *R*-matrix calculations [11].

A novel approximation procedure for constructing sufficiently accurate asymptotic solutions for problems involving a superposition of power-law potentials was introduced by Cavagnero [12]. The method, a modified form of perturbation theory, is distinguished by the introduction of shifted orbital quantum numbers and, being algebraic, has the attractive feature that higher-order corrections, beyond the Born approximation, are obtained very easily. With this attractive feature as motivation, an extension of the method has been developed [13], in terms of a specific model based on two coupled partial waves, with orbital quantum numbers differing by two units and with the channels having identical threshold energies. Summation techniques based on the introduction of level shifts (in conjunction with the angular-momentum renormalization central to the method) allow, in principle, for inclusion of arbitrarily high orders of perturbation theory. Our purpose here is to extend the analysis of Ref. [13] in a number of ways. In Sec. II, after a review of the formalism, it is shown how a wider class of power-law potentials, as well as the coupling of more than two degenerate channels, may be accommodated. The asymptotic solutions are calculated to second order in the modified perturbation expansion and their zero-energy limits are displayed. Since the nonanalytic energy-dependent factors associated with the threshold anomaly can be factored out, solutions obtained this way provide the basis for a modified effective-range expansion. The scattering formalism is developed in Sec. III. This material completes and corrects a treatment covering similar ground in Sec. III of Ref. [13] and is meant to replace it [14]. The modified effective-range expansion is derived from a variational principle that provides the basis for determining the parameters appearing in the expansion. As shown in Sec. IV, the leading terms in the modified effective-range expansion describe the threshold behavior of the scattering amplitude that is associated directly with the long-range potentials of the model. The existence of a zero-energy bound state induces resonant behavior that modifies the energy dependence at threshold. For clarity of presentation a number of calculational details are placed in four appendixes.

II. DISTORTED WAVES

We consider a model scattering system generated by reduction of the Schrödinger equation to two coupled radial equations of the matrix form $L\psi=0$, where, in atomic units,

$$L_{ji}=-\frac{1}{2}\left[\frac{d^2}{dr^2}+k^2-l_i(l_i+1)/r^2\right]\delta_{ji}+V_{ji}, \quad i,j=1,2, \tag{2.1}$$

with $l_2=l_1+2$. The energy, the same for each channel, is $k^2/2$. In the region $r>r_0$ the real, symmetric potential matrix V takes on the power-law form

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

Formal extensions of the model can be made without difficulty, as demonstrated below.

Two linearly independent approximate solutions of the wave equation in the region $r>r_0$, denoted here as f_{ji} and g_{ji}, may be found in the form of a superposition of Bessel

functions of the first and second kind, respectively. Starting with the former, we define $z=kr$ and write

$$f_{ji}(z)=C_i(\pi z/2)^{1/2}m_{ji}(z), \tag{2.3}$$

where C_i is a normalization constant to be fixed later on. The wave equation then takes the form

$$\left[z^2\frac{d^2}{dz^2}+z\frac{d}{dz}+z^2-\left(l_j+\frac{1}{2}\right)^2\right]m_{ji}(z) = -\left(\frac{\Delta_3}{z}+\frac{\Delta_4}{z^2}\right)\sum_{j'}(1-\delta_{j'j})m_{j'i}(z)-\frac{D_j}{z^2}m_{ji}(z), \tag{2.4}$$

where we have introduced the dimensionless parameters $\Delta_3=\beta_3 k$, $\Delta_4=(\beta_4' k)^2$, and $D_j=(\beta_4^{(j)}k)^2$. We look for a solution generated by iteration based on a first approximation corresponding to a particular linear combination of degenerate states, labeled by the mode index $s=1$, 2, with amplitudes a_{1s} and a_{2s} to be determined, as shown below. The expansion is taken to be of the form

$$m_{ji}(z)=a_{is}J_{\eta_{is}+1/2}(z)\,\delta_{ji}+\sum_{p\neq 0}a_{is}\alpha_{ji}^{(p)}J_{\eta_{js}+p+1/2}(z), \tag{2.5}$$

where $\eta_{js}=l_j-(2/\pi)\delta_s$. The phase shift δ_s plays the role of an eigenvalue to be chosen in a manner that renders consistent the coupled equations satisfied by the 2×2 matrix a_{js}. [The combination of indices $\{i,s\}$ appearing in the first term in the expansion (2.5), with i denoting one of the target states in mode s, will serve to label an entrance or exit channel in the distorted-wave scattering formalism developed in Sec. III. Since the mode remains fixed in the discussion in this section, the index s is omitted in labeling mode-dependent quantities in Eq. (2.3) and elsewhere when the meaning is clear.]

The coefficients $\alpha_{ji}^{(p)}$ may be determined at any stage of the iteration procedure by inserting a truncated version of the expansion (2.5) into Eq. (2.4) and making use of the Bessel function properties

$$z^{-1}J_{\eta+1/2}(z)=(2\eta+1)^{-1}[J_{\eta+3/2}(z)+J_{\eta-1/2}(z)]$$

and

$$\left[z^2\frac{d^2}{dz^2}+z\frac{d}{dz}+z^2-\left(l_j+\frac{1}{2}\right)^2\right]J_{\eta+1/2}(z) =[(\eta+1/2)^2-(l_j+1/2)^2]J_{\eta+1/2}(z).$$

One then requires that the coefficient of each function $J_{\eta+p+1/2}$ must vanish. Setting the coefficient of $J_{\eta+1/2}$ equal to zero we arrive at coupled equations of the form

$$[(\eta_{js}+1/2)^2-(l_j+1/2)^2]a_{js}+\sum_{j'=1}^{2}\Gamma_{jj'}a_{j's}=0, \quad j=1,2. \tag{2.6}$$

The parameter Δ_3 will be treated as a quantity of first order with Δ_4 and D_j taken to be of second order. While a systematic (nonlinear) procedure is available for constructing solutions to arbitrarily high order [13], we confine the present treatment to second order (allowing us to ignore the dependence of the Γ matrix on the phase δ_s). To simplify notation we define an ''interaction''

$$v(j,p)=[2(\eta_{js}+p)+1]^{-1}, \tag{2.7}$$

and ''propagator''

$$g(j,p)=[(l_j+1/2)^2-(\eta_{js}+p+1/2)^2]^{-1}. \tag{2.8}$$

In applications of the modified perturbation theory, such as those summarized below, a diagrammatic representation of interactions and propagators, set up previously [13] and reviewed in Appendix B in the notation of Eqs. (2.7) and (2.8), is very helpful. Consider first an application to the matrix Γ. There is no contribution to Γ in first order. In second order we find

$$\Gamma_{21}=\Delta_4 v(1,0)v(1,1) \quad \Gamma_{12}=\Delta_4 v(2,0)v(2,-1), \tag{2.9a}$$

$$\Gamma_{11}=\Delta_3^2[v(1,0)g(2,-1)v(2,-1)+v(1,0)g(2,-3)v(2,-3)]+D_1[v(1,0)v(1,1)+v(1,0)v(1,-1)], \tag{2.9b}$$

$$\Gamma_{22}=\Delta_3^2[v(2,0)g(1,1)v(1,1)+v(2,0)g(1,3)v(2,3)]+D_2[v(2,0)v(2,1)+v(2,0)v(2,-1)]. \tag{2.9c}$$

The off-diagonal elements are seen to vanish for $\Delta_4=0$, i.e., in the absence of the off-diagonal inverse-fourth-power potential. This remains true in higher orders. In that case Eqs. (2.6) are uncoupled, the distinction between target and mode indices vanishes, and the formulation simplifies to some extent [15]. An attempt to construct the solution in the form (2.5) for $\Delta_4\neq 0$ without imposing the eigenvalue conditions shown in Eq. (2.6) fails due to the appearance of singularities. [It will be recognized that the prediagonalization procedure involved in the solution of Eq. (2.6), with Γ serving as an effective-potential matrix, bears some analogy to that encountered in standard degenerate perturbation theory.]

With the above approximation to the Γ matrix in hand, Eqs. (2.6) may be solved for the coefficients a_{js} after being made consistent by suitable choice of phases δ_1 and δ_2; results are given in Appendix A. The expansion coefficients in first order are determined to be

$$\alpha_{12}^{(3)}=\Delta_3 v(2,0)g(1,3), \quad \alpha_{12}^{(1)}=\Delta_3 v(2,0)g(1,1),$$

$$\alpha_{21}^{(-1)}=\Delta_3 v(1,0)g(2,-1), \quad \alpha_{21}^{(-3)}=\Delta_3 v(1,0)g(2,-3). \tag{2.10}$$

Coefficients obtained in second order are recorded in Appendix B. To all orders, the functions $\bar{f}_{ji}=k^{-(\eta_{is}+1)}f_{ji}$ and $\bar{g}_{ji}=k^{\eta_{is}}g_{ji}$ vary smoothly with energy and have well-defined zero-energy limits; the limiting values are listed, to second

order, in Appendix B. These results form the basis of our later discussion of the threshold behavior of the scattering matrix.

Extensions of these procedures to account for additional power-law potentials and coupling of more than two channels are straightforward. Thus we may assume that the long-range potential includes a diagonal inverse-sixth-power component that we write as $-\beta_6^{(j)4}/r^6$, $j=1, 2$, requiring the addition of a term $-(D_j'/z^4)m_{ji}$ to the right-hand side of Eq. (2.4), with $D_j'=(\beta_6^{(j)}k)^4$. Then Γ_{11}, for example, would contain the additional contribution

$$D_1'v(1,0)[v(1,1)v(1,2)v(1,1)+v(1,-1)v(1,-2)\times v(1,-1)],$$

generating, along with the corresponding addition to Γ_{22}, corrections of order k^4 to the phases δ_s. Inclusion of fourth-order contributions to Γ_{jj} arising from combinations of $1/r^3$ and $1/r^4$ would be required for consistency. Modifications of Γ_{12} and Γ_{21} enter only in sixth order.

The model may be extended to include more than two degenerate channels, as would be required by the coupling of partial waves generated by a $P_2(\cos\theta)$ angular dependence contained in the original effective potential [6]. In a three-channel approximation, with $l_3=l_2+2$, new types of couplings appear that involve all three channels. The leading contribution to m_{31}, for example, would be of second order, taking the form

$$a_{1s}\Delta_3 v(1,0)g(2,-1)\Delta_3' v(2,-1)g(3,-2)J_{\eta_{3s}-2+1/2}(z),$$

where we distinguish between parameters Δ_3 and Δ_3' corresponding to the (1, 2) and (2, 3) channel couplings, respectively. The leading contribution to Γ_{31} is only of fourth order.

With the asymptotic solutions determined to a certain order their behavior at great distances may be obtained by replacing the Bessel and Neumann functions by their large-argument limits. We represent the standing-wave solutions that are found in this way as

$$f_{ji}\sim c_{ji}\sin(kr-l_j\pi/2+\delta_s)+d_{ji}\cos(kr-l_j\pi/2+\delta_s), \tag{2.11a}$$

$$g_{ji}\sim -c_{ji}\cos(kr-l_j\pi/2+\delta_s)+d_{ji}\sin(kr-l_j\pi/2+\delta_s). \tag{2.11b}$$

It proves convenient to define the matrix

$$B^T=(c+id)e^{i\delta_s}, \tag{2.12}$$

where the superscript T denotes transpose. A proof that B is unitary (after a normalization condition is imposed) is given in Appendix C. The unitarity property implies the relations

$$cc^T+dd^T=1, \quad c^Tc+d^Td=1, \tag{2.13a}$$

$$c^Td=d^Tc, \quad dc^T=cd^T. \tag{2.13b}$$

Traveling-wave solutions are defined as $I=-g-if$ and $O=-g+if$ with asymptotic forms

$$I\sim\exp[-i(kr-l_j\pi/2)](B^\dagger)_{ji},$$

$$O\sim\exp[i(kr-l_j\pi/2)](B^T)_{ji}. \tag{2.14}$$

The first-order approximations for the expansion coefficients are determined as

$$c_{ji}=C_{is}a_{is}\delta_{ji}, \tag{2.15a}$$

$$d_{21}=C_{1s}a_{1s}\Delta_3 v(1,0)[g(2,-1)-g(2,-3)], \tag{2.15b}$$

$$d_{12}=C_{2s}a_{2s}\Delta_3 v(2,0)[g(1,3)-g(1,1)], \tag{2.15c}$$

with $d_{11}=d_{22}=0$. The normalization condition contained in Eq. (2.13a) requires that $c_{ji}=\delta_{ji}$ to first order and (since δ_s is of second order, as shown in Appendix A) we have the first-order approximation $d_{12}=d_{21}=\Delta_3[6l_2(l_2-1)]^{-1}$.

III. DISTORTED-WAVE SCATTERING FORMALISM

We set up a scattering formalism in terms of standing waves distorted by the long-range potential V^L. The reaction matrix accounting for scattering by the short-range component of the potential in the presence of V^L is denoted as $K_{js;iq}$, where j and i are final and initial target indices, respectively. Since the short-range interaction can cause transitions between modes, we must distinguish between final and initial mode indices, s and q, respectively. The scattering wave function in the region $r>r_0$ has the form

$$U_{js;iq}=f_{ji,s}\delta_{sq}-\sum_{i'} g_{ji',s}K_{i's;iq}, \tag{3.1}$$

where the functions f and g now carry the mode indices previously omitted. To simplify notation target and mode indices will often be combined in a single index, for example, as $\rho=\{i,q\}$ or $\sigma=\{j,s\}$, with $f_{ji,s}\delta_{sq}$ written as $f_{\sigma\rho}$. Then Eq. (3.1) will be understood to be equivalent to

$$U_{\sigma\rho}=f_{\sigma\rho}-\sum_{\rho'} g_{\sigma\rho'}K_{\rho'\rho}, \quad r>r_0, \tag{3.2}$$

where the sum runs over target and mode indices. The matrix notation $U=f-gK$ allows even further notational simplification. The solution in the region $r>r_0$ may, alternatively, be expressed in terms of traveling waves as $\Psi=I-OS$. From the relations $f=(O-I)/2i$ and $g=-(O+I)/2$ we find the correspondence $S=(1+iK)(1-iK)^{-1}$ and, with $S=1+2iT$, we have $T=K(1-iK)^{-1}$. Then, defining $\Psi^0=\Psi B$, we find, using the unitarity property of the matrix B, that at great distances the function Ψ^0 is expressed in terms of undistorted traveling waves as

$$\Psi^0_{js;iq}=\exp[-i(kr-l_j\pi/2)]\delta_{ji}\delta_{sq}-\exp[i(kr-l_j\pi/2)]S^0_{js;iq}, \tag{3.3}$$

with

$$S^0=B^TSB. \tag{3.4}$$

As shown below, K is both real and symmetric. It follows that S is unitary, a property passed on to S^0, since (as shown in Appendix C) B is a unitary matrix.

To begin the derivation of a variational identity for the K matrix we introduce a trial wave function U_t, regular at the origin and passing smoothly into the form $U_t = f - gK_t$ for $r \geqslant r_0$, with K_t a trial K matrix; we also introduce the notation $L_{js;iq} \equiv L_{ji}\delta_{sq}$. Now consider the expression

$$R_{\sigma\rho} = \sum_{\rho'} \sum_{\omega'} \int_0^{r_0} dr [U_{\rho'\sigma} L_{\rho'\sigma'} U_{\sigma'\rho,t} - (L_{\sigma'\rho'} U_{\rho'\sigma}) U_{\sigma'\rho,t}], \tag{3.5}$$

to be evaluated in two ways; equating the results gives the desired identity. First, since U satisfies the wave equation the second term in the integrand vanishes. Alternatively, integration by parts, using the boundary condition at the origin, results in the form

$$R_{\sigma\rho} = \frac{1}{2} \sum_{\rho'} \left[\left(\frac{d}{dr} U_{\rho'\sigma} \right) U_{\rho'\rho,t} - U_{\rho'\sigma} \left(\frac{d}{dr} U_{\rho'\rho,t} \right) \right]_{|r=r_0} \equiv W[U, U_t]_{\sigma\rho}. \tag{3.6}$$

As a first step in evaluating this Wronskian-like quantity using the boundary conditions at $r = r_0$ we set $U_t = U$ so that $R = 0$ and $W[U,U]_{\sigma\rho} = 0$. Inserting the form (3.2) in this last relation we isolate the terms independent of K and require that they vanish independently of the remaining terms. The expression obtained this way is $W[f,f]_{\sigma\rho} = 0$. In the next step we will show that $W[g,g]_{\sigma\rho}$ vanishes as well. To do this we first verify that $W[g,g]_{\sigma\rho}$, defined at $r = r_0$, is unchanged when evaluated for any $r > r_0$. To accomplish this we return to an expression similar to that in Eq. (3.5), but with U and U_t each replaced by g and with the integration running from r_0 to r. Since g satisfies the wave equation in this region, the integral vanishes and integration by parts leads to the stated result that $W[g,g]_{\sigma\rho}$ is independent of r for $r > r_0$. We may then evaluate this quantity by substituting the asymptotic form shown in Eq. (2.11b). Using the first of Eqs. (2.13b), the stated result, $W[g,g]_{\sigma\rho} = 0$, follows. [The same procedure provides an independent verification of the relation $W[f,f]_{\sigma\rho} = 0$.] A similar argument shows that $W[g,f]_{\sigma\rho}$, defined for $r = r_0$, may be evaluated for any $r > r_0$; in particular we may let $r \to \infty$ and do the calculation using the asymptotic forms shown in Eqs. (2.11). Then, with the aid of the second of Eqs. (2.13a), we find that

$$W[g,f]_{\sigma\rho} \equiv \frac{1}{2} \sum_{i'} \left[\left(\frac{d}{dr} g_{i'j,s} \right) f_{i'i,s} - g_{i'j,s} \left(\frac{d}{dr} f_{i'i,s} \right) \right]_{|r=r_0} = \frac{k}{2} \delta_{ji} \delta_{sq}. \tag{3.7}$$

With these results in hand the surface terms in Eq. (3.6) may be evaluated, yielding the relation $(2/k) W[U,U_t]_{\sigma\rho} = -K_{\rho\sigma} + K_{\sigma\rho,t}$. Now setting $U_t = U$ the symmetry condition $K_{\sigma\rho} = K_{\rho\sigma}$ is verified. Combining this result with Eqs. (3.5) and (3.6) we obtain the useful identity

$$K_{\sigma\rho} = K_{\sigma\rho,t} - \frac{2}{k} \sum_{\rho'} \sum_{\sigma'} \int_0^{r_0} dr\, U_{\rho'\sigma} L_{\rho'\sigma'} U_{\sigma'\rho,t}. \tag{3.8}$$

Replacement of the exact solution on the right-hand side by a trial function provides a variational expression for the reaction matrix (as elaborated on in Appendix D).

To prepare for an analysis of threshold behavior it is convenient to define a reduced wave function $\overline{U}_{js;iq} = U_{js;iq}/k^{\eta_{is}+1}$ and K matrix

$$\overline{K}_{js;iq} = k^{-(\eta_{js}+1/2)} K_{js;iq} k^{-(\eta_{iq}+1/2)}. \tag{3.9}$$

Then Eq. (3.8) implies that

$$\overline{K}_{\sigma\rho} = \overline{K}_{\sigma\rho,t} - 2 \sum_{\rho'} \sum_{\sigma'} \int_0^{r_0} dr\, \overline{U}_{\rho'\sigma} L_{\rho'\sigma'} \overline{U}_{\sigma'\rho,t}. \tag{3.10}$$

We now consider a trial function defined for *all* r as

$$\overline{U}_{\sigma\rho,t} = \phi_{\sigma\rho} - \sum_{\rho'} \xi_{\sigma\rho'} \overline{K}_{\rho'\rho,t}, \tag{3.11}$$

where the trial functions ϕ and ξ are regular at the origin and, as r approaches r_0 from below, merge continuously into the forms $\phi = \overline{f}$ and $\xi = \overline{g}$. (As previously defined, $\overline{f}_{ji} = k^{-(\eta_{is}+1)} f_{ji}$ and $\overline{g}_{ji} = k^{\eta_{is}} g_{ji}$ vary smoothly with energy near threshold, with well-defined zero-energy limits.) To arrive at a version of the variational approximation from which threshold properties may be deduced most readily we first introduce some simplifying notation. We define the matrix

$$X_{\sigma\rho} = \sum_{\rho'} \sum_{\sigma'} \int_0^{r_0} dr\, \xi_{\rho'\sigma} L_{\rho'\sigma'} \xi_{\sigma'\rho}, \tag{3.12}$$

the function $w_{\sigma\rho} = \Sigma_{\rho'} L_{\sigma\rho'} \phi_{\rho'\rho}$, and the scalar product

$$(a_\sigma, b_\rho) \equiv \sum_{\rho'} \int_0^{r_0} dr\, a_{\rho'\sigma} b_{\rho'\rho}. \tag{3.13}$$

As shown in Appendix D, a variational determination of the trial reaction matrix leads to a variational approximation $\overline{K}_v$ for the reduced $\overline{K}$ matrix of the form

$$\overline{K}_{\sigma\rho,v} = -2 \left\{ (\phi_\sigma, w_\rho) - \sum_{\rho'} \sum_{\sigma'} (w_\sigma, \xi_{\rho'}) \times (X^{-1})_{\rho',\sigma'} (\xi_{\sigma'}, w_\rho) \right\}. \tag{3.14}$$

It is readily verified that such an approximation satisfies the required symmetry property (thereby guaranteeing unitarity). The energy dependence near threshold may be determined from that of the trial functions, which are matched at the boundary to functions analytic in the neighborhood of zero energy. With boundary-condition constraints satisfied, any residual energy dependence of the trial functions may be

ignored following the standard effective-range approximation [16] that treats the scattering energy term in the wave equation as negligible compared to the potential energy term in the region $r<r_0$ of strong interaction. A trial function chosen in this manner introduces an error of order k^2, leading to an error in the variational approximation $\overline{K}_v$ of order k^4. Thus the first two terms in an expansion of $\overline{K}_v$ in powers of the energy will provide variational approximations for the coefficients, the scattering-length and effective-range matrices. In fact, the diagonal elements of the scattering-length matrix satisfy a minimum principle [17]. A zero-energy resonance corresponds to a divergence in the determinant of the scattering-length matrix. The variational principle for the scattering length, closely related to the Rayleigh-Ritz principle for bound states, allows for a direct connection between the resonance condition and the appearance of a zero-energy bound state.

IV. THRESHOLD BEHAVIOR

With the replacement $S=1+2iT$ in Eq. (3.4) we have $S^0=1+2iT^0$ with

$$T^0=T^L+B^TTB. \tag{4.1}$$

The first term, directly reflecting the presence of the long-range potential, is given by

$$T^L=\frac{(B^TB-1)}{2i}, \tag{4.2}$$

while T may be expressed in terms of the reduced K matrix as

$$T=k^{\eta+1/2}(\overline{K}^{-1}-ik^{2\eta+1})^{-1}k^{\eta+1/2}. \tag{4.3}$$

From the definition (2.12) of B we have

$$B^TB=(c+id)e^{i\delta_s}e^{i\delta_s}(c^T+id^T). \tag{4.4}$$

Combining this form with Eq. (4.2), and making use of the properties shown in Eqs. (2.13), we may put the expression for T^L in the form

$$T^L=(c+id)\left(\frac{e^{2i\delta_s}-1}{2i}\right)(c^T+id^T)+idd^T+cd^T. \tag{4.5}$$

This is exact, but written in a way that leads very directly to a simple approximation correct to second order, that is,

$$T^L\cong\delta_s+idd^T+cd^T. \tag{4.6}$$

Here we have recognized that the phase shift δ_s is of second order (as shown in Appendix A) so that the matrices $c+id$ and its transpose may each be replaced by unity. Then, with the last two terms on the right in Eq. (4.6) evaluated using the approximations given just below Eqs. (2.15), we have, with corrections of order k^3 ignored,

$$(T^L)_{ji}=\delta_s\delta_{ji}+\frac{\Delta_3}{6l_2(l_2-1)}(1-\delta_{ji})+\left(\frac{\Delta_3}{6l_2(l_2-1)}\right)^2\delta_{ji}. \tag{4.7}$$

We now consider the contribution from the second term in Eq. (4.1), using the expression in Eq. (4.3) for the T matrix. In its conventional form, the effective-range approximation is

$$\overline{K}^{-1}=-A^{-1}+\tfrac{1}{2}R_0k^2, \tag{4.8}$$

with the scattering length A and effective range R_0 appearing as constant matrices. Terms of order k^3 will be ignored in our approximation for T, in which case the k^2 term in Eq. (4.8) may be omitted and we need only consider scattering with $l_1=0$, $l_2=2$. Further, the Heitler equation for T reduces to the second iteration $T\cong K+iK^2$. Now from Eq. (3.9) along with the threshold behavior $-(2/\pi)\delta_s=\gamma_sk^2$, with γ_s a constant (see Appendix A), we have, to the order considered here,

$$K_{1s;1q}=-[k+(\gamma_s+\gamma_q)k^3\ln k]A, \tag{4.9}$$

where $A_{1s,1q}$ has been written as A for brevity [18]. We note, finally, that the matrix B appearing in Eq. (4.1) may be represented, to the required accuracy, as $B_{ji}\cong\delta_{ji}+i(\Delta_3/12)(1-\delta_{ji})$. The threshold behavior of the T^0 matrix obtained in this way may be represented as

$$T^0_{1s;1q}=\left[\delta_s+i\left(\frac{\Delta_3}{12}\right)^2\right]\delta_{sq}-[k+(\gamma_s+\gamma_q)k^3\ln k]A+ik^2A^2, \tag{4.10a}$$

$$T^0_{2s;1q}=T^0_{1q;2s}=\frac{\Delta_3}{12}[\delta_{sq}+i(-kA)], \tag{4.10b}$$

$$T^0_{2s;2q}=\left[\delta_s+i\left(\frac{\Delta_3^2}{12}\right)\right]\delta_{sq}. \tag{4.10c}$$

This form shows the required symmetry and correctly reproduces the threshold law obtained some time ago for the case of single-channel scattering with a pure $1/r^4$ long-range potential [2]. As a final check, we may verify that, to the order considered, unitarity is satisfied. One way to accomplish this is to introduce the real symmetric reaction matrix K^0 with elements

$$K^0_{1s;1q}=\delta_s\delta_{sq}-[k+(\gamma_s+\gamma_q)k^3\ln k]A, \tag{4.11a}$$

$$K^0_{2s;1q}=K^0_{1q;2s}=\frac{\Delta_3}{12}\delta_{sq}, \tag{4.11b}$$

$$K^0_{2s;2q}=\delta_s\delta_{sq}. \tag{4.11c}$$

With this choice of reaction matrix the Heitler equation in the form

$$T^0_{\sigma\rho}=K^0_{\sigma\rho}+i\sum_{\rho'}K^0_{\sigma\rho'}T^0_{\rho'\rho} \tag{4.12}$$

is satisfied and this guarantees that T^0 is unitary, to the order of approximation maintained here. For $l_1>0$ the second term on the right-hand side of Eq. (4.1) is of the order of k^3 or higher, in which case long-range effects, generating terms of the order of k and k^2 appearing in the expression for T^L in Eq. (4.5), are dominant. The Wigner threshold law [1] is inapplicable here.

The above discussion must be modified for resonant scattering. Considering the zero-energy limit in Eq. (4.3), for example, with $\det \bar{K}=\infty$, the T matrix, rather than vanishing, takes on its maximum value allowed by unitarity. In the variational approximation of Eq. (3.14), this corresponds to the condition $\det X=0$, signaling the entrance of a bound state at threshold.

V. SUMMARY

The threshold behavior of transition amplitudes for scattering interactions of short range has a universal character [1], largely independent of the form of the potentials. Interactions of long range, however, must be accounted for in the asymptotic solutions appearing in the scattering formalism in order to determine threshold behavior. With analytic solutions unavailable in general, a number of approximation techniques have been developed. Since application of standard perturbation theory can be cumbersome in going beyond lowest orders, alternative procedures can be useful. The modified perturbation theory of Ref. [12] has the attractive feature that the calculational procedure is algebraic in nature, is applicable to a variety of scattering systems, and is readily extended beyond the lowest orders with the aid of diagram summation methods [13]. The method has been adopted here to treat a coupled-channel problem representing the scattering of an electron from a neutral atom with a permanent quadrupole moment. The detailed form of the asymptotic solutions, including their zero-energy limits, have been worked out in second order for a simplified two-channel version of the system. Possible extensions of the model, allowing for additional long-range potentials as well as multichannel generalizations, were indicated. A scattering formalism was outlined, in which these asymptotic solutions are incorporated as constituents of trial functions in a variational construction that preserves the unitarity of the scattering matrix. The variational principle provides the basis for an effective-range approximation, differing from the standard form in that it contains terms reflecting the presence of the long-range potentials. A procedure for calculating such terms directly from a knowledge of the asymptotic solutions was provided, and was illustrated using the explicit form of the second-order solutions derived here.

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APPENDIX A: PREDIAGONALIZATION

An explicit solution of the coupled homogeneous Eqs. (2.6), correct to second order, is obtained by requiring the matrix of coefficients to have vanishing determinant. This corresponds to the condition $a\,\delta_s^2+b\,\delta_s+c=0$, with

$$a=\left(\frac{4}{\pi}\right)^2\left(l_1+\frac{1}{2}\right)\left(l_2+\frac{1}{2}\right), \tag{A1a}$$

$$b=-\frac{4}{\pi}\left[\left(l_1+\frac{1}{2}\right)\Gamma_{22}+\left(l_2+\frac{1}{2}\right)\Gamma_{11}\right]. \tag{A1b}$$

$$c=\Gamma_{11}\Gamma_{22}-\Gamma_{12}\Gamma_{21}. \tag{A1c}$$

and with the Γ_{ji} given in Eqs. (2.9). The solution shows the threshold behavior $\delta_s\sim k^2$ referred to in the text. In the limit $\Delta_4\to 0$ the two solutions are seen to correspond to the uncoupled relations

$$[l_j-(2/\pi)\,\delta_j+1/2]^2-(l_j+1/2)^2-\Gamma_{jj}=0,\quad j=1,2, \tag{A2}$$

with $a_{js}=0$, $j\neq s$. Following the convention stated in the text, the mode index s has been identified in Eq. (A2) with the channel index in the limit $\Delta_4\to 0$ considered here. The positive root of the quadratic equation for δ_s corresponds to $s=2$ and the negative root to $s=1$.

With the phases determined in this approximation the ratios $a_{2s}/a_{1s}\equiv r_s$ may be calculated and the coefficients fixed by the normalization condition $a_{1s}^2+a_{2s}^2=1$ and sign convention

$$a_{1s}=\frac{1}{\sqrt{1+r_s^2}},\quad a_{2s}=\frac{r_s}{\sqrt{1+r_s^2}}. \tag{A3}$$

We set $r_1=\tan\varepsilon_1$, $r_2=\cot\varepsilon_2$ and verify, using the properties $\delta_1+\delta_2=-b/a$, $\delta_1\delta_2=c/a$, that $r_1r_2=-1$, from which we conclude that $\varepsilon_1=-\varepsilon_2\equiv\varepsilon$. We then have the result

$$\begin{pmatrix}a_{11}\\ a_{21}\end{pmatrix}=\begin{pmatrix}\cos\varepsilon\\ -\sin\varepsilon\end{pmatrix},\quad \begin{pmatrix}a_{12}\\ a_{22}\end{pmatrix}=\begin{pmatrix}\sin\varepsilon\\ \cos\varepsilon\end{pmatrix}. \tag{A4}$$

The coefficients a_{is} are energy-independent in second order; an explicit evaluation gives

$$\Delta_4\cot 2\varepsilon=\frac{1}{\pi}\left(-\frac{b}{a}-\Gamma_{11}\right)(2l_2+1)(2l_2-1). \tag{A5}$$

APPENDIX B: ZERO-ENERGY LIMIT

The expansion coefficients appearing in Eq. (2.5) of the text are evaluated in second order and listed below using the notation introduced in Eqs. (2.7) and (2.8). As a first entry we have

$$\alpha_{21}^{(-2)}=\Delta_4 v(1,0)[v(1,1)+v(1,-1)]g(2,-2), \tag{B1}$$

with the first and second term represented by Figs. 1(a) and 1(b), respectively. These diagrams are quite helpful in keeping track of the contributions, as is their purely formal interpretation in the language of ''states'' and ''propagators.'' The first of these diagrams is interpreted as a sequence consisting of a transition from a ''state'' (1,0) to (1,1), then a transition

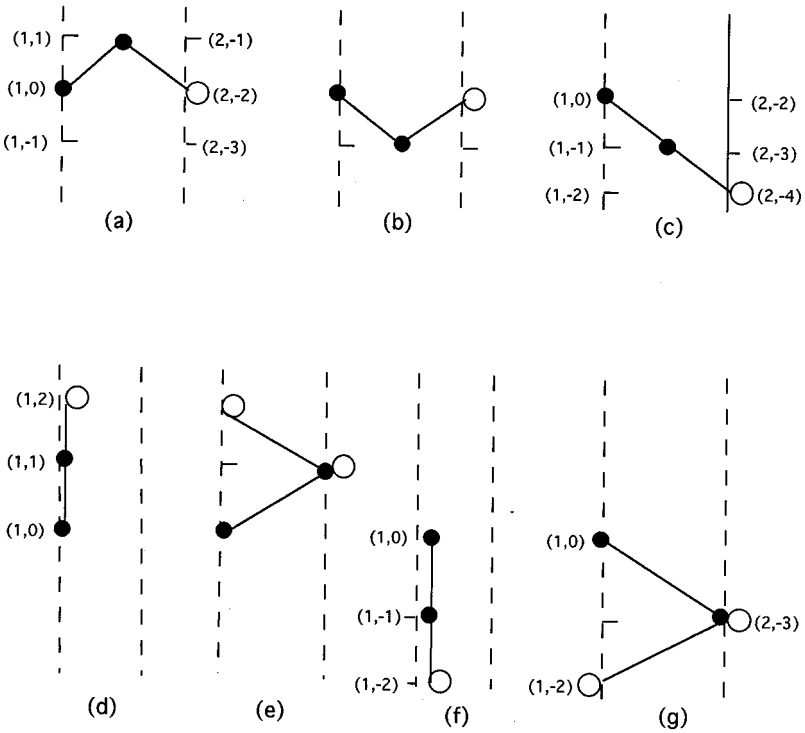

FIG. 1. The second-order expansion coefficients given in Eqs. (B1) through (B4) are represented by diagrams (a) through (g). Interactions and propagators may be read off from the positions of the filled and open circles in the diagrams using rules given in the text.

from (1,1) to (2,−2), followed by propagation in state (2, −2). An interaction leading to a transition from state (j, p) is represented by a filled circle in the diagram, while propagation in state (j, p) is represented by a larger open circle. In general, the sequence of transitions representing the coefficient $\alpha_{ji}^{(p)}$ begins with the reference state (i,0) and ends with propagation in state (j, p). Figure 1(c) corresponds to the expression

$$\alpha_{21}^{(-4)}=\Delta_4 v(1,0)v(1,-1)g(2,-4), \tag{B2}$$

while Figs. 1(d) and 1(e) correspond to the two terms in the expression

$$\alpha_{11}^{(2)}=D_1 v(1,0)v(1,1)g(1,2)+\Delta_3 v(1,0)g(2,-1)\times\Delta_3 v(2,-1)g(1,2). \tag{B3}$$

The diagrams in Figs. 1(f) and 1(g) correspond to the two terms in appearing in the coefficient

$$\alpha_{11}^{(-2)}=D_1 v(1,0)v(1,-1)g(1,-2)+\Delta_3 v(1,0)\times g(2,-3)\Delta_3 v(2,-3)g(1,-2). \tag{B4}$$

The remaining second-order coefficients are listed as follows:

$$\alpha_{12}^{(2)}=\Delta_4 v(2,0)[v(2,1)+v(2,-1)]g(1,2), \tag{B5}$$

$$\alpha_{12}^{(4)}=\Delta_4 v(2,0)v(2,1)g(1,4), \tag{B6}$$

$$\alpha_{22}^{(2)}=D_2 v(2,0)v(2,1)g(2,2)+\Delta_3 v(2,0)g(1,3)\Delta_3 v(1,3)g(2,2), \tag{B7}$$

$$\alpha_{22}^{(-2)}=D_2 v(2,0)v(2,-1)g(2,-2)+\Delta_3 v(2,0)g(1,1)\Delta_3 v(1,1)g(2,-2). \tag{B8}$$

With these results in hand the asymptotic solutions $\overline{f}_{ji}=k^{-(\eta_{is}+1)}f_{ji}$ and $\overline{g}_{ji}=k^{\eta_{is}}g_{ji}$ may be constructed in second order and their low-energy behavior determined by replacing the Bessel and Neumann functions, appearing in the expansions of these functions, by their small-argument approximations. Here we list the zero-energy limit of these functions. For notational convenience in this listing we write $\overline{f}_{ji}=C_{is}a_{is}[(2l_i+1)!!]^{-1}\bar{\bar{f}}_{ji}$ and $\overline{g}_{ji}=-C_{is}a_{is}(2l_i-1)!!\bar{\bar{g}}_{js}$ and continue to use the notation of Eq. (2.8) for the propagator with the understanding that for $k=0$, η_{js} reduces to l_j since the phase δ_s vanishes in that limit. We find that

$$\bar{\bar{f}}_{11}=r^{l_1+1}+[\beta_4^{(1)^2}g(1,-2)+\beta_3^2 g(2,-3)g(1,-2)]r^{l_1-1}, \tag{B9}$$

$$\bar{\bar{f}}_{21}=\beta_3 g(2,-3)r^{l_1}+\beta_4'^2 g(2,-4)r^{l_1-1}, \tag{B10}$$

$$\bar{\bar{f}}_{12}=\beta_3 g(1,1)r^{l_2}, \tag{B11}$$

$$\bar{\bar{f}}_{22}=r^{l_2+1}+[\beta_4^{(2)^2}g(2,-2)+\beta_3^2 g(1,1)g(2,-2)]r^{l_2-1}, \tag{B12}$$

$$\bar{\bar{g}}_{11}=r^{-l_1}+[\beta_4^{(1)^2}g(1,2)+\beta_3^2 g(2,-1)g(1,2)]r^{-(l_1+2)}, \tag{B13}$$

$$\bar{\bar{g}}_{21}=\beta_3 g(2,-1)r^{-(l_1+1)}, \tag{B14}$$

$$\bar{\bar{g}}_{12}=\beta_3 g(1,3)r^{-(l_2+1)}, \tag{B15}$$

$$\bar{g}_{22}=r^{-l_2}+[\beta_4^{(2)^2}g(2,2)+\beta_3^2 g(1,3)g(2,2)]r^{-(l_2+2)}. \tag{B16}$$

Extensions of this procedure provide higher-order terms in the asymptotic expansion in powers of r as well as corrections of order k^2 and higher.

APPENDIX C: UNITARITY

We prove here that the matrix B, whose transpose is given in Eq. (2.12), is unitary. The matrices c and d appear in Eqs. (2.11). These equations, providing the asymptotic forms of the basis functions f and g, may be expressed equivalently as

$$f_{ji}\sim \overline{c}_{ji}\sin(kr-l_j\pi/2)+\overline{d}_{ji}\cos(kr-l_j\pi/2), \tag{C1a}$$

$$g_{ji}\sim -\overline{c}_{ji}\cos(kr-l_j\pi/2)+\overline{d}_{ji}\sin(kr-l_j\pi/2), \tag{C1b}$$

obtained by expanding the trigonometric functions and redefining the coefficients according to

$$\overline{c}_{ji}=c_{ji}\cos\delta_s-d_{ji}\sin\delta_s, \tag{C2a}$$

$$\overline{d}_{ji}=c_{ji}\sin\delta_s+d_{ji}\cos\delta_s. \tag{C2b}$$

A new set of basis functions is obtained by defining $f^L=f\overline{c}^{-1}$ and $g^L=g\overline{c}^{-1}$. These functions are seen to have the asymptotic forms

$$f^L_{ji}\sim\sin(kr-l_j\pi/2)\,\delta_{ji}+\cos(kr-l_j\pi/2)K^L_{ji}, \tag{C3a}$$

$$g^L_{ji}\sim-\cos(kr-l_j\pi/2)\,\delta_{ji}+\sin(kr-l_j\pi/2)K^L_{ji}, \tag{C3b}$$

with $K^L=\overline{d}\overline{c}^{-1}$. The symmetry property of the matrix K^L, a key element in the unitarity proof, is verified using the Wronskian relation

$$\sum_{i'}\left[\frac{df^L_{i'j}}{dr}f^L_{i'i}-f^L_{i'j}\frac{df^L_{i'i}}{dr}\right]=0, \tag{C4}$$

satisfied for all $r>r_0$. The proof runs parallel to the derivation, given below Eq. (3.6), of an identical relation satisfied by the matrix function f. The argument is modified here by the replacement of f and g with the alternative sets f^L and g^L, respectively. The symmetry relation $K^L_{ji}=K^L_{ij}$ follows directly upon substitution of the asymptotic form (C3a) into Eq. (C4). We may conclude that an orthogonal matrix x exists such that $K^Lx=x\tan\delta^L$, with $\tan\delta^L$ diagonal.

We now observe that the relations $\overline{c}_{ji}=x_{ji}\cos\delta^L_i$ and $\overline{d}_{ji}=x_{ji}\sin\delta^L_i$ guarantee that the solutions $(f^Lx)_{ji}\cos\delta^L_i$ and f_{ji} have the same asymptotic forms and are therefore seen to be identical. The equality $(g^Lx)_{ji}\cos\delta^L_i=g_{ji}$ follows in a similar way. It then follows that

$$x_{ji}e^{i\delta^L_i}=\overline{c}_{ji}+i\overline{d}_{ji}=(c_{ji}+id_{ji})e^{i\delta_s}\equiv B^T_{ji} \tag{C5}$$

The unitarity of B follows directly from the fact that x is orthogonal and δ_s is real.

APPENDIX D: VARIATIONAL PRINCIPLE

As discussed in the text, the basis for the modified effective-range expansion is provided by the version of the variational principle shown in Eq. (3.14). Its derivation, starting with the identity (3.10), is sketched here. A trial function is chosen of the form shown in Eq. (3.11), and a variational approximation is obtained with the replacement of the exact solution by a trial function of the same form, but with $\overline{K}_t$, the trial reaction matrix, replaced by $\overline{K}_\tau$, with the two different matrices representing variational parameters. One of the terms encountered after these replacements has the form

$$\sum_{\rho'}\sum_{\sigma'}\sum_{\lambda}\int_0^{r_0}dr\;\phi_{\sigma'\sigma}L_{\sigma'\rho'}\xi_{\rho'\lambda}\overline{K}_{\lambda\rho,t}\equiv(\phi_\sigma,[L\xi\overline{K}_t]_\rho), \tag{D1}$$

where the abbreviated notation defined in Eq. (3.13) has been adopted to simplify the writing. With the aid of an integration-by-parts procedure of the type employed in the derivation of the variational identity we establish the relation

$$\overline{K}_{\sigma\rho,t}+2(\phi_\sigma,[L\xi\overline{K}_t]_\rho)=2([L\phi]_\sigma,[\xi\overline{K}_t]_\rho). \tag{D2}$$

Then, with the definition $w_{\sigma\rho}=\Sigma_{\rho'}L_{\sigma\rho'}\phi_{\rho'\rho}$, introduced in the text, the variational approximation takes the form

$$\begin{aligned}\overline{K}_{\sigma\rho,v}=-2\{&-([L\phi]_\sigma,[\xi\overline{K}_t]_\rho)+(\phi_\sigma,w_\rho)\\&-([\xi\overline{K}_\tau]_\sigma,[L\phi]_\rho)+([\xi\overline{K}_\tau]_\sigma,[L\xi\overline{K}_t]_\rho)\}.\end{aligned} \tag{D3}$$

The requirement that this expression be stationary with respect to variations in $\overline{K}_t$ leads to the condition

$$-(w_\sigma,\xi_\lambda)+([\xi\overline{K}_\tau]_\sigma,[L\xi]_\lambda)=0, \tag{D4}$$

which may be used to determine $\overline{K}_\tau$ as

$$\overline{K}_{\sigma\rho,\tau}=\sum_\lambda(w_\sigma,\xi_\lambda)(X^{-1})_{\lambda\rho}, \tag{D5}$$

where $X_{\sigma\rho}=(\xi_\sigma,[L\xi]_\rho)$, as in Eq. (3.12). With this form for $\overline{K}_\tau$ substituted into Eq. (D3) we observe that the first and last terms on the right-hand side of that equation cancel, leaving the form of the variational principle shown in Eq. (3.14).

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