Effect of long-range interactions on low-energy scattering parameters: Variational formulation

Leonard Rosenberg
Department of Physics, New York University, New York, New York 10003
(Received 6 December 1996)

A systematic treatment is presented of near-threshold electron-atom scattering based on a variational principle. Results obtained here extend the modified effective-range theory derived some time ago (in which long-range polarization forces are taken into account) by providing a prescription, based on a minimum principle, for calculating the effective-range parameters. With the aid of perturbation-theory methods introduced recently for obtaining asymptotic solutions of the wave equation for scattering by a superposition of long-range power-law potentials [see M. J. Cavagnero, Phys. Rev. A **50**, 2841 (1994)], higher-order corrections to the modified effective-range expansion in powers of the polarizability parameters are readily obtained. Explicit examples are provided. The theory is developed for both single-channel and multichannel scattering. [S1050-2947(97)06304-X]

PACS number(s): 34.80.Bm, 03.65.Nk, 34.10.+x

I. INTRODUCTION

The effect of a long-range polarization potential on the low-energy behavior of electron-atom scattering parameters was described some time ago in the context of a modified effective-range theory [1]. The original formulation, applicable to scattering by a $1/r^4$ potential, was expressed in terms of Mathieu functions. A multichannel extension of the theory was developed subsequently by Watanabe and Greene [2]. To simplify the analysis, freeing it from a dependence on special functions and allowing for application to a general class of power-law potentials, Hinckelmann and Spruch applied a distorted-wave perturbation theory, taken in lowest order in the strength of the polarization potential [3]. Recently, Cavagnero [4] has provided a convenient version of perturbation theory for the construction of asymptotic solutions for systems interacting with power-law potentials. Results are expressed in terms of relatively simple (Bessel) functions and the procedure for generating higher-order terms in the expansion in powers of the polarization parameters is fairly straightforward. With accurate analytic representations of the asymptotic solutions available, in an approximation that can be improved systematically, the task of constructing trial functions in a variational treatment of the low-energy scattering problem is simplified considerably. This observation is used here as the basis for the development of a variational approach to the low-energy scattering problem. Results of this work encompass earlier treatments of modified effective-range theory and allow for a variational determination of the effective-range parameters—for single-channel scattering these are the scattering length and effective range, appropriately redefined to account for the presence of the long-range polarization potential. The minimum principle for the scattering length [5] plays a useful role in providing a means to optimize the variational parameters appearing in the (positive-energy) trial function. An analogous treatment of multichannel scattering is given here in terms of a suitably defined reaction matrix. We recall that a variational derivation of ordinary effective-range theory (for short-range potentials) was given many years ago by Schwinger [6]. The derivation is constructive, providing a method for calculating the effective-range parameters. That approach, based on Green's functions, is more difficult to extend to allow for long-range interactions than is the Kohn version of the variational principle [7] adopted here.

The single-channel potential-scattering problem is discussed in Sec. II. As an illustration of the calculational procedure, explicit forms of the effective-range expansions for s-wave and p-wave scattering are provided that include corrections of second order in a $1/r^4$ component of the long-range potential and of first order in the $1/r^6$ component. The multichannel version of the theory is treated in Sec. III, for the case where the long-range potential is diagonal in channel space. Two appendixes are devoted to applications of the perturbation theory of Ref. [4] to cases that may be of use in the study of scattering by targets that are not spherically symmetric. Approximate asymptotic solutions for the $1/r^3$ potential are derived in Appendix A. In Appendix B an eigenphase shift extension of the method of Ref. [4] is applied to the problem of determining the asymptotic solutions for multichannel scattering, valid when the long-range potential is not diagonal. The procedure is illustrated in a first-order treatment of the $1/r^4$ potential.

II. SINGLE-CHANNEL SCATTERING

We consider the Schrödinger equation $(H-E)u=0$ in a given partial wave (the orbital angular momentum index l is suppressed), with a central potential $V(r)$ behaving as $-(\hbar^2/2m)\beta^2/r^4$ asymptotically [8]. Inclusion of additional components of the long-range potential will be discussed later on. The boundary conditions are $u(0)=0$ and, in the region where the potential has achieved its long-range form,

$$u(r)\sim\phi(r)+K\xi(r). \tag{2.1}$$

Here ϕ and ξ are linearly independent solutions of the wave equation accounting for the long-range potential. A successive approximation procedure for constructing these solutions has been described in Ref. [4] and will be briefly summarized below. As will be seen, the asymptotic forms of the solutions may be taken as

$$\phi \sim \sin(kr - l\pi/2 + \delta),$$

$$\xi \sim \cos(kr - l\pi/2 + \delta + \pi\gamma)/\cos(\pi\gamma), \tag{2.2}$$

where δ is the polarization phase, $\gamma = l - 2\delta/\pi$, and $E = (\hbar^2/2m)k^2$. The relation between the scattering parameter K and the physical phase shift η is obtained by comparing the asymptotic form (2.1) with

$$u \sim a[\sin(kr - l\pi/2) + \tan\eta \cos(kr - l\pi/2)]. \tag{2.3}$$

This leads to the relation

$$\tan\eta = \frac{\tan\delta + K/\cos 2\delta}{1 + K \tan\delta/\cos 2\delta}. \tag{2.4}$$

Following the method of Ref. [4] one transforms the equation

$$\left(\frac{d^2}{dr^2} + k^2 - \frac{l(l+1)}{r^2} + \frac{\beta^2}{r^4}\right)\phi(r) = 0 \tag{2.5}$$

by substituting $\phi = C(\pi z/2)^{1/2} M(z)$ and $z = kr$, with C a normalization constant. Then, with $\Delta = (\beta k)^2$, $M(z)$ is seen to satisfy

$$\left[z^2 \frac{d^2}{dz^2} + z \frac{d}{dz} + z^2 - \left(l + \frac{1}{2}\right)^2\right] M(z) = -\frac{\Delta}{z^2} M(z). \tag{2.6}$$

One seeks a series solution $M(z) = M^{(0)}(z) + \Delta M^{(1)}(z) + \Delta^2 M^{(2)}(z) + \cdots$, and writes

$$(l + 1/2)^2 = (\gamma + 1/2)^2 + \Delta\Gamma^{(1)} + \Delta^2\Gamma^{(2)} + \cdots. \tag{2.7}$$

In lowest order Eq. (2.6) gives $M_\gamma^{(0)}(z) = J_{\gamma+1/2}(z)$, and the equation for $M^{(1)}$ becomes

$$\left[z^2 \frac{d^2}{dz^2} + z \frac{d}{dz} + z^2 - \left(\gamma + \frac{1}{2}\right)^2\right] M_\gamma^{(1)}(z) = \left(\Gamma^{(1)} - \frac{1}{z^2}\right) M_\gamma^{(0)}(z). \tag{2.8}$$

With the aid of the Bessel-function recursion relation, the function $z^{-2} J_{\gamma+1/2}$, appearing on the right in Eq. (2.8), may be expressed as a sum of terms involving $J_{\gamma+1/2}$, $J_{\gamma+5/2}$, and $J_{\gamma-3/2}$. A key point in the method of Ref. [4] is the observation that the choice $\Gamma^{(1)} = [2(\gamma - 1/2)(\gamma + 3/2)]^{-1}$ eliminates the term $J_{\gamma+1/2}$, thus avoiding a spurious singularity and allowing one to solve for $M_\gamma^{(1)}$ by inspection, as shown in Eq. (12) of Ref. [4]. The parameter γ is thereby determined implicitly, to first order in Δ, by Eq. (2.7), above. To the same order, the polarization phase is found to be

$$\delta = \frac{\pi(\beta k)^2}{(2l+1)(2l+3)(2l-1)}. \tag{2.9}$$

A similar procedure may be followed, with the replacement $\gamma \to -\gamma - 1$, to determine the function $\xi(r)$; in lowest order we have $M_{-\gamma-1}^{(0)}(z) = J_{-\gamma-1/2}(z)$. An essential point to recognize here is that the solution may be carried out in a straightforward way to higher orders, leading to a convergent expansion [4], and r^{-6} and higher-order terms may be included in the long-range interaction—no special functions, such as Mathieu functions, need be introduced. Equally important is the recognition that the Bessel functions, in terms of which the solutions are expressed, have simple analytic properties. As will be demonstrated below, this allows for the identification of the nature of the threshold singularity which, once isolated, leaves a scattering parameter that has a smooth energy dependence.

To study the near-threshold behavior it is convenient to define the functions $\phi(r) = (\beta k)^{-(\gamma+1)}\phi(r)$ and $\xi(r) = (\beta k)^{\gamma}\xi(r)$. As seen from the form of the series solutions discussed above, these renormalized functions may each be represented as a convergent power series in k^2. It follows from Eq. (2.1), along with the definition $K(k) = (\beta k)^{-(2\gamma+1)} K(k)$, that $\overline{u(r)} = (\beta k)^{-(\gamma+1)} u(r)$ has the asymptotic form

$$\overline{u(r)} \sim \overline{\phi(r)} + \overline{K\xi(r)}. \tag{2.10}$$

We now introduce a trial function $\overline{u_t(r)}$ which vanishes at the origin and has the asymptotic form (2.10) with K replaced by K_t. Following a standard procedure, one readily obtains an identity which is a generalization of one introduced by Kato [9] for scattering by short range potentials. To simplify notation we write $L = -(2m/\hbar^2)(H - E)$ and denote the scalar product as $\int_0^\infty \underline{f(r)}\underline{g(r)}dr \equiv (\underline{f},\underline{g})$. The identity is derived by evaluating $(u, Lu_t) - (\underline{u_t}, Lu)$ in two ways, first by applying the wave equation $Lu = 0$ and then by integrating by parts and evaluating surface terms with the aid of the boundary conditions. In this way one finds that

$$\overline{K} = \overline{K_t} + \beta(\overline{u}, L\overline{u_t}). \tag{2.11}$$

A version of the Kohn variational principle is obtained with the replacement of $\overline{u(r)}$ by $\overline{u_t(r)}$ in Eq. (2.11); that is, it leads to an approximation K_v with an error of second order in $\overline{u} - \overline{u_t}$. While greater flexibility is possible, let us consider, for definiteness, a trial function that for all values of r has the specific form

$$\overline{u_t(r)} = y_s(r) + \overline{K_t} y_c(r), \tag{2.12}$$

with $y_s(r) = \overline{\phi(r)}$ and $y_c(r) = \overline{\xi(r)}$ for $r > d$. Here d is taken to be large enough so that for $r > d$ $V(r)$ is well approximated by its long-range form; with this condition satisfied results will be insensitive to the specific value of d. The variational approximation may then be expressed as

$$\overline{K_v}/\beta = (y_s, Ly_s) - \frac{(y_c, Ly_s)^2}{(y_c, Ly_c)}. \tag{2.13}$$

Here, to gain some simplification in form, the relation

$$1 + \beta(y_s, Ly_c) = \beta(y_c, Ly_s), \tag{2.14}$$

obtained by integration by parts, has been used; $\overline{K_t}$ was then evaluated by requiring that K_v be stationary with respect to

variations in this parameter. For $r<d$, continuity of value and slope is required, with $\overline{u_t}(0)=0$. One way to accomplish this is to set

$$y_s(r)=\overline{\phi}(d)[-(r/d)^2+2(r/d)]+\overline{\phi'}(d)r(r/d-1)+g_s(r)(r-d)^2. \quad (2.15)$$

The ''inside'' function $g_s(r)$ must vanish at the origin and decay asymptotically, but is otherwise unconstrained; $y_c(r)$ takes a similar form with ϕ and g_s replaced by ξ and g_c, respectively. In the spirit of the effective-range approximation [6,10] we may choose $g_s(r)$ and $g_c(r)$ to be independent of energy near threshold. Since the variational principle at zero energy is in fact an extremum principle, which allows for systematic improvement of the trial function, we may expect that accurate approximations for these functions may be obtained. With the threshold behavior properly accounted for, the error in the trial function will be of order, k^2 and the error in the variationally determined function $\overline{K}(k)$ will be of order k^4; we write

$$\overline{K_\nu}=-\frac{1}{\beta}[A+\tfrac{1}{2}r_0A^2k^2]+O(k^4). \quad (2.16)$$

The parameters (scattering length A and effective range r_0) appearing here have been chosen to conform to standard notation.

We emphasize that the asymptotic solutions need not be known exactly [11]. In applying the zero-energy minimum principle for the scattering length (a *maximum* principle for K), asymptotic solutions of sufficient accuracy may be constructed by taking the zero-energy limit of the positive-energy solutions. These assume the form of expansions in inverse powers of r and are accurate to a given order in each of the polarization parameters. The coefficients appearing in these expansions may be obtained more directly by analyzing the zero-energy form of the wave equation. (For example, for $l=1$ and a pure $1/r^4$ potential, sufficient accuracy is achieved by choosing the approximation to ϕ to be proportional to $r^2+\beta^2/2$.) Once the inside functions $g_s(r)$ and $g_c(r)$ are chosen the variational calculation is repeated at a positive energy with the same choice of inside functions. The integration range may be broken up into two regions; for $r>d$ we write $(H-E)\phi=V^S\phi$, where V^S is the short-range component of the potential (assumed to vanish sufficiently rapidly at great distances to assure convergence of the variational integrations), and similarly for $H-E$ operating on ξ. At this stage we insert for ϕ and ξ the approximate forms obtained by the perturbation procedure, with the Bessel functions appearing there replaced by their small-argument expansions. By retaining only the k^2 correction terms in these expansions in the evaluation of the variational expression (2.13) an explicit expression for the effective range is readily obtained.

In the following we examine the form taken by the effective-range expansion for $\tan\eta$ for s-wave and p-wave scattering; with terms of order k^4 ignored in the expansion (2.16). Then terms of order k^5 and k^7 for $l=0$ and $l=1$, respectively, may be omitted in the modified effective-range expansion of $\tan\eta$. Along with the β^2/r^4 component of the long-range interaction, a component of form β'^4/r^6 will be included; the appropriate extension of the procedure for generating the asymptotic solutions for this superposition of potentials can be made without difficulty [4]. Thus for $l=0$ one finds that

$$\delta=-\frac{\pi}{3}(\beta k)^2+\frac{\pi}{135}(\beta k)^4+\frac{\pi}{15}(\beta' k)^4. \quad (2.17)$$

The relation (2.4) may now be replaced, to sufficient accuracy, by

$$\tan\eta\cong\tan\delta+K-K^2\tan\delta. \quad (2.18)$$

We combine with this expression the approximation

$$K\cong-\frac{1}{\beta}\beta k^{2\gamma+1}[A+\tfrac{1}{2}r_0A^2k^2], \quad (2.19)$$

introduce the expansion

$$\beta k^{2\gamma+1}\cong\beta k\left[1-\frac{4\delta}{\pi}\ln\beta k+\frac{1}{2}\left(\frac{4\delta}{\pi}\ln\beta k\right)^2\right], \quad (2.20)$$

and write $\tan\delta\cong\delta+\delta^2/2$. The modified effective-range expansion for the s-wave scattering parameter then takes the form

$$\tan\eta/k=-A-\frac{\pi}{3}\beta^2k-\tfrac{4}{3}A\beta^2k^2\ln\beta k-\tfrac{1}{2}r_0A^2k^2+c_1k^3-\tfrac{8}{9}A\beta^4k^4(\ln\beta k)^2+c_2k^4\ln\beta k+O(k^5), \quad (2.21a)$$

where

$$c_1=\frac{\pi}{3}A^2\beta^2+\frac{\pi}{135}\beta^4+\frac{\pi^2}{18}\beta^4+\frac{\pi}{15}\beta'^4, \quad (2.21b)$$

and

$$c_2=\tfrac{4}{135}A\beta^4+\tfrac{4}{15}A\beta'^4-\tfrac{2}{3}r_0A^2\beta^2. \quad (2.21c)$$

Turning now to p-wave scattering, and ignoring terms of order k^6 for simplicity, we find for the tangent of the polarization phase the expression

$$\tan\delta\cong0.6283(\beta k)^2+0.1677(\beta k)^4-(\pi/35)(\beta' k)^4, \quad (2.22)$$

where rational coefficients have been replaced by approximate decimal equivalents. To the accuracy required here, Eq. (2.4) may be replaced by

$$\tan\eta=\tan\delta+K. \quad (2.23)$$

The p-wave version of the effective-range expansion is obtained by combining Eqs. (2.22) and (2.23) with the expansion

$$K=-A\beta^2k^3+\tfrac{4}{5}A\beta^4k^5\ln\beta k-\tfrac{1}{2}r_0A^2\beta^2k^5-\tfrac{8}{25}A\beta^6k^7(\ln\beta k)^2+[\tfrac{2}{5}r_0A^2\beta^4-0.3776A\beta^6-\tfrac{4}{35}A\beta^2\beta'^4]k^7\ln\beta k+O(k^6). \quad (2.24)$$

III. MULTICHANNEL SCATTERING

To focus on its essential features, the multichannel extension of the theory will be presented in the context of a simple two-channel model in which degenerate states of orbital quantum numbers l_1 and l_2 are mixed by the short-range component of the potential, but not by the long-range component. The total potential, a matrix in channel space, has the large-distance behavior $V_{ij}(r)\to V^L(r)\delta_{ij}$. The inverse-fourth power potential is again taken to be dominant at great distances, but longer-range components may be present as well. The wave function for a particle, incident in channel j, and corresponding to an outgoing wave in channel i, has the asymptotic form

$$u_{ij}\sim \phi_j\delta_{ij}+K_{ij}\xi_i, \tag{3.1}$$

where the asymptotic functions are just are those introduced earlier in Sec. II, now with channel indices attached. (Asymptotic solutions corresponding to a long-range potential that is not diagonal in channel space are derived in Appendix B.) In a matrix notation in which u_{ij} is the ith element of the column vector u_j, the wave equation becomes $Lu_j=0$, where $L_{ij}=[d^2/dr^2+k^2-l_i(l_{i-1})/r^2]\delta_{ij}-(2m/\hbar^2)V_{ij}$.

To set up a variational procedure we introduce a trial function $u_{j,t}$, and corresponding trial matrix K_t, and, by straightforward generalization of the procedure that led to Eq. (2.11), obtain the identity

$$K_{j'j}=K_{j'j,t}+\frac{1}{k}\sum_{i,i'}(u_{i'j'},L_{i'i}u_{ij,t}). \tag{3.2}$$

Actually, it is the matrix element $K_{jj'}$ that originally appears on the left-hand side; the symmetry property of the K matrix (verified by performing the above calculation with the trial function replaced by the exact solution), was used in obtaining Eq. (3.2). To relate the K matrix to the physical reaction matrix, denoted here as K^0, we rewrite the sum over outgoing-wave channels of the asymptotic form shown in Eq. (3.1) as [12]

$$\begin{aligned}&\sin(kr-l_j\pi/2+\delta_j)\\&\quad+\sum_i K_{ij}\cos(kr-l_i\pi/2+\delta_i+\pi\gamma_i)/\cos(\pi\gamma_i)\\&=\sum_i[a_{ij}\sin(kr-l_i\pi/2)+b_{ij}\cos(kr-l_i\pi/2)].\end{aligned} \tag{3.3}$$

When the trigonometric functions are expanded and coefficients compared, one finds that

$$a_{ij}=(\cos\delta_j)\delta_{ij}+K_{ij}\sin\delta_i/\cos2\delta_i, \tag{3.4}$$

and

$$b_{ij}=(\sin\delta_i)\delta_{ij}+K_{ij}\cos\delta_i/\cos2\delta_i. \tag{3.5}$$

Using the matrix relation $b=K^0a$, we obtain the solutions

$$K^0_{11}=(\det a)^{-1}(a_{22}b_{11}-a_{21}b_{12}), \tag{3.6}$$

and (employing the relation $-a_{12}b_{11}+a_{11}b_{12}=1$ which is verified directly)

$$K^0_{12}=(\det a)^{-1}K_{12}. \tag{3.7}$$

The remaining two elements of K^0 are obtained by interchange of indices. The expected symmetry property of K^0 is confirmed by these results.

The variational approximation K_v for the K matrix is obtained from the identity (3.2) by replacing the true wave function by the trial function, now written as $u_{j,t}(r)=(\beta k)^{\gamma_j+1}\overline{u_{j,t}}(r)$, with the trial K matrix expressed as

$$K_{ij,t}=(\beta k)^{\gamma_i+\gamma_j+1}\overline{K_{ij,t}}. \tag{3.8}$$

The shifted orbital quantum number is $\gamma_j=l_j-2\delta_j/\pi$; the polarization phase is determined for each channel using the method reviewed in Sec. II. We further specify that, for all r,

$$\overline{u_{ij,t}}(r)=y_{s,ij}(r)+\overline{K_{ij,t}}y_{c,ij}(r), \tag{3.9}$$

where, in the region where the potential is well approximated by its long-range form, we have $y_{s,ij}(r)\sim(\beta k)^{-(\gamma_j+1)}\phi_j(r)\delta_{ij}$ and $y_{c,ij}(r)\sim(\beta k)^{\gamma_i}\xi_i(r)$. (As discussed in Sec. II, these asymptotic wave functions need not be known exactly, but can be calculated, in principle, to any desired order in powers of the polarization strength parameters.) In recasting the variational expression into a more useful form we follow fairly closely the procedure of Sec. II, leading to Eq. (2.13). That is, we insert the trial function in the form (3.9) into the variational integral and require that, $K_{j'j,v}=(\beta k)^{-(\gamma_j+\gamma_j+1)}K_{j'j,v}$ be stationary under variations in elements of the trial matrix K_t. To simplify the writing we introduce the matrix function

$$w_{ij}=\sum_{i'}L_{ii'}y_{s,i'j}. \tag{3.10}$$

The variational expression then becomes

$$\begin{aligned}\overline{K_{j'j,\nu}}/\beta=&\sum_{i'}(y_{s,i'j'},w_{i'j})-\sum_{i,i'}(w_{i'j'},y_{c,i'j})\\&\times(m^{-1})_{i'i}(y_{c,ij'},w_{ij}),\end{aligned} \tag{3.11}$$

where the matrix m (with channel indices j and j' suppressed) is defined as

$$m_{i'i}=(y_{c,i'j'},Ly_{c,ij}). \tag{3.12}$$

The asymptotic forms of the trial matrices y_s and y_c are to be connected smoothly to inside functions that vanish at the origin and, in line with the effective-range approximation, are chosen to be slowly varying in energy near threshold. It then follows from the structure of the variational expression (3.11) that K_v can be put in the form of an expansion in powers of k^2. While it is not necessary to do so, one could maintain an analogy with the single-channel result, Eq. (2.16), by writing

$$(\beta\overline{K_v})^{-1}\cong[-A^{-1}+\tfrac{1}{2}r_0k^2], \tag{3.13}$$

where now the scattering length A and effective range r_0 are matrices. Diagonal elements of the scattering length matrix satisfy a minimum principle. The trial functions, optimized

by application of this principle, may be used in the estimation of the effective range. The calculation introduces an error of order k^4.

With the energy dependence of the K matrix determined, and with ''shape-dependent'' terms of order k^4 in the effective-range expansion ignored, the expressions given above for the physical reaction matrix K^0 in terms of the matrix K and the polarization phases may be simplified without further loss of accuracy. For example, taking $l_1=0$ and $l_2=2$ we find, after a brief calculation, that

$$\begin{aligned} K^0_{11}&=\tan\delta_1+K_{11}-(K_{11})^2\tan\delta_1+O(k^5),\\ K^0_{12}&=K_{12}-K_{12}K_{11}\tan\delta_1+O(k^7),\\ K^0_{21}&=K_{21}-K_{21}K_{11}\tan\delta_1+O(k^7),\\ K^0_{22}&=\tan\delta_2+K_{22}-K_{21}K_{12}\tan\delta_2-(K_{11}\tan\delta_1)^2\tan\delta_2\\ &\quad+O(k^9). \end{aligned} \tag{3.14}$$

For $l_1\geq 1$ and $l_2=l_1+2$, we have, more simply, $K^0_{ij}\cong(\tan\delta_i)\,\delta_{ij}+K_{ij}$ to sufficient accuracy. While we shall not do so here, a more explicit form for the modified effective-range expansion may be derived by introducing the effective-range approximation for K along with the values of the polarization phases; the latter are obtained by application of the perturbation theory of Ref. [4]

IV. SUMMARY

While the effect of long-range interactions on low-energy scattering parameters is a subject with a long history, efforts are still being made to extend the range of validity of the theory and to develop new applications. Until recently, one limitation on such extensions has been the dependence of the formulation of the theory on special functions appearing in the solution of the wave equation in the presence of the long-range forces The procedure introduced by Cavagnero [4] for generating approximations for these solutions goes a long way toward lifting this limitation. A natural way to exploit this approximation procedure is to place it in the context of a variational formulation, which depends for its effectiveness on the availability of trial functions sufficiently accurate to account for the interactions at large as well as small projectile-target separations. The modified perturbation theory of Ref. [4] provides a means for systematically improving the asymptotic behavior of the trial function, a feature that gains crucial importance in applications to scattering by highly polarizable systems. Here, to take advantage of this capability, we have reformulated one of the standard variational procedures [7] by allowing for distorted waves at great distances. This enables us to separate off factors that are singular at threshold, leaving trial functions, and auxiliary scattering parameters, depending only weakly on the energy. In this context, a suitably generalized version of effective-range theory is applicable. An additional advantage of the variational approach applied to the low-energy scattering problem is the availability of a minimum principle that provides upper bounds on diagonal elements of the scattering-length matrix [defined in Eq. (3.13)] and allows for the improvement of the accuracy of the trial function in the interior region. Since the wave function (with near-singularities removed) is expected to be slowly varying in energy, these optimized zero-energy inside functions can be useful in some range above threshold. These ideas have been illustrated here in the context of rather simple single-channel and multichannel models of the scattering process. A promising direction to take for further development of this approach is the study of scattering by targets that are not spherically symmetric [13]. New features appear, arising from the effect of a target with a permanent electric quadrupole moment, and the appearance of a long-range interaction that can induce transitions. These are matters that have been touched on in the two appendixes of this paper, and will require further study.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation under Grant No. PHY-9400673. Helpful conversations with Larry Spruch during early stages of this work are gratefully acknowledged.

APPENDIX A: THE INVERSE-CUBE POTENTIAL

If the target in its ground state has a permanent quadrupole moment the effective potential behaves as $-(\hbar^2/2m)\beta_3/r^3$ at great distances. Modifications of the perturbation theory of Ref. [4] are required to construct the asymptotic solutions. Ignoring longer-range components at this time, we look for a solution of

$$\left[z^2\frac{d^2}{dz^2}+z\frac{d}{dz}+z^2-\left(l+\frac{1}{2}\right)^2\right]M(z)=-\frac{\Delta_3}{z}M(z), \tag{A1}$$

with $\Delta_3=\beta_3 k$. In lowest order we have $M^{(0)}(z)=J_{l+1/2}(z)$, so that the polarization phase vanishes in this order. Using the relation $z^{-1}J_{l+1/2}=(2l+1)^{-1}[J_{l+3/2}+J_{l-1/2}]$, we find the first-order correction to be

$$\begin{aligned} M^{(1)}(z)=(2l+1)^{-1}&[(2l)^{-1}J_{l-1/2}(z)\\ &-(2l+2)^{-1}J_{l+3/2}(z)]. \end{aligned} \tag{A2}$$

Note that this procedure breaks down for s-wave scattering, a case considered separately below. From the asymptotic form $M^{(1)}\sim[2l(l+1)]^{-1}\cos(kr-l\pi/2)$ we conclude that, to first order, the polarization phase δ satisfies

$$\tan\delta=\beta_3 k[2l(l+1)]^{-1}. \tag{A3}$$

A first-order solution behaving as $\sin(kr-l\pi/2+\delta)$ asymptotically is given by

$$\phi(r)=(\pi kr/2)^{1/2}\cos\delta[M^{(0)}_l(kr)+\beta_3 kM^{(1)}_l(kr)]. \tag{A4}$$

A linearly independent solution $\xi(r)$, behaving as $\cos(kr-l\pi/2+\delta)$, is obtained by replacing l by $-l-1$ in the above expression for $\phi(r)$ and then multiplying the result by $(-1)^l$. Following the discussion in the text leading from Eq. (2.2) to (2.4), with γ replaced by l, we find that

$$\tan\ \eta = \frac{\tan\delta + K}{1 - K\ \tan\delta}. \tag{A5}$$

Since the leading term near threshold is $\tan\delta$, we expect that this will agree with the Born approximation

$$\tan\eta_{\rm Born} = \beta_3 k \int_d^\infty [krj_l(kr)]^2/r^3 dr, \tag{A6}$$

for the inverse-cube potential cut off for $r<d$ and evaluated to lowest order in k; this is indeed verified [14]. A variational principle for the K matrix can be set up as described in Sec. II. The extension of this analysis to include $1/r^4$ and $1/r^6$ potentials is straightforward.

A different method is required for $l=0$ and to deal with this case we resort to ordinary perturbation theory, confining our attention here to the evaluation of the first Born approximation for scattering by a $1/r^3$ potential cut off for $r<d$. Introducing the free-particle Green's function

$$G(r,r') = k^{-1}\ \sin kr_<\ \cos kr_>, \tag{A7}$$

we write the solution of the wave equation as

$$u(r) = \sin kr + \int_d^\infty G(r,r')\ \frac{\beta_3}{r'^3}\ \phi(r')dr'. \tag{A8}$$

In the Born approximation the unperturbed wave function is introduced in place of the exact solution on the right-hand side, yielding

$$u(r) \cong \sin kr\left(1 + \frac{\beta_3}{k}\int_r^\infty \cos kr'\ \frac{\theta(r'-d)}{r'^3}\ \sin kr' dr'\right) + \frac{\beta_3}{k}\cos kr \int_d^r \sin^2(kr')\ \frac{1}{r'^3}\ dr'. \tag{A9}$$

Thus $u(r) \sim \sin kr + \tan\eta \cos kr$ asymptotically, with

$$\tan\eta \cong \frac{\beta_3}{k}\int_d^\infty \sin^2(kr)\ \frac{1}{r^3}\ dr = -\beta_3 k\ \ln k + O(k). \tag{A10}$$

The zero-energy limiting value of the integral recorded above is obtained using an integration-by-parts method described in Ref. [3].

APPENDIX B: EIGENPHASE SHIFT METHOD FOR MULTICHANNEL SCATTERING

We look for asymptotic solutions for a two-channel scattering problem of the type considered in Sec. III, but with a long-range component of the potential that is not diagonal in channel space. For simplicity and definiteness we assume that $V_{ij}(r) \to -(\hbar^2/2m)\beta^2/r^4$ for large r. An appropriate asymptotic solution may be obtained from linear combinations of basis functions behaving at great distances as

$$\psi_{ij}(r) \sim \sin(kr - l_j\pi/2)\,\delta_{ij} + K^L_{ij}\cos(kr - l_i\pi/2). \tag{B1}$$

In order to apply a direct generalization of the perturbation theory of Ref. [4], as reviewed here in Sec. II, we take the linear combination that leaves the matrix K^L diagonal. Thus we attempt to find an orthogonal matrix

$$x = \begin{pmatrix} \cos\varepsilon & -\sin\varepsilon \\ \sin\varepsilon & \cos\varepsilon \end{pmatrix} \tag{B2}$$

and eigenphases δ_j, such that $(K^L x)_{ij} = \tan\delta_j x_{ij}$. Noting that

$$(\psi x)_{ij} \sim x_{ij}[\sin(kr - l_i\pi/2) + \tan\delta_j \cos(kr - l_i\pi/2)], \quad r\to\infty, \tag{B3}$$

we take as the transformed basis function $\phi_{ij} = \cos\delta_j (\psi x)_{ij}$ with asymptotic form

$$\phi_{ij} \sim x_{ij}\sin(kr - l_i\pi/2 + \delta_j). \tag{B4}$$

In a natural extension of the method reviewed in the text we set, $\phi_{ij} = C_j(\pi z/2)^{1/2} M_{ij}(z)$ and consider the wave equation for the matrix M. The solution is expanded in powers of $\Delta = (\beta k)^2$ as $M = M^{(0)} + \Delta M^{(1)} + \Delta^2 M^{(2)} + \cdots$, and a shifted orbital quantum number γ_{ij}, defined implicitly by the relation

$$(l_i + 1/2)^2 = (\gamma_{ij} + 1/2)^2 + \Delta\Gamma^{(1)}_{ij} + \Delta^2\Gamma^{(2)}_{ij} + \cdots, \tag{B5}$$

is introduced. In lowest order we have $M^{(0)}_{ij}(z) = x_{ij} J_{\gamma_{ij}+1/2}(z)$ and the equation satisfied by the first-order correction is found to be

$$\left[z^2\frac{d^2}{dz^2} + z\frac{d}{dz} + z^2 - \left(\gamma_{ij} + \frac{1}{2}\right)^2\right] M^{(1)}_{ij} = \Gamma^{(1)}_{ij} - \frac{1}{z^2}(M^{(0)}_{1j} + M^{(0)}_{2j}). \tag{B6}$$

The last term on the right-hand side is expanded with the aid of the Bessel-function recursion relation and $\Gamma^{(1)}_{ij}$ is chosen such that the coefficient of $J_{\gamma_{ij}+1/2}$, vanishes. Specifying that $l_2 = l_1 + 2$, and making use of the relation

$$(l_i - \gamma_{ij})\pi/2 = \delta_j, \tag{B7}$$

we see that $\gamma_{2j} = \gamma_{1j} + 2$. It then follows that

$$\begin{aligned} \Gamma^{(1)}_{11} &= [2(\gamma_{11} - 1/2)(\gamma_{11} + 3/2)]^{-1} \\ &\quad + \tan\varepsilon[4(\gamma_{11} + 5/2)(\gamma_{11} + 3/2)]^{-1}, \\ \Gamma^{(1)}_{21} &= [2(\gamma_{21} - 1/2)(\gamma_{21} + 3/2)]^{-1} \\ &\quad + \cot\varepsilon[4(\gamma_{21} - 3/2)(\gamma_{21} - 1/2)]^{-1}. \end{aligned} \tag{B8}$$

We may now solve Eq. (B6) for $M^{(1)}_{11}(z)$ and $M^{(1)}_{21}(z)$ and require that the value of the eigenphase shift δ_1 appearing in the asymptotic form of each solution be the same. In this

way, after a brief calculation, we find the polarization eigenphase δ_1, determined to first order from the defining relation (B7), to be

$$\delta_1=\frac{\pi\Delta}{2l_1+1}\left[\frac{1}{(2l_1-1)(2l_1+3)}+\frac{\tan\varepsilon}{2}\,\frac{1}{(2l_1+5)(2l_1+3)}\right]. \tag{B9}$$

The mixture parameter is found to satisfy the relation

$$\tan\varepsilon=-q/2+[(q/2)^2+1]^{1/2}, \tag{B10}$$

where

$$q=\frac{24(2l_1+3)}{(2l_1-1)(2l_1+7)}. \tag{B11}$$

With the calculation repeated for the mode $j=2$, the expression for δ_2 is found to be of the form (B9), but with $\tan\varepsilon\rightarrow-\cot\varepsilon$, corresponding to the choice of the negative square root in Eq. (B10).

In any given approximation for x_{ij} and $\tan\delta_j$ we have

$$K^L=\begin{pmatrix}\cos^2\varepsilon\,\tan\delta_1+\sin^2\varepsilon\,\tan\delta_2 & \sin2\varepsilon(\tan\delta_1-\tan_2)/2\\ \sin2\varepsilon(\tan\delta_1-\tan\delta_2)/2 & \sin^2\varepsilon\,\tan\delta_1+\cos^2\varepsilon\,\tan\delta_2\end{pmatrix}. \tag{B12}$$

In our first-order approximation, we find that

$$K^L_{11}\cong\frac{\pi(\beta k)^2}{(2l_1+1)(2l_1+3)(2l_1-1)}, \tag{B13}$$

which agrees with the single-channel result, as it must in first order, and K^L_{22} is obtained by interchanging indices 1 and 2 in Eq. (B13). The off-diagonal elements are

$$K^L_{21}=K^L_{12}\cong\frac{\pi(\beta k)^2}{2l_1+1}\,\frac{1}{2}\,\frac{1}{(2l_1+5)(2l_1+3)}. \tag{B14}$$

This latter expression reduces to that obtained in Born approximation by Bardsley and Nesbet [16] by setting $l_p=l_q+2$ in their Eq. (8). In the present approach, inclusion of higher-order corrections is straightforward, as is the extension to account for longer-range components of the potential.

[1] T. F. O'Malley, L. Spruch, and L. Rosenberg, J. Math. Phys. **2**, 491 (1961).

[2] S. Watanabe and C. H. Greene, Phys. Rev. A **22**, 158 (1980).

[3] O. Hinckelmann and L. Spruch, Phys. Rev. A **3**, 642 (1971).

[4] M. J. Cavagnero, Phys. Rev. A **50**, 2841 (1994).

[5] L. Rosenberg, L. Spruch, and T. F. O'Malley, Phys. Rev. **119**, 164 (1960).

[6] J. Schwinger, lectures, Harvard University, 1947 (unpublished). See also, L. C. Biedenharn and J. M. Blatt, Phys. Rev. **95**, 1387 (1954).

[7] W. Kohn, Phys. Rev. **74**, 1763 (1948).

[8] Here we adopt a simplified form of the actual electon-atom effective potential, which is in general energy-dependent and nonlocal. Derivations of the form of the long-range potential leading, in particular, to the relation between the strength parameter β^2 and the polarizability of the target, can be found in Ref. [2] and references contained therein.

[9] T. Kato, Progr. Theoret. Phys. (Kyoto) **6**, 394 (1951).

[10] H. A. Bethe, Phys. Rev. **76**, 38 (1949).

[11] If the long-range potential has a pure $1/r^n$ form, the zero-energy asymptotic solutions $\phi(r)$ and $\xi(r)$ can be determined exactly in terms of Bessel functions. [See N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon, Oxford, 1965), p. 44. For example, the regular and irregular solutions for a $1/r^4$ potential are proportional to $n_l(\beta/r)$ and $j_l(\beta/r)$, respectively.] Exact zero-energy solutions are otherwise not available. With approximations introduced, one requires, for the validity of the minimum principle of Ref. [5] to be maintained, that the error in $\phi(r)$ vanish at great distances. In practice, this requirement will cause no real difficulty.

[12] See also Eq. (3.5) of Ref. [2]. Omitted here for simplicity are the target wave functions appropriate to each channel in the asymptotic form of the complete physical wave function. Note that this wave function, in the asymptotic domain, is properly given as a coherent *sum* over outgoing-wave channels since, in our model, all such states occupy the same region in configuration space.

[13] Long-range interactions for such systems have been studied recently by W. Clark, C. H. Greene, and G. Miecznik, Phys. Rev. A **53**, 2248 (1996).

[14] The integral is performed with the aid of Eq. 6.574-2 of I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series, and Products*, 4th ed. (Academic, New York, 1980).

[15] The threshold behavior given by Eqs. (A3) and (A10) agrees with results obtained by B. R. Levy and J. B. Keller, J. Math. Phys. **4**, 54 (1963).

[16] J. N. Bardsley and R. K. Nesbet, Phys. Rev. A **8**, 203 (1973).