Electron–positive-ion scattering near reaction thresholds: Effect of long-range polarization forces

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A multichannel version of effective-range theory is developed, applicable to electron scattering by positive ions. The formalism allows for the inclusion of the effect of long-range inverse-power-law interactions arising from target distortion in the field of the projectile. A perturbation theory is described for the construction of asymptotic states accounting for the combined effect of Coulomb and polarization forces. The explicit extraction of threshold branch-point singularities leaves modified reaction-matrix elements that vary slowly with energy, thereby permitting the smooth extrapolation of scattering parameters through reaction thresholds. A systematic procedure is made available to determine the effect of long-range forces on quantum defects and resonance level shifts; it is applied here, as an illustration, in first order. The theory provides an extension, to a wider class of scattering systems and long-range interactions, of an analysis of threshold behavior in electron-ion reactions given some time ago [M. Gailitis, Sov. Phys. JETP **17**, 1328 (1963)]. [S1050-2947(98)03010-8]

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I. INTRODUCTION

The theory of electron scattering by positive ions at energies near reaction thresholds has been a subject of intensive study over the years, primarily in the context of quantum-defect theory [1]. The effective potential acting on the electron at great distances from the target includes, in addition to the Coulomb interaction, a superposition of inverse power-law contributions. For spherically symmetric targets, and in the absence of target-state degeneracies (the present study is restricted to such systems for simplicity) the dominant term is the $1/r^4$ polarization potential. Long-range power-law interactions can play an important role, particularly in states of high orbital quantum numbers. The effect of the $1/r^4$ potential (in the presence of the Coulomb field) on threshold scattering parameters has been considered, in lowest-order perturbation theory, by Seaton [2]. Our aim here is to provide a systematic treatment of the multichannel scattering problem, accounting for the presence of a superposition of long-range potentials. A perturbation expansion developed previously for scattering by a neutral, polarizable target [3] is extended here to the Coulomb problem, thus allowing for the treatment of the distortion of asymptotic states to an arbitrary order. A third-order calculation of the zero-energy polarization phase shift over a range of interaction strengths is reported below, in Sec. III, as an illustration of the significance of higher-order perturbations in physically relevant situations. This calculational procedure is algebraic and is therefore much simpler to perform than that of standard perturbation theory. Of course, a long-range potential can be accounted for in all orders through the numerical solution of a one-body scattering problem; such an approach was developed years ago in the form of a modified effective-range theory [4]. The alternative analytic approach adopted here has certain advantages, particularly in the treatment of resonance theory by extrapolation of scattering parameters through reaction thresholds.

Coulomb wave functions, satisfying different boundary conditions, play a prominent role in the theory. While their properties have been well described in the literature [5,6], those that are required in our presentation are briefly summarized, for convenience and to establish notation, in Sec. II, with some details relegated to Appendix A. In Sec. III the perturbation theory applicable to the construction of the distorted asymptotic wave functions is described and the analytic properties of these solutions are determined; some details are given in Appendix B. With this accomplished, the application to the study of threshold behavior follows along fairly standard lines, with earlier work [1,8] suitably modified to allow for the distortion of the asymptotic Coulomb wave functions. In Sec. IV the nature of the branch-point singularities of the scattering matrix for energies near reaction thresholds is considered. As in standard effective-range theory [7], such an analysis leads to the identification of a modified reaction matrix that has a smooth dependence on energy near thresholds and may therefore be conveniently modeled with a few parameters. Moreover, it may be continued through thresholds, thus providing the basis for an examination of the resonance structure of the cross section below an excitation threshold. A study of this type was made by Gailitis [8] for electron scattering by hydrogenic ions, taking into account both the Coulomb field and the inverse-square potential arising from the degeneracy of excited states of the ion. Expressions were obtained for the energy-averaged cross section, widths, and shifts of the resonances. An extension of this procedure, applicable to a wider class of scattering systems and long-range interactions, is made available by the approach developed here, and a simple illustration of this extension is given in Sec. V. Results are summarized in Sec. VI.

II. PRELIMINARIES: COULOMB WAVE FUNCTIONS

Here we summarize those properties of Coulomb solutions that will be required later on. The wave equation describing an electron in an attractive Coulomb potential is (in atomic units)

$$\frac{d^2U}{dr^2}+\left[k^2+\frac{2Z}{r}-\frac{\gamma(\gamma+1)}{r^2}\right]U=0, \tag{2.1}$$

where the restriction to integral values of the orbital quantum number γ is relaxed here in anticipation of subsequent developments. In terms of the parameters

$$z=(8Zr)^{1/2}, \quad n=-i\eta, \quad \eta=-Z/k, \tag{2.2}$$

we define a Coulomb solution

$$J(n,\gamma;z)=\frac{n^{\gamma+1}}{\Gamma(2\gamma+2)}\,M_{n,\gamma+1/2}\left(\frac{z^2}{4n}\right), \tag{2.3}$$

where $M_{n,\gamma+1/2}$ is the regular Whittaker function [9,10]. The large-distance behavior is

$$J(n,\gamma;z)\underset{z\to\infty}{\sim}A(n,\gamma)\sin\,\theta, \tag{2.4a}$$

with the proportionality factor given by

$$A(n,\gamma)=\frac{2|\eta|^{\gamma+1}e^{\eta\pi/2}}{|\Gamma(\gamma+1+n)|}, \tag{2.4b}$$

and phases defined as

$$\theta=kr-\gamma\pi/2-\eta\,\ln 2kr+\sigma_\gamma, \tag{2.5}$$

and

$$\sigma_\gamma=\arg\,\Gamma(\gamma+1+i\eta). \tag{2.6}$$

We record for later reference the series expansion, in terms of regular Bessel functions,

$$J(n,\gamma;z)=\sum_{p=0}^{\infty}a_p z^{p+1}J_{2\gamma+1+p}(2z), \tag{2.7}$$

with

$$a_0=1, \quad a_1=0, \quad a_2=(\gamma+1)/4n^2,$$

$$a_p=(4n^2p)^{-1}[(p+2\gamma)a_{p-2}-a_{p-3}], \quad p\geqslant 3. \tag{2.8}$$

Convergence and analyticity properties of the expansion are derived in Ref. [5]. If $2\gamma+1$ is not an integer an independent solution is obtained from the above results by replacing γ with $-\gamma-1$.

A second solution of Eq. (2.1) that is independent of $J(n,\gamma;z)$ for all values of $2\gamma+1$ may be defined as [11]

$$N(n,\gamma;z)=[\sin\,\pi(2\gamma+1)]^{-1}\times\left[\frac{\Gamma(\gamma+1+n)}{n^{2\gamma+1}\Gamma(n-\gamma)}\,J(n,\gamma;z)\cos\,\pi(2\gamma+1)-J(n,-\gamma-1;z)\right]. \tag{2.9}$$

The Wronskian is determined to be $JN'-NJ'=2Z/\pi$, where the prime denotes differentiation with respect to r. It is not possible to obtain a series expansion of the function $N(n,\gamma;z)$ that is convergent for all γ. To surmount this difficulty one defines [5] an irregular solution of Eq. (2.1) as

$$Q(n,\gamma;z)\equiv N(n,\gamma;z)-G(n,\gamma)J(n,\gamma;z), \tag{2.10a}$$

with

$$G(n,\gamma)=\left[\frac{\Gamma(\gamma+1+n)}{n^{2\gamma+1}\Gamma(n-\gamma)}-\sum_{p=0}^{l}\,\frac{b_p(\gamma)}{n^{2p}}\right]\frac{\cos\,\pi(2\gamma+1)}{\sin\,\pi(2\gamma+1)}. \tag{2.10b}$$

Here the $b_p(\gamma)$ are polynomials in γ with $b_0(\gamma)=1$; the procedure for calculating these parameters is given by Ham [5]. The integer l is the orbital quantum number of interest in the limit of vanishing polarization forces. The limiting form $G(n,l)$ is well defined and is given in Appendix A. The function $Q(n,\gamma;z)$ is an entire analytic function; it may be represented as an absolutely convergent series in powers of the scattering energy [12].

One may also introduce outgoing- and incoming-wave Coulomb solutions. Expressed in terms of Whittaker functions we have

$$O(n,\gamma;z)=e^{\eta\pi/2}e^{-i\gamma\pi/2}e^{i\sigma_\gamma}W_{n,\gamma+1/2}(z^2/4n), \tag{2.11}$$

with asymptotic form $O(n,\gamma;z)\sim e^{i\theta}$; the incoming-wave solution, $I(n,\gamma;z)=O^*(n,\gamma;z)$, has the form $e^{-i\theta}$ at great distances.

III. DISTORTED ASYMPTOTIC WAVES

For definiteness and simplicity we assume that beyond a certain radius r_0 the effective potential matrix is diagonal, with the Coulomb potential modified only by the addition of the polarization interaction $-\beta^2/2r^4$. It will be clear how to include additional terms of longer range. For the lth partial wave, and with the abbreviations $\rho=kr$ and $\Delta=(\beta k)^2$, the radial equation of interest is

$$\left(\frac{d^2}{d\rho^2}-\frac{l(l+1)}{\rho^2}-\frac{2\eta}{\rho}+1+\frac{\Delta}{\rho^4}\right)\phi(\rho)=0 \tag{3.1}$$

in the region $r>r_0$. With C a normalization constant to be determined, the substitution $\phi(\rho)=C(\pi\rho/2)^{1/2}m_l(\rho)$ leads to the transformed equation

$$L_l m_l(\rho)\equiv\left[\rho^2\,\frac{d^2}{d\rho^2}+\rho\,\frac{d}{d\rho}+\rho^2-2\,\eta\rho-(l+1/2)^2\right]\times m_l(\rho)=-\frac{\Delta}{\rho^2}\,m_l(\rho). \tag{3.2}$$

Generalizing the procedure described (for the case $\eta=0$) in Ref. [3], we look for a solution in the form of a series $m_l(\rho)=\Sigma_{j=0}^{\infty}\Delta^j m_l^{(j)}(\rho)$. Coulomb wave functions that are sinusoidal at great distances, with unit amplitude, satisfy a useful recurrence relation [13]. It will be available to us if we take the lowest-order solution of Eq. (3.1), corresponding to $\Delta=0$, to be the function $O(n,l;z)$ (in the notation of Sec. II) behaving asymptotically as an outgoing wave. In the version of the recurrence relation given in Ref. [13] an integral value for the orbital quantum number is assumed. However, the relation can be shown to hold for nonintegral values as well, in the form

$$\frac{1}{\rho}\, m_\gamma^{(0)} = e(\gamma) m_{\gamma+1}^{(0)} + e(-\gamma-1) m_{\gamma-1}^{(0)} + e_0(\gamma) m_\gamma^{(0)}, \tag{3.3a}$$

with

$$e(\gamma) = \frac{[(\gamma+1)^2+\eta^2]^{1/2}}{(2\gamma+1)(\gamma+1)}, \quad e_0(\gamma) = -\frac{\eta}{\gamma(\gamma+1)}. \tag{3.3b}$$

Here the notation for the orbital quantum number anticipates a shift induced by the polarization potential [3]. The unit amplitude condition is preserved in higher orders by suitable normalization of $\phi(\rho)$. The normalized solution will be denoted as $O(n,\gamma;z)$. It has the asymptotic form $\exp(i\theta)$, where $\theta = \theta + \tau$. Here θ is given by Eq. (2.5) and the phase shift τ is to be determined. An incoming wave solution of Eq. (3.1) is defined in a similar way, with $I(n,\gamma;z) \sim \exp(-i\theta)$ for $r \to \infty$. The overbar notation will be used to distinguish distorted waves from their pure Coulomb counterparts introduced in Sec. II. Once the functions O and I are determined, in some approximation, J is constructed as $A(n,\gamma)[O-I]/2i$, the distorted-wave version of Eq. (A3). The expression that relates N to the functions $J(n,\gamma;z)$ and $J(n,-\gamma-1;z)$ is of the form (2.9) with the *same* linear coefficients, and Wronskian relations are unchanged [14].

If, in Eq. (3.2), one makes the replacement

$$(l+1/2)^2 = (\gamma+1/2)^2 + \sum_{j=0}^{\infty} \Delta^j \Gamma^{(j)}, \tag{3.4}$$

one arrives at a sequence of perturbation equations, the first three of which are

$$L_\gamma m_\gamma^{(0)}(\rho) = 0, \tag{3.5a}$$

$$L_\gamma m_\gamma^{(1)}(\rho) = (\Gamma^{(1)} - \rho^{-2}) m_\gamma^{(0)}(\rho), \tag{3.5b}$$

$$L_\gamma m_\gamma^{(2)}(\rho) = \Gamma^{(2)} m_\gamma^{(0)}(\rho) + (\Gamma^{(1)} - \rho^{-2}) m_\gamma^{(1)}(\rho). \tag{3.5c}$$

With the lowest-order solution chosen as indicated above, the recurrence relation (3.3) may be applied to determine the coefficients in the expansion

$$\frac{1}{\rho^2}\, m_\gamma^{(0)}(\rho) = \sum_{p=-2}^{2} d_p m_{\gamma+p}^{(0)}(\rho). \tag{3.6}$$

The term on the right corresponding to $p=0$ must be eliminated by suitable choice of $\Gamma^{(1)}$ to avoid the appearance of a spurious singularity [3]; this yields

$$\Gamma^{(1)} = d_0 = e(\gamma)e(-\gamma-2) + e(-\gamma-1)e(\gamma-1) + [e_0(\gamma)]^2. \tag{3.7}$$

The remaining coefficients d_p are listed in Appendix B item 1. In terms of these coefficients, and with $\lambda = \gamma + 1/2$, the solution of Eq. (3.5b) is obtained immediately as

$$m_\gamma^{(1)}(\rho) = \sum_{p=-2}^{2} (1-\delta_{p0})[(\lambda+p)^2 - \lambda^2]^{-1} d_p m_{\gamma+p}^{(0)}(\rho). \tag{3.8}$$

The lowest-order solution on the right is assumed to be known in terms of the Whittaker function in Eq. (2.11) or, to the desired accuracy, from Eqs. (A4) and (2.7) as an expansion in powers of the energy. Examination of the asymptotic form of the first-order solution provides us with an expression, given in Appendix B item 3, of the first-order phase shift $\tau^{(1)}$. One sees that this phase vanishes at threshold and is invariant under the replacement $\gamma \to -\gamma - 1$; these properties hold to all orders.

From the first-order version of Eq. (3.4) the shifted orbital quantum number is obtained from that solution of

$$l^2 + l = \lambda^2 - \frac{1}{4} + \frac{\Delta}{\lambda^2 - 1}\left(\frac{1}{2} + \frac{6\eta^2}{4\lambda^2 - 1}\right) \tag{3.9}$$

which approaches l in the limit $\Delta \to 0$. The result is expected to be most useful for $l \gg 1$; the polarization potential will have a dominant effect in that domain. However, for polarizabilities of physical interest the first-order approximation is essentially useless for $l=0$ and $l=1$. With the approximation (3.9) adopted, and for $|l-\gamma| \ll 1$ (a relation that holds over a wide range of interaction strengths) one finds, to first order in $l-\gamma$,

$$l - \gamma = \frac{2\beta^2 k^2 l(l+1) + 6\beta^2 Z^2}{l(l+1)(2l+3)(2l+1)(2l-1)}. \tag{3.10}$$

As seen here, the renormalization of the orbital quantum number introduces a dependence on energy; this has a significant influence on threshold behavior.

The argument $\bar{\theta} = \theta + \tau$ of the distorted wave may be written in the form $kr - l\pi/2 - \eta \ln 2kr + \sigma_l + \bar{\delta}$, thereby defining a polarization phase as

$$\bar{\delta} = (l-\gamma)\pi/2 + \sigma_\gamma - \sigma_l + \tau. \tag{3.11}$$

As shown in Appendix B item 4, the relation $\sigma_\gamma - \sigma_l = (l-\gamma)\pi/2$ holds in the limit $k=0$, and since the phase τ vanishes in that limit the total polarization phase takes on the value $\delta = (l-\gamma)\pi$ at threshold. This point is discussed further in Sec. V in connection with Seaton's theorem [6] relating phase shifts and quantum defects at threshold. To gain some numerical orientation regarding the effect of higher-order perturbations we have carried the calculation of the polarization phase up to third order, over a range of values of $\beta^2 Z^2$, for the case $k=0$ and several partial waves. The result for $l=3$ appears in Fig. 1 as the solid curve obtained by interpolation; the dashed line represents the first-order polarization phase given in Eq. (3.10) and the individual points represent values found in second order. Convergence improves rapidly with l. For $l=4$ the lowest-order calculation agrees with the third-order result to within 0.5% for $\beta^2 Z^2 = 30$. A similar calculation for $l=2$ provides an indication that to obtain an accuracy of better than 10% in third order one is restricted to the range $\beta^2 Z^2 < 5$. Greater reliability of

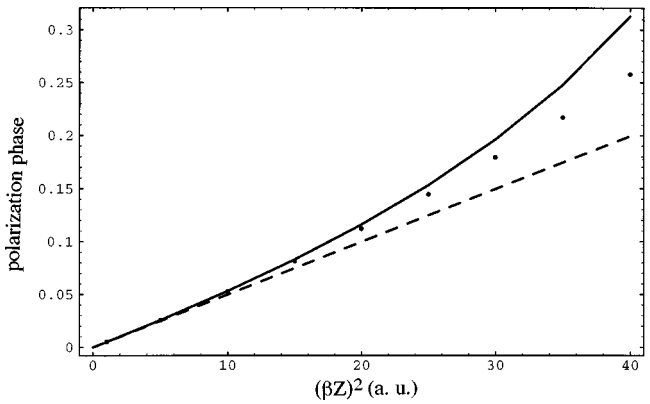

FIG. 1. f-wave polarization phase for the potential $-\beta^2/2r^4 - Z/r$ (atomic units) at zero energy as a function of $(\beta Z)^2$, evaluated in third order (solid curve). The individual points represent results obtained in second order and the dashed line gives the result of the lowest-order approximation obtained by including a factor of π in Eq. (3.10) of the text.

this approximation procedure is expected for applications to potentials of longer range than the $1/r^4$ potential discussed above.

The perturbation calculations are simplified in practice if one takes advantage of the invariance of $\Gamma^{(j)}$ under the replacement $\gamma \rightarrow -\gamma - 1$. This property is verified explicitly in first order by the result shown in Eq. (3.7). A proof to all orders is sketched in Appendix B item 2. Note that since the invariance property carries over to the determination of γ according to Eq. (3.4), the same value of γ is to be used in the construction of the two distorted waves $\bar{J}(n,\gamma;z)$ and $\bar{J}(n,-\gamma-1;z)$, as has been anticipated by our choice of notation. The perturbation theory plays another useful formal role in establishing the analytic properties of the distorted waves in each order. One observes that if the correction is analytic in the energy to a given order this property is preserved in the next higher order since the perturbing factor $\Delta\rho^{-2}$ is energy independent, and possible singularities arising from the inversion of the operator L_γ are avoided through the choice of $\Gamma^{(n)}$. This remark is developed in more detail in Appendix B item 5.

IV. SCATTERING MATRICES

Having introduced basis functions for electron-ion scattering that account for Coulomb and longer-range interactions it is now possible to define a scattering matrix from which factors are removed that contain branch point singularities at thresholds. This leaves a function that varies smoothly with energy, thus providing the basis for a multichannel effective-range theory that extends earlier formulations [7,8,15]. Our treatment follows closely that of Ref. [15], differing from it by the inclusion of the combined effect of the Coulomb tail and polarization forces of longer range. Target states are assumed to be spherically symmetric and nondegenerate. We suppose that the scattering problem has been reduced to one defined by a set of N coupled radial equations, involving a real, symmetric effective potential matrix; all N channels are assumed to be open. The wave function then appears as a square matrix consisting of N columns, each corresponding to a different entrance channel. The rows represent the open channels.

Following standard procedure [16] we represent the multichannel scattering matrix as $S^c = e^{i\sigma} S^0 e^{i\sigma}$. Here σ is a diagonal matrix with the Coulomb phase appropriate to each channel as diagonal elements. [The Coulomb phase is given by Eq. (2.6) where in the present context γ is replaced by the orbital quantum number l_i for the ith channel]. The scattering matrix S^0 is defined in terms of the asymptotic form of the wave function with pure Coulomb solutions representing the incoming and outgoing waves. When reexpressed in terms of the distorted waves defined in Sec. II the asymptotic form becomes

$$\psi_{ji} \sim \bar{I}_i \delta_{ji} - \bar{O}_j S_{ji}. \tag{4.1}$$

By comparison of the asymptotic forms of the wave functions defined with and without the inclusion of polarization interactions one arrives at the relation $S^0 = e^{i\bar{\delta}} S e^{i\bar{\delta}}$, where $\bar{\delta}$ is the diagonal phase matrix [17] with elements defined for each channel in Eq. (3.11). As an alternative to Eq. (4.1) we may write the asymptotic form, with $S = 1 + 2iT$, as

$$-(2i)^{-1}\psi_{ji} \sim \bar{F}_i \delta_{ji} + \bar{O}_j T_{ji}, \tag{4.2}$$

where $\bar{F}$ is a diagonal matrix the nonvanishing elements of which are distorted-wave versions of the regular Coulomb solution defined in Eq. (A2). Additional transformations are useful at this point. By extension of Eqs. (A5) we have $\bar{O} = c_3 \bar{J} + c_4 \bar{N}$. With this replacement made in Eq. (4.2) along with the substitution $\bar{N} = G\bar{J} + Q$ [a distorted-wave extension of Eq. (2.10a)] we have, after a suitable renormalization, a wave function behaving at great distances as

$$u_{ji} \sim \bar{J}_j M_{ji} - \bar{Q}_i \delta_{ji}. \tag{4.3}$$

The relation connecting the matrices T and M is found (after some algebra) to be

$$T = f^{1/2}[M - (h + if)]^{-1} f^{1/2}. \tag{4.4}$$

Here we have set $-(c_3/c_4 + G) = h + if$ where f and h are the real, diagonal matrices

$$f = (2\pi)^{-1} e^{-\eta\pi} |\Gamma(1 + \gamma + i\eta)|^2 |\eta|^{-(2\gamma+1)} \tag{4.5}$$

and

$$h = -\mathrm{Re}\ G(n,\gamma) + f\ e^{2\pi\eta} \sin 2\pi\gamma. \tag{4.6}$$

As will be discussed further below, the matrix M is a smooth function of the energy in the neighborhood of reaction thresholds. Hence Eq. (4.4) exhibits threshold singularities explicitly, thereby providing the basis for an effective range theory. As a partial check on these developments we note that in the absence of polarization forces, γ is replaced by the integer l and the limiting relation shown in Eq. (A1) for the function G is employed. One then verifies that Eq. (4.4) reduces to Eq. (10) of Ref. [8], the version appropriate to standard multichannel Coulomb scattering. Further reduction, in which the effect of the Coulomb tail is not included, leads to the effective-range formalism of Ross and Shaw [7].

The unitarity of the scattering matrix implies the relation $T-T^{\dagger}=2iTT^{\dagger}$. With the T matrix given by Eq. (4.4), unitarity will be satisfied if M is Hermitian. In fact M must be real and symmetric to satisfy the symmetry property of T. For single-channel scattering in a given partial wave, unitarity allows for the representation $T=e^{i\delta}\sin\delta$ with the real phase shift δ accounting for the short-range interaction. From the single-channel version of Eq. (4.4) it follows that

$$M=f\cot\delta+h. \tag{4.7}$$

Writing $T^0=e^{i\delta^0}\sin\delta^0$, we find that the phase shift δ^0 relative to pure Coulomb scattering is given by the sum $\delta+\bar{\delta}$ of the short-range and polarization contributions.

Returning to the general multichannel problem we remark that the variational procedure provides an effective method for constructing approximations to M that preserve not only the reality and symmetry properties but the analyticity of the M matrix as well. With regard to this latter property, one observes that threshold singularities can appear in the variational representation of the M matrix only through the behavior of the trial functions in the asymptotic region. These trial functions, however, have the asymptotic form shown in Eq. (4.3), expressed in terms of distorted waves J and Q that are analytic in the energy variable. Such a trial function may be connected smoothly to an inside function that is weakly energy-dependent thereby providing a variational formulation of the effective-range approximation. In its simplest version this approximation leads to a representation of M as a two-term expansion in powers of the excitation energy near a reaction threshold with coefficients, variationally determined, that are matrix generalizations of the scattering length and effective range parameters. The formulation of the variational principle for the problem considered here is essentially identical to that described previously for scattering by a neutral target [15] and need not be repeated. One need only account for an altered normalization factor arising from the Wronskian relation $\bar{J}\bar{Q}'-\bar{J}'\bar{Q}=2Z/\pi$ between the basis functions.

V. CONTINUATION BELOW THRESHOLD

Owing to the presence of a Rydberg series of resonances just below an excitation threshold the scattering amplitude T^b in this domain will vary rapidly with energy. A knowledge of the amplitude T^a above threshold, obtained either by calculation or deduced from experiment can, by analytic continuation, give useful information on the resonance structure of T^b. Effective-range theory, based on the smooth energy dependence of the M matrix, provides the basis for the analytic continuation process. Such a procedure, described by Gailitis [8] for the problem of electron scattering by hydrogenic ions (accounting for both the Coulomb and long-range inverse-square potentials), may now be extended to the wider class of problems under consideration here. While greater generality is possible, we shall limit the present discussion to energies sufficiently close to threshold so that the energy variation of the M matrix may be ignored completely, that is, we set $M^a=M^b$. In addition, it is assumed that only one channel opens at the threshold under consideration.

We first consider single-channel scattering at the continuum threshold in order to determine the effect of long-range polarization forces on the relation between scattering parameters and bound-state energies. At an energy corresponding to a bound state the scattering amplitude has a pole so that

$$M-h-if=0. \tag{5.1}$$

For M we use the expression (4.7), evaluated at an energy just *above* threshold. In that limit the function f, given by Eq. (4.5), goes to unity [18] and, as seen from Eq. (4.6) with $e^{2\pi\eta}$ set equal to zero, $h\rightarrow-\mathrm{Re}\,G(n,\gamma)$. This latter function vanishes in the limit considered, as may be seen by making use of the identity

$$\Gamma(n-\gamma)\Gamma(\gamma+1-n)=\pi\csc\pi(n-\gamma) \tag{5.2}$$

in the defining relation (2.10b), and evaluating the result at threshold. Thus M in Eq. (5.1) is replaced by $\cot\delta$, where δ now represents the threshold value of the short-range phase shift. The calculation below threshold of $h+if\equiv-(c_3/c_4+G)$ is performed by setting $k=i\kappa$, with κ real and positive, and approaching zero from above. Referring to Eqs. (A5b) we find, after a brief calculation, that

$$\frac{c_3}{c_4}\cong\cot\pi\left[\frac{Z}{\kappa}-(\gamma-l)\right] \tag{5.3}$$

and that G vanishes. The parameter κ, the threshold energy E_t, and the bound-state energy E_b satisfy the relation $\kappa^2=2(E_t-E_b)$. With E_t-E_b expressed in terms of the quantum defect μ evaluated at threshold, Eq. (5.1) becomes

$$\cot\delta=\cot\pi(\mu+\gamma-l). \tag{5.4}$$

If one interprets this result as an example of Seaton's theorem [6] relating the phase shift at threshold to the quantum defect one should identify $\mu+\gamma-l$ as the *short*-range contribution to the quantum defect and hence $l-\gamma$ should be identified as the polarization contribution. We denote this latter quantity as $\bar{\mu}$ so that (recalling our earlier evaluation of the polarization phase at threshold) we can write $\delta=\pi\bar{\mu}$ relating the polarization contributions to the phase shift and quantum defect at threshold. This relation agrees with that obtained by Seaton [2] using ordinary first-order perturbation theory for the effect of the polarization interaction on phase shifts and quantum defects. For high partial waves one may expect the $1/r^4$ potential to provide the dominant contribution to the quantum defect. A very early first-order perturbative calculation based on this idea [19] gives a value $\bar{\mu}=l-\gamma$ with $l-\gamma$ given by Eq. (3.10). These results provide consistency checks on the formalism developed here, which is not restricted to calculations done at threshold in lowest-order perturbation theory. [This is true, in particular, of the parameter γ appearing in Eq. (5.4), as discussed in Sec. III and illustrated in Fig. 1.]

The shift in the quantum defect arising from the polarization potential may be expected to play an analogous role in the multichannel scattering problem, leading to a corresponding shift in the positions of the Rydberg resonances lying just below an excitation threshold. This matter is most simply studied by suitable modification of the resonance

analysis given by Gailitis [8], who traced the source of rapid oscillation of the cross section to the presence of a term $\cot\pi Z/\kappa_t$ in a resonance denominator. Here $\kappa_t=[2(E_t-E)]^{1/2}$, the energy E being measured from the threshold of the new channel. Without repeating the details of the argument given in Ref. [8], we remark that inclusion of the polarization interaction has the effect of replacing the cotangent function by $\cot[\pi Z/\kappa_t+\overline{\mu}]$, where $\overline{\mu}=l-\gamma$ is just the polarization contribution introduced above in the discussion of discrete states. The expression for the resonance width [20] is unaltered by this modification but the resonance pattern is shifted by an amount $-D\overline{\mu}$, where D is the distance between resonances. This result follows from the fact that the reference level from which resonance positions are reckoned has been shifted. The main conclusion reached in Ref. [8] is unaltered, namely, that the total cross section, its value below threshold taken to be an average over resonances, is continuous across the threshold

VI. SUMMARY

The standard theory of scattering by a modified Coulomb interaction is formulated in terms of distorted asymptotic solutions that account for the presence of the Coulomb tail. This allows for the introduction of a reaction matrix that is free of threshold singularities and hence serves as the basis for simple parametrizations of the scattering data as well as an analytic continuation below excitation thresholds. This approach has been carried a step further here through the inclusion of long-range polarization interactions in the definition of the asymptotic states. In the absence of exact analytic solutions for potentials of this type, a previously developed perturbation theory for inverse power-law potentials [3] has been extended to include the Coulomb potential. It appears, from numerical tests, that this version of the approximation procedure for determining the asymptotic solutions, while quite effective for the higher orbital quantum numbers, will have to be supplemented by some other technique (such as direct numerical solution of a one-body radial Schrödinger equation [4]) for the lowest few partial waves. While thus limited to some extent, the perturbation theory serves a useful formal role, allowing for the examination of analyticity and invariance properties of the asymptotic solutions. Based on this analysis, the analytic form of the threshold singularities of the scattering matrix is determined and this permits the introduction of a modified reaction matrix that is free of such singularities. With this ''M matrix'' properly defined, approximation techniques, such as the variational method [15], are available for its construction and the basis for an effective-range theory applicable to electron scattering by positive ions is thereby provided. A particular application of interest would be a study of the effect of long-range polarization interactions on resonance parameters. As an illustration, a preliminary treatment of this problem has be given here, leading to expressions for near-threshold modifications of quantum defects and resonance level shifts.

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APPENDIX A: COULOMB FUNCTIONS

Some properties of Coulomb wave functions that are referred to in the text are listed here for the convenience of the reader.

(1) The limiting form of the function $G(n,\gamma)$, given in Eq. (2.10b), for $\gamma\to l$, is

$$2\pi G(n,l)=\frac{\Gamma(\gamma+1+n)}{n^{2\gamma+1}\Gamma(n-\gamma)}\times[\Psi(\gamma+1+n)+\Psi(n-\gamma)-2\ln n]-\sum_p^l n^{-2p}\left.\frac{db_p(\gamma)}{d\gamma}\right|_{\gamma=l}, \tag{A1}$$

where Ψ is the logarithmic derivative of the Γ function [21].

(2) The standard regular solution, satisfying

$$F(n,\gamma;z)=(2i)^{-1}[O(n,\gamma;z)-I(n,\gamma;z)], \tag{A2}$$

behaves as $\sin\theta$ asymptotically, with θ given by Eq. (2.5). From Eq. (2.4) we have

$$J(n,\gamma;z)=A(n,\gamma)F(n,\gamma;z). \tag{A3}$$

The outgoing wave solution may be expressed as the linear combination

$$O(n,\gamma;z)=c_1J(n,\gamma;z)+c_2J(n,-\gamma-1;z), \tag{A4a}$$

with linear coefficients given by

$$c_1=-e^{\eta\pi/2}e^{-i\gamma\pi/2}\pi\ \csc[\pi(2\gamma+1)]\times n^{-(\gamma+1)}(|\Gamma(-\gamma-n|)^{-1},$$

$$c_2=e^{\eta\pi/2}e^{-i\gamma\pi/2}\pi\ \csc[\pi(2\gamma+1)]n^{\gamma}(|\Gamma(\gamma+1-n|)^{-1}. \tag{A4b}$$

Another useful relation is

$$O(n,\gamma;z)=c_3J(n,\gamma;z)+c_4N(n,\gamma;z), \tag{A5a}$$

where

$$c_3=e^{\eta\pi/2}e^{-i\gamma\pi/2}|\Gamma(\gamma+1+n)|n^{-\gamma-1}\ \cos\ \pi(-\gamma-1+n),$$

$$c_4=e^{\eta\pi/2}e^{-i\gamma\pi/2}|\Gamma(-\gamma+n)|n^{\gamma}\ \sin\ \pi(-\gamma-1+n). \tag{A5b}$$

APPENDIX B: PERTURBATION THEORY

(1) To complete the specification of the first-order correction, shown in Eq. (3.8), of the outgoing Coulomb wave function we list the expansion coefficients as

$$d_2(\gamma)=e(\gamma)e(\gamma+1),\quad d_{-2}(\gamma)=d_2(-\gamma-1),$$

$$d_1(\gamma)=e(\gamma)[e_0(\gamma+1)+e_0(\gamma)],\quad d_{-1}(\gamma)=d_1(-\gamma-1), \tag{B1}$$

with $e(\gamma)$ and $e_0(\gamma)$ defined in Eq. (3.3b).

(2) The invariance property of the functions $\Gamma^{(1)}$ under the exchange $\gamma \rightarrow -\gamma-1$ is evident in the first-order result shown in Eq. (3.7). We examine this property more explicitly, emphasizing those features that allow us to extend it to all orders. To begin we note that the coefficient $e(\gamma)$ of the term that raises the index by unity and the coefficient $e(-\gamma-1)$ of the lowering term transform one into the other while the coefficient $e_0(\gamma)$ of the term that leaves the index unchanged is invariant under the exchange $\gamma \rightarrow -\gamma-1$. An iteration of the operation is required in first order; the result is shown in Eq. (3.7). It is helpful to adopt a diagrammatic view of this iteration process, in which index shifts are related to upward, downward, and horizontal steps that start and end at a given reference level, corresponding to the initial value of the index γ. The pattern of steps thus generated has a reflection symmetry about that reference level; for example, along with a step up ($\gamma \rightarrow \gamma+1$) and then down ($\gamma \rightarrow \gamma-1$) one includes a step down and then up. [This picture is justified by the form of the first-order Eqs. (3.7) and (B1), and applies to higher orders as well.] The analysis may be simplified at the outset by recognizing that horizontal steps ($\gamma \rightarrow \gamma$)—in first order these lead to the last term in Eq. (3.7)—preserve the invariance property of interest [since $e_0(\gamma)$ is invariant] and may therefore be safely be ignored in the proof. Each upward step may be paired with a downward partner obtained by reflection through the reference level. The coefficients $e(\gamma)$ and $e(-\gamma-1)$ associated with these steps are transformed into one another under the exchange $\gamma \rightarrow -\gamma-1$, as noted above. This observation is sufficient to verify the invariance property of $\Gamma^{(1)}$. Extension of the analysis to higher orders follows along very similar lines, with the paired steps having associated with them the coefficients $e(\gamma+p)$ and $e(-\gamma-1+p)$, with p an integer, which are transformed into one another.

(3) The first-order contribution, $\tau^{(1)}$, to the phase shift τ in Eq. (3.11) is obtained by examining the asymptotic form of the function $m_\gamma^{(1)}(\rho)$, appearing in Eq. (3.8). With the aid of Eqs. (B1) and the relation

$$\sigma_{\gamma+1} = \sigma_\gamma + \tan^{-1} \frac{\eta}{\gamma+1}, \tag{B2}$$

we find that

$$\tau^{(1)} = \tan^{-1} \frac{a_c}{1+a_s}. \tag{B3}$$

To make the invariance of $\tau^{(1)}$ with respect to the interchange $\gamma \rightarrow -\gamma-1$ manifest we express the coefficients a_c and a_s in terms of the variable $\lambda = \gamma + \frac{1}{2}$ and obtain the relations

$$\begin{aligned} a_c &= \Delta\eta[a_{c1}(\lambda) + a_{c1}(-\lambda) + a_{c2}(\lambda)], \\ a_{c1}(\lambda) &= 2\lambda(\lambda+1)(2\lambda+1)(2\lambda+3), \\ a_{c2}(\lambda) &= -[(\lambda^2-1/4)(\lambda^2-9/4)]^{-1}, \\ a_s &= \Delta a_{s1}(\lambda) + \Delta\eta^2[a_{s2}(\lambda) + a_{s2}(-\lambda) + 2a_{c2}(\lambda)], \\ a_{s1}(\lambda) &= -[2(\lambda^2-1)]^{-2}, \\ a_{s2}(\lambda) &= -[16(\lambda+1)^2\lambda(\lambda+1/2)(\lambda+3/2)]^{-1}. \end{aligned} \tag{B4}$$

(4) In determining the threshold value of the polarization phase, defined in Eq. (3.11), the relation $\sigma_\gamma - \sigma_l = (l-\gamma)\pi/2$, valid in the limit $k=0$, was used. This relation may be verified by examining the expansion $\sigma_\gamma - \sigma_l = (\lambda-l)\sigma' + 1/2(\lambda-l)^2\sigma'' + \cdots$, where

$$\sigma' \equiv \left.\frac{d\sigma_\gamma}{d\gamma}\right|_{\gamma=l} = -\,\mathrm{Im}\,\Psi(1+l-i\eta). \tag{B5}$$

Using the relations [21]

$$\Psi(1+l-i\eta) = (l-i\eta)^{-1} + (l-1-i\eta)^{-1} + \cdots + \Psi(1-i\eta), \tag{B6a}$$

and

$$\mathrm{Im}\,\Psi(1-i\eta) = -\frac{1}{2|\eta|} + \frac{\pi}{2}\coth\pi|\eta|, \tag{B6b}$$

we find that $\sigma' = -\pi/2$ in the limit $|\eta| \rightarrow \infty$. It remains to show that higher orders in the Taylor series expansion of $\sigma_\gamma - \sigma_l$ vanish. This follows from the threshold behavior of the coefficients $\sigma'' = -\,\mathrm{Im}\,\Psi^{(1)}$, $\sigma''' = -\,\mathrm{Im}\,\Psi^{(2)}$, etc.; these coefficients vanish since the polygamma functions [21]

$$\Psi^{(n)}(z) \equiv \frac{d^n}{dz^n}\Psi(z) \tag{B7}$$

vanish as z^{-n} for $z \rightarrow \infty$ in $|\arg z| < \pi$ and here $z = 1 + l + i|\eta|$.

(5) The distorted wave $\bar{F}(n,\gamma;z)$, behaving asymptotically as $\sin\theta$, is not analytic in the energy, but each term in the perturbation expansion of the renormalized function $\bar{J}(n,\gamma;z) = A(n,\gamma)\bar{F}(n,\gamma;z)$ is analytic. As mentioned earlier, and proved in Ref. [5], the unperturbed function is analytic. [It is represented in Eq. (2.7) as a convergent expansion of analytic functions.] We now show explicitly that this property is preserved in first order; the procedure for extending this demonstration to higher orders should then be clear.

The perturbation theory was formulated in terms of the function $m(\rho)$, satisfying Eq. (3.2). For our present purposes we identify $F(n,\gamma;z) = (\pi\rho/2)^{1/2} m_\gamma^{(0)}(\rho)$; since the two functions are related by the same factor $(\pi\rho/2)^{1/2}$ in each order and $\bar{F}(n,\gamma;z)$ is ultimately normalized to unit amplitude this factor plays no role in the discussion and will be ignored. The function $m_\gamma^{(1)}(\rho)$ given in Eq. (3.8) is to be multiplied by the strength parameter $\Delta = \beta^2 k^2$. We wish to convert the resultant expression to one relating the first-order correction to $J(n,\gamma;z)$ to a combination of the unperturbed functions $J(n,\gamma+p;z)$. For this purpose we multiply both sides by $A(n,\gamma)$, and on the right-hand side we replace $m_{\gamma+p}^{(0)}(\rho)$ by $A^{-1}(n,\gamma+p)J(n,\gamma+p;z)$. [A factor $(\pi\rho/2)^{1/2}$ enters but is canceled]. We now collect and list all energy-dependent factors that appear in each of the four terms ($p = \pm 2, p = \pm 1$) in the expansion.

$p=2$: Along with the factor

$$\Delta A(n,\gamma)A^{-1}(n,\gamma+2)=\beta^2k^2|\gamma+2-i\eta||\gamma+1-i\eta|\eta^{-2}$$

we must include the energy-dependent contribution arising from the coefficient d_2, which is seen from Eq. (B1) to be $[(\gamma+2)^2+\eta^2]^{1/2}[(\gamma+1)^2+\eta^2]^{1/2}$. These factors combine to give the analytic function $[(\gamma+2)^2k^2+(\eta k)^2][(\gamma+1)^2k^2+(\eta k)^2]$. $p=1$: The factor $\Delta A(n,\gamma)A^{-1}(n,\gamma+1)=\Delta|\gamma+1-i\eta|\eta^{-1}$ combines with the factor $\eta[(\gamma+1)^2+\eta^2]^{1/2}$ contributed by the coefficient d_1 to give $[(\gamma+1)^2k^2+(\eta k)^2]$. $p=-1$: The product of $\Delta\eta|\gamma-i\eta|^{-1}$ and $\eta(\gamma^2+\eta^2)^{1/2}$ is a constant. $p=-2$: The product of $\Delta\eta^2|\gamma-i\eta|^{-1}|\gamma-1-i\eta|^{-1}$ and $(\gamma^2+\eta^2)^{1/2}[(\gamma-1)^2+\eta^2)]^{1/2}$ is a constant.

Note that when $\Gamma^{(1)}$, given in Eq. (3.7), is multiplied by Δ the result is a sum of three terms each of which being analytic. The analysis of the structure of $\Gamma^{(j)}$ given in item 2 of this appendix can be used to show that $\Delta^j\Gamma^{(j)}$ is analytic. Since the higher-order functions $m_\gamma^{(j)}$ are expressed as linear combinations of lowest-order functions we are led to apply an analysis similar to that outlined above to functions of the form $\Delta\rho^{-2}m_{\gamma+p}^{(0)}$ and arrive at the conclusion that each term in the perturbation expansion of $\bar{J}(n,\gamma;z)$ is analytic in energy. In a similar way one may show that the function $Q(n,\gamma;z)$ is analytic. The analyticity in lowest order of this function was established by Ham [5] and is preserved in higher orders.

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