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Bound-state methods for low-energy electron-ion scattering

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An effective-potential formalism, previously developed for electron scattering by a neutral target, is extended to apply to electron-ion scattering, with the requirement of antisymmetrization now accounted for explicitly. A minimum principle for the effective potential is derived, valid for scattering below the ionization threshold and applicable when, as is usually the case, the target wave functions are imprecisely known. The basis for the minimum principle is the Rayleigh-Ritz property that is satisfied by the modified Hamiltonian in terms of which the effective potential is defined. An analysis of single-channel, zero-energy scattering for a particular partial wave is presented; it is based on the effective-potential formalism and leads to an absolute definition of the zero-energy phase shift $\delta(0)$ of the form $\delta(0)=\mu(\infty)\pi$, where $\mu(n)$ is the quantum defect of the nth energy level. This result may be thought of as an extension of Levinson's theorem for scattering by short-range potentials.

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I. INTRODUCTION

Minimum principles, of the Rayleigh-Ritz type, were developed some years ago as a tool for the systematic improvement of trial functions in variational treatments of low-energy electron and positron scattering by light atoms [1,2]. Such methods have, in recent years, played a less significant role than originally anticipated. One reason for this is the subsequent introduction of alternative techniques, such as close-coupling and R-matrix methods [3], that very effectively take advantage of the ever-increasing power of computers. Partly as a result of this, procedures based on the minimum-principle idea, originally presented in the context of scattering by hydrogenic targets, have not been further developed to apply to more complex atomic and negative-ion targets. Moreover, the extension of the theory to electron scattering by *positive* ions—a class of problems of considerable current interest—has not been previously made. In the search for reliable calculational methods applicable to multiparticle scattering systems, where computational limits of existing methods begin to be felt, it appears likely that the particular merits of the variational approach, developed to its full potential, can be exploited. With this as motivation, a generalized version of the minimum-principle approach to low-energy multiparticle scattering calculations will be given here.

In Sec. II an effective-potential formulation of the scattering problem, which provides the basis for the minimum principle, will be presented in a form that is applicable to multichannel scattering by complex targets, with resonance effects accounted for in a natural way, for scattering energies below the ionization threshold. The theory is an extension of that given in Ref. [2], with the requirement of antisymmetry now explicitly accounted for, and applicable to electron scattering by positive ions. As in the analogous case of scattering by a neutral target, the spectrum of the modified Hamiltonian in terms of which the effective potential is defined has a continuum of states removed that, in the physical spectrum, contains energies lying below the scattering energy. In addition, an infinite series of Rydberg states, corresponding to the projectile electron weakly bound to the positively charged target, is removed in the construction of the effective potential. The essence of the calculational procedure is the application of the minimum principle for the effective potential. Since this principle is rigorously valid even when the target states are imprecisely known, and since the modified Hamiltonian is obtained directly through the subtraction of known separable interactions, the method has certain advantages over those based on the Feshbach projection-operator formalism [4]. It should be emphasized that the minimum principle is of a subsidiary nature, useful in optimizing the choice of trial functions. With the variational construction of the effective potential accomplished the equivalent one-body integral equation for the reaction matrix can be solved numerically, with high accuracy, using standard methods [5]. Since, in going beyond hydrogen, one deals with inexact target wave functions, a rigorous bound on diagonal elements of the reaction matrix is not guaranteed. However, the *accuracy* of the scattering calculation, which is now very similar to a Rayleigh-Ritz calculation of the energy of an $(N+1)$-particle bound state, can in general be comparable to that achieved in the determination of the binding energy of the N-particle target.

The phase shift is the parameter of interest for single-channel scattering in a particular partial wave and the availability of an absolute definition of this parameter can be useful in the interpretation of results obtained from applications of the minimum principle [6]. Levinson's theorem, suitably generalized, relating the zero-energy phase shift to the number of bound states, provides the basis for such an absolute definition. The theorem was originally derived for scattering by a short-range potential [7], and has recently been extended to apply to the case where the target is a neutral atom [8]. When the potential contains an attractive Coulomb tail the zero-energy phase shift $\delta(0)$ can be defined (relative to the Coulomb phase) as $\delta(0)=\mu(\infty)\pi$ by analytic continuation of the quantum defect function to the series limit [9]. This result, which removes the ambiguity in the definition of the phase shift regarding the addition of arbitrary multiples of π, was recently given a purely scattering-theoretic derivation (not involving analytic continuation) valid for one-body potential scattering [10]. Its extension to apply to electron scattering by positive ions is conveniently obtained with the aid of the effective-potential formalism, as shown in Sec. III. The definition arrived at in this way is therefore the appropriate one to use in scattering calculations based on the effective-potential method.

II. EFFECTIVE-POTENTIAL FORMALISM

A. Definition of the effective potential

While greater generality is possible in setting up an effective-potential formalism that allows for the use of Rayleigh-Ritz methods, we focus our attention here on the scattering of an electron by a target consisting of N electrons bound to a fixed nucleus of charge $Z|e|$. The Hamiltonian of this system may be written (in $N+1$ different ways) as

$$H=h(n)+K(n)+V(n). \tag{2.1a}$$

Here $K(n)$ is the sum of the kinetic energy of the nth electron and its monopole Coulomb interaction with the residual system, $h(n)$ is the Hamiltonian of that residual system (in which electron n has been removed), and $V(n)$ is the interaction, with the monopole Coulomb component subtracted off, of the nth electron with the residual system. In configuration space we have

$$V(n)=-\frac{Ne^2}{r_n}+\sum_{j=1}^{N+1}(1-\delta_{nj})\frac{e^2}{|\mathbf{r}_n-\mathbf{r}_j|}, \tag{2.1b}$$

where $\mathbf{r}_j$ is the distance of the jth electron from the nucleus. The target states associated with open channels satisfy

$$h(n)|\chi_\gamma(\bar{n})\rangle=\varepsilon_\gamma|\chi_\gamma(\bar{n})\rangle, \tag{2.2}$$

with negative eigenvalues $\varepsilon_1\leqslant\varepsilon_2\leqslant\cdots\leqslant\varepsilon_p$. We use the notation

$$\chi_\gamma(\bar{n})=\chi_\gamma(1,2,\ldots,n-1,n+1,\ldots,N+1) \tag{2.3}$$

for the antisymmetrized target wave function; for simplicity, we frequently represent the space and spin coordinates of the jth particle by the symbol j. More often, the coordinates will be suppressed. [In accordance with convention, the *function* $\chi_\gamma(\bar{n})$ is interpreted as the coordinate-space representation of the Dirac *ket* $|\chi_\gamma(\bar{n})\rangle$.] An essential feature of the effective-potential formalism is the introduction of a modified Hamiltonian which has the branches of its continuous spectrum starting not at the physical thresholds of the various channels but at a higher threshold lying above the scattering energy E. As a first step in this direction, we define the modified target Hamiltonian

$$\hat{h}(n)=h(n)-\sum_{\gamma=1}^{p}\varepsilon_\gamma|\chi_\gamma(\bar{n})\rangle\langle\chi_\gamma(\bar{n})|. \tag{2.4}$$

(This is an alternative to working with the standard Feshbach projection operators which are difficult to construct in general, when exchange and rearrangement processes are possible and when exact target solutions are not available.) As seen from the eigenvalue equation $\hat{h}(n)|\chi_\gamma(\bar{n})\rangle=0$, $\varepsilon_\gamma\leqslant\varepsilon_p$, the target energies associated with open channels have been displaced upward to zero, so that $\hat{h}(n)-\varepsilon_{p+1}$ is a non-negative operator. At this point we must be concerned with the fact that the target states are imprecisely known. Let us assume that an orthonormal set of trial functions $\chi_{\gamma t}(\bar{n})$ have been found (by the Hylleraas-Undheim construction [11], for example) that are sufficiently accurate to give binding, that is, which provide a $p\times p$ diagonal matrix representation of $h(n)$ with ordered eigenvalues $\varepsilon_{\gamma t}$ all less than zero. The definition (2.4) is then replaced with

$$\hat{h}(n)=h(n)-\sum_{\gamma=1}^{p}\frac{h(n)|\chi_{\gamma t}(\bar{n})\rangle\langle\chi_{\gamma t}(\bar{n})|h(n)}{\langle\chi_{\gamma t}(\bar{n})|h(n)|\chi_{\gamma t}(\bar{n})\rangle}. \tag{2.5}$$

It has been shown [2] that with the energy $\overline{\varepsilon_{p+1}}$ determined to satisfy

$$\overline{\varepsilon_{p+1}}\leqslant\frac{\varepsilon_1}{\varepsilon_{1t}}\frac{\varepsilon_2}{\varepsilon_{2t}}\cdots\frac{\varepsilon_p}{\varepsilon_{pt}}\varepsilon_{p+1}, \tag{2.6}$$

the operator $\hat{h}(n)-\overline{\varepsilon_{p+1}}$ is non-negative. (We assume that $\overline{\varepsilon_{p+1}}$ lies above ε_{pt}.) This suggests that we introduce the modified Hamiltonian

$$\hat{H}=H-\sum_{n=1}^{N+1}\sum_{\gamma=1}^{p}\frac{h(n)|\chi_{\gamma t}(\bar{n})\rangle\langle\chi_{\gamma t}(\bar{n})|h(n)}{\langle\chi_{\gamma t}(\bar{n})|h(n)|\chi_{\gamma t}(\bar{n})\rangle}. \tag{2.7}$$

From an examination of the asymptotic solutions of the Schrödinger equation associated with this Hamiltonian, one sees that the threshold of the continuous spectrum of $\hat{H}$ lies above $\overline{\varepsilon_{p+1}}$. It follows that if $\hat{H}$ has no discrete states below E (we briefly discuss the more general case below) then the operator inequality $\hat{H}-E>0$ is satisfied for scattering energies $E<\overline{\varepsilon_{p+1}}$. This is the key property in the development of the minimum principle. To simplify notation in the following we work, formally, with exact target wave functions with the understanding that in an actual calculation trial target functions are employed, with the modified Hamiltonian given by Eq. (2.7).

We now show how the scattering problem may be reformulated in such a way that virtual excitations of the system are described in terms of the modified Hamiltonian $\hat{H}$ introduced above. The scattering wave function corresponding to an incident channel with index ν is represented as

$$\Psi_\nu(1,2,\ldots,N+1)=\mathscr{A}\sum_\gamma\chi_\gamma(\bar{1})f_{\gamma\nu}(1)+M_\nu(1,2,\ldots,N+1), \tag{2.8}$$

where the residual antisymmetrizer $\mathscr{A}$ is defined by the relation

$$\mathscr{A}\chi(\bar{1})f(1)=\sum_{n=1}^{N+1}(-1)^{n+1}\chi(\bar{n})f(n). \tag{2.9}$$

The function $f_{\gamma\nu}(n)$ in Eq. (2.8) is a one-body radial wave function for electron n propagating in channel γ, and the normalizable, completely antisymmetric, function M_ν contains the effects of virtual excitations. While not indicated explicitly, the product $\chi_\gamma f_{\gamma\nu}$ is to be understood as a vector-coupled product combining the orbital and spin angular momenta of the target and projectile to give a state of definite total orbital angular momentum and spin, along with their projections [12]. The channel index γ now stands for all the quantum numbers of the system, not only that which labels the energy level of the target.

The wave function represented in Eq. (2.8) satisfies the Schrödinger equation

$$
\begin{aligned}
0=(H-E)|\Psi_\nu\rangle=&\sum_n \sum_\gamma (-1)^{n+1}\\
&\times[V(n)+K(n)-E_\gamma]|\chi_\gamma(\bar{n})\rangle|f_{\gamma\nu}(n)\rangle\\
&+(\hat{H}-E)|M_\nu\rangle+\sum_n \sum_\gamma \varepsilon_\gamma|\chi_\gamma(\bar{n})\rangle\langle\chi_\gamma(\bar{n})|M_\nu\rangle,
\end{aligned}
\tag{2.10}
$$

where $E_\gamma = E-\varepsilon_\gamma$ is the energy available to the projectile in channel γ. In line with remarks made above, the target wave functions have been taken to be exact, with the understanding that the modified Hamiltonian will be replaced by the form (2.7) in calculations. To find a formal solution to Eq. (2.10) we first write down an equation to be satisfied by M_ν, for which approximate solutions may be obtained with the aid of a subsidiary minimum principle, and then deduce the coupled equations to be satisfied by the one-body scattering functions $f_{\gamma\nu}$. Based on considerations of simplicity for the form of the effective potential that emerges from this analysis, we make the choice

$$
(\hat{H}-E)M_\nu=-\sum_n \sum_\gamma (-)^{n+1}\hat{V}(n)\chi_\gamma(\bar{n})f_{\gamma\nu}(n), \tag{2.11}
$$

where

$$
\hat{V}(n)=\hat{H}-\hat{h}(n)-K(n). \tag{2.12}
$$

Combining Eqs. (2.10)–(2.12), we have

$$
\begin{aligned}
0=&\sum_n \sum_\gamma (-1)^{n+1}[V(n)-\hat{V}(n)+K(n)-E_\gamma]\\
&\times|\chi_\gamma(\bar{n})\rangle|f_{\gamma\nu}(n)\rangle+\sum_n \sum_\gamma \varepsilon_\gamma|\chi_\gamma(\bar{n})\rangle\langle\chi_\gamma(\bar{n})|M_\nu\rangle;
\end{aligned}
\tag{2.13}
$$

the relation

$$
V(n)-\hat{V}(n)=\sum_{n'\neq n} \sum_\gamma \varepsilon_\gamma|\chi_\gamma(\bar{n}')\rangle\langle\chi_\gamma(\bar{n}')|, \tag{2.14}
$$

which follows from the definition (2.12), will be useful in what follows.

As the final step in the derivation we write the formal solution of Eq. (2.11) as

$$
M_\nu=\hat{G}(E)\sum_n \sum_\gamma (-1)^{n+1}\hat{V}(n)\chi_\gamma(\bar{n})f_{\gamma\nu}(n), \tag{2.15}
$$

where $\hat{G}(E)=(E-\hat{H})^{-1}$ is the Green's function associated with the modified Hamiltonian, and insert it into Eq. (2.13). The result is evaluated with the aid of the resolvent equation

$$
\begin{aligned}
(E-\hat{H})^{-1}=&[E-\hat{h}(n)-K(n)]^{-1}\\
&+[E-\hat{h}(n)-K(n)]^{-1}\\
&\times\hat{V}(n)(E-\hat{H})^{-1},
\end{aligned}
\tag{2.16}
$$

which is used, along with the eigenvalue equation for $\hat{h}(n)$ noted above, to deduce the relation

$$
\langle\chi_\gamma(\bar{n})|\hat{G}(E)=\frac{1}{E-K(n)}\langle\chi_\gamma(\bar{n})|[1+\hat{V}(n)\hat{G}(E)]. \tag{2.17}
$$

Consider now the result obtained by replacing $V(n)-\hat{V}(n)$ in Eq. (2.13) by the expression given in Eq. (2.14). It proves useful to transform this result by writing

$$
\begin{aligned}
&\sum_{\gamma,\gamma'} \sum_n \sum_{n'} (-1)^{n+1}(1-\delta_{nn'})|\chi_\gamma(\bar{n}')\rangle\\
&\qquad\times\langle\chi_\gamma(\bar{n}')|\chi_{\gamma'}(\bar{n})\rangle|f_{\gamma'\nu}(n)\rangle\\
&\quad=\sum_n \sum_{\gamma,\gamma'} |\chi_\gamma(\bar{n})\rangle\langle\chi_\gamma(\bar{n})|[\mathscr{A}|\chi_{\gamma'}(\overline{1})\rangle|f_{\gamma'\nu}(1)\rangle\\
&\qquad-(-1)^{n+1}|\chi_{\gamma'}(\bar{n})\rangle|f_{\gamma'\nu}(n)\rangle],
\end{aligned}
\tag{2.18}
$$

where the right-hand member was obtained by interchanging indices n and n'. In addition, the Dirac-ket version of Eq. (2.9) has been applied. At this stage the Schrödinger equation has the structure

$$
\sum_n \sum_\gamma |\chi_\gamma(\bar{n})\rangle|L_\gamma(n)\rangle=0,
$$

which, owing to the identity of the particles, can be satisfied by setting *each* of the vectors $|L_\gamma(n)\rangle$ equal to zero. The relation $|L_\gamma(1)\rangle=0$ provides us with the coupled one-body wave equations

$$
[K(1)-E_\alpha]|f_{\alpha\nu}(1)\rangle+\frac{\varepsilon_\alpha}{E-K(1)}\sum_\gamma \mathscr{V}_{\alpha\gamma}(E)|f_{\gamma\nu}(1)\rangle=0, \tag{2.19}
$$

where

$$
\begin{aligned}
\mathscr{V}_{\alpha\gamma}(E)|f_{\gamma\nu}(1)\rangle=&\langle\chi_\alpha(\overline{1})|\{\mathscr{A}\hat{V}(1)+[E-K(1)](\mathscr{A}-1)\\
&+\hat{V}(1)\hat{G}(E)\mathscr{A}\hat{V}(1)\}|\chi_\gamma(\overline{1})\rangle|f_{\gamma\nu}(1)\rangle.
\end{aligned}
\tag{2.20}
$$

To obtain a manifestly Hermitian form for the effective potential, we make use of the relation $\hat{G}(E)=(N+1)^{-1}\mathscr{A}\hat{G}(E)$, which holds since the resolvent has an eigenfunction expansion involving totally antisymmetric states. We may then express the effective-potential operator as

$$
\begin{aligned}
\mathscr{V}_{\alpha\gamma}(E)=&\langle\chi_\alpha(\overline{1})|\{\mathscr{A}\hat{V}(1)+[E-K(1)](\mathscr{A}-1)\\
&+(N+1)^{-1}\hat{V}(1)\mathscr{A}\hat{G}(E)\mathscr{A}\hat{V}(1)\}|\chi_\gamma(\overline{1})\rangle.
\end{aligned}
\tag{2.21}
$$

B. Reaction matrix

It will be convenient to convert Eq. (2.19) to an integral equation, in a representation in which the operator K is diagonal. Toward this end we introduce a complete set of (discrete and continuum) solutions of the homogeneous radial equation $(K-E)F(E,r)=0$ for the lth partial wave (the index l is suppressed), where

$$K=-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}-\frac{ze^2}{r}+\frac{\hbar^2 l(l+1)}{2mr^2} \tag{2.22}$$

and $z=Z-N$. With the continuum solutions normalized on the energy scale, they have the asymptotic form

$$F\left(\frac{\hbar^2k^2}{2m},r\right)\sim\left(\frac{2m}{\hbar^2\pi k}\right)^{1/2}\sin(kr-l\pi/2-\eta\ \ln 2kr+\sigma), \tag{2.23}$$

with

$$\eta=-1/ka,\quad a=\hbar^2/me^2z,\quad \sigma=\arg\Gamma(l+1+i\eta). \tag{2.24}$$

The integral equation for the one-body wave function may be written as

$$f_{\alpha\nu}(r)=F(E_\alpha,r)\delta_{\alpha\nu}+\sum_\gamma\int_0^\infty dr'\int_0^\infty dr''\mathcal{G}(r,r';E_\alpha)\times\mathcal{V}_{\alpha\gamma}(r',r'';E)f_{\gamma\nu}(r''). \tag{2.25}$$

The propagator has the eigenfunction expansion

$$\mathcal{G}(r,r';E_\alpha)=P\int dE'\frac{F(E',r)F(E',r')}{E_\alpha-E'}\frac{\varepsilon_\alpha}{E-E'}, \tag{2.26}$$

where the generalized energy integral is understood to include a sum over discrete states, and the singularity at $E_\alpha-E'=0$ is treated by the principal-value prescription. The (somewhat unconventional) factor $\varepsilon_\alpha/(E-E')$ is unity at the singularity so that, while it modifies the off-shell extension of the wave function, it can be ignored in evaluating the asymptotic behavior of the wave function and hence the determination of the physical reaction matrix $R_{\alpha\nu}$. Following standard methods, we obtain the identity

$$R_{\alpha\nu}(E_\alpha,E_\nu;E)=\sum_\gamma\int_0^\infty dr\int_0^\infty dr' F(E_\alpha,r)\times\mathcal{V}_{\alpha\gamma}(r,r';E)f_{\gamma\nu}(r'). \tag{2.27}$$

After a single iteration using Eq. (2.26), we arrive at an integral equation for the off-shell reaction matrix of the form

$$\begin{aligned}R_{\alpha\nu}(E_\alpha,E_\nu;E)={}&R^{\rm Born}_{\alpha\nu}(E_\alpha,E_\nu;E)\\&+\sum_\gamma\int dE' R^{\rm Born}_{\alpha\gamma}(E_\alpha,E';E)\\&\times P\frac{1}{E_\gamma-E'}\frac{\varepsilon_\gamma}{E-E'}R_{\gamma\nu}(E',E_\nu;E).\end{aligned} \tag{2.28}$$

The leading term $R^{\rm Born}_{\alpha\nu}$ is obtained from Eq. (2.27) by replacing the exact solution $f_{\gamma\nu}(r')$ on the right-hand side by its Born approximation $F(E_\gamma,r')\delta_{\gamma\nu}$. Here again the integration over energies is meant to include a sum over discrete eigenstates of K. Such discrete-state contributions can be accounted for in an approximate but highly accurate manner in numerical solutions of integral equations of this type, in which the continuum itself is replaced by a sequence of discrete states [5].

C. Minimum principle

We now briefly review a variational procedure, based on a subsidiary minimum principle, for evaluating the resolvent $\hat{G}(E)$ appearing in the definition (2.21) of the effective potential. One introduces a trial resolvent $\hat{G}_t(E)$ and resolvent identity

$$\hat{G}(E)=\hat{G}_t(E)+\hat{G}(E)[(\hat{H}-E)\hat{G}_t(E)+1]. \tag{2.29}$$

By writing $\hat{G}=\hat{G}_t+\Delta\hat{G}$ on the right-hand side, the identity takes the form of the sum of the variational approximation

$$\hat{G}_v=2\hat{G}_t+\hat{G}_t(\hat{H}-E)\hat{G}_t \tag{2.30}$$

and a second-order error term; one finds that

$$\hat{G}=\hat{G}_v+\Delta\hat{G}(E-\hat{H})\Delta\hat{G}. \tag{2.31}$$

With the energy assumed to lie below the minimum eigenvalue of the modified Hamiltonian $\hat{H}$, the error term in the resolvent will be a negative operator. Replacement of the exact resolvent in Eq. (2.21) by the variational approximation $\hat{G}_v$ provides us with a minimum principle for the effective potential and a prescription for a variational construction of the reaction matrix [13]. If, for example, the trial resolvent is chosen as

$$\hat{G}_t=\sum_i c_i|\Phi_i\rangle\langle\Phi_i|, \tag{2.32}$$

where the Φ_i form an orthonormal set of trial functions, and the linear parameters c_i are chosen variationally, Eq. (2.30) becomes

$$\hat{G}_v(E)=\sum_i|\Phi_i\rangle\frac{1}{\langle\Phi_i|E-\hat{H}|\Phi_i\rangle}\langle\Phi_i|. \tag{2.33}$$

The trial functions may be improved systematically by minimization of diagonal elements of the variational expression for the effective potential. If the modified Hamiltonian has one or more discrete states with eigenenergy below E, the minimum principle must be modified; the subtraction procedure that may be used to arrive at this modified version has been described elsewhere [2]. Here we merely remark that this procedure leads not only to a valid minimum principle but also to a description of resonances of the "closed-channel" type [4].

Single-channel scattering in a given partial wave is characterized by a real phase shift. The utility of the minimum principle is greatly enhanced by a removal of the ambiguity with regard to multiples of π in the determination of the phase shift. In this regard an absolute determination of the phase shift at zero energy (coupled with the assumption of continuity in the energy variable) can be helpful. Levinson's theorem provides such an absolute determination for scattering potentials of short range. The extension to the case where the potential has an attractive Coulomb tail is discussed below.

III. ABSOLUTE DETERMINATION OF THE PHASE SHIFT: LEVINSON-SEATON THEOREM

We consider the single-channel scattering of an electron of zero energy by a positive ion. We wish to establish the relation $\delta(0)=\mu(\infty)\pi$ between the zero-energy phase shift (relative to the Coulomb phase) and the limiting value of the quantum defect, thereby obtaining the multiparticle generalization of a result derived earlier for potential scattering [10]. As remarked above, such a Levinson-type theorem, of interest in its own right, would provide a reference value for the phase shift, thus removing the ambiguity with regard to multiples of π, and this can be helpful in analyzing results of numerical calculations of the phase shift. The basis for the analysis is most conveniently taken to be the integrodifferential equation (2.19), subjected to the transformations

$$f_{\gamma\nu}=\left(\frac{\varepsilon_{\gamma}}{E-K}\right)^{1/2}\tilde{f}_{\gamma\nu};$$

$$\tilde{\mathscr{V}}_{\alpha\gamma}(E)=\left(\frac{\varepsilon_{\alpha}}{E-K}\right)^{1/2}\mathscr{V}_{\alpha\gamma}(E)\left(\frac{\varepsilon_{\gamma}}{E-K}\right)^{1/2}. \tag{3.1}$$

Note that (in accordance to an earlier observation) while the off-shell extensions of the wave functions and potentials are changed by this transformation, the physical scattering parameters are unaltered since the factors introduced are unity on the energy shell. With channel labels dropped, and with the scattering energy set at the threshold value ε corresponding to the target in its ground state, the scattering equation becomes

$$K\tilde{f}(r)+\int_0^{\infty}\tilde{\mathscr{V}}(r,r';\varepsilon)\tilde{f}(r')dr'=0. \tag{3.2}$$

The solution, consistent with the normalization established above, behaves asymptotically as

$$\tilde{f}(r)\sim(r/a^2z^2R)^{1/2}\{J_{2l+1}[(8r/a)] -\tan\delta(0)Y_{2l+1}[(8r/a)]\}, \tag{3.3}$$

where J_{2l+1} and Y_{2l+1} are Bessel functions of the first and second kinds, respectively, and $R=me^4/2\hbar^2$. We now consider a class of solutions $\tilde{f}(\lambda,r)$ corresponding to the introduction of a potential-strength parameter λ. Associated with these solutions is a family of phase shifts $\delta(0,\lambda)$. The definition of the phase shift adopted here is such that $\delta(0,\lambda)$ is a continuous function of λ with $\delta(0,0)=0$ and $\delta(0,1)\equiv\delta(0)$. The version of Eq. (3.2) that we study is, in operator notation,

$$[K+\lambda\tilde{\mathscr{V}}(\varepsilon)]\tilde{f}(\lambda)=0. \tag{3.4}$$

With the replacement $\lambda\rightarrow\lambda+d\lambda$, Eq. (3.4) becomes

$$[K+(\lambda+d\lambda)\tilde{\mathscr{V}}(\varepsilon)]\tilde{f}(\lambda+d\lambda)=0. \tag{3.5}$$

A standard manipulation is now employed, in which Eq. (3.4) is premultiplied by $\tilde{f}(\lambda+d\lambda)$, Eq. (3.5) is premultiplied by $\tilde{f}(\lambda)$, an integration is performed, and the two equations are subtracted. A partial integration is carried out in the term containing the kinetic energy, taking into account the asymptotic form (3.3), and the Hermiticity property of the effective potential $\mathscr{V}(\varepsilon)$ is invoked. The resultant relation, correct to first order in $d\lambda$, is

$$\tan\,\delta(0,\lambda+d\lambda)-\tan\,\delta(0,\lambda)=-\pi d\lambda\langle\tilde{f}(\lambda)|\tilde{\mathscr{V}}(\varepsilon)|\tilde{f}(\lambda)\rangle, \tag{3.6}$$

where we use the notation

$$\langle\tilde{f}(\lambda)|\tilde{\mathscr{V}}(\varepsilon)|\tilde{f}(\lambda)\rangle =\int_0^{\infty}dr\int_0^{\infty}dr'\tilde{f}(\lambda,r)\tilde{\mathscr{V}}(r,r';\varepsilon)\tilde{f}(\lambda,r'). \tag{3.7}$$

Alternatively, we may write, in the limit $d\lambda\rightarrow 0$,

$$\frac{1}{\pi}\frac{d\delta(0,\lambda)}{d\lambda}=-\langle\varphi(0,\lambda)|\mathscr{V}(\varepsilon)|\varphi(0,\lambda)\rangle, \tag{3.8}$$

in terms of the wave function $\varphi(0,\lambda,r)=\tilde{f}(\lambda,r)\cos\,\delta(0,\lambda)$. This latter function is recognized [9] as the zero-energy limit of the positive-energy continuum wave function normalized according to

$$\int_0^{\infty}\varphi(E',\lambda,r)\varphi(E,\lambda,r)dr=\delta(E'-E). \tag{3.9}$$

A closely analogous treatment may be given for the bound-state problem, defined by the eigenvalue equation

$$K\varphi_n(\lambda)+\lambda\tilde{\mathscr{V}}[E_n(\lambda)+\varepsilon]\varphi_n(\lambda)=E_n(\lambda)\varphi_n(\lambda), \tag{3.10}$$

for the energy $E_n(\lambda)$, measured relative to the continuum threshold energy, as a function of the potential-strength parameter; the energy eigenfunction is assumed to be normalized to unity. A similar equation may be written down with λ replaced by $\lambda+d\lambda$. After performing the standard manipulation of these two equations, making use of the fact that both the kinetic-energy and potential-energy operators are Hermitian, we obtain the relation

$$\langle \varphi_n(\lambda + d\lambda)|\lambda\tilde{\mathscr{V}}[E_n'(\lambda)]|\varphi_n(\lambda)\rangle - \langle \varphi_n(\lambda)|(\lambda + d\lambda)\tilde{\mathscr{V}}[E_n'(\lambda + d\lambda)]|\varphi_n(\lambda + d\lambda)\rangle$$
$$= [E_n(\lambda) - E_n(\lambda + d\lambda)]\langle \varphi_n(\lambda)|\varphi_n(\lambda + d\lambda)\rangle. \quad (3.11)$$

For brevity we have expressed the total energy of the system, appearing as the energy argument of the effective potential, as $E_n'(\lambda) = E_n(\lambda) + \varepsilon$. To first order in $d\lambda$, Eq. (3.11) becomes

$$\langle \varphi_n(\lambda)|\left\{ \tilde{\mathscr{V}}[E_n'(\lambda)] + \lambda \frac{\partial \tilde{\mathscr{V}}[E_n'(\lambda)]}{\partial \lambda} \right\}|\varphi_n(\lambda)\rangle = \frac{dE_n(\lambda)}{d\lambda}. \quad (3.12)$$

We now write $E_n(\lambda) = -z^2R/n^{*2}$, where the effective quantum number is defined as $n^*(\lambda) = n - \mu(n,\lambda)$. The quantum defect $\mu(n,\lambda)$ is taken to be a continuous function of λ with $\mu(n,0)=0$ and $\mu(\infty,1)=\mu(\infty)$. With the energy represented in this way, we have

$$\frac{dE_n(\lambda)}{d\lambda} = \frac{2z^2R}{n^{*3}} \frac{d\mu(n,\lambda)}{d\lambda}, \quad (3.13)$$

so that Eq. (3.12) becomes

$$\frac{d\mu(n,\lambda)}{d\lambda} = -\frac{\langle \varphi(E_n,\lambda)|\tilde{\mathscr{V}}[E_n'(\lambda)]|\varphi(E_n,\lambda)\rangle}{1 - \lambda \dfrac{2z^2R}{n^{*3}} \left\langle \varphi(E_n,\lambda)\left|\dfrac{\partial \tilde{\mathscr{V}}(E)}{\partial E}\right|\varphi(E_n,\lambda)\right\rangle\Bigg|_{E=E_n'(\lambda)}}. \quad (3.14)$$

Here we have introduced the renormalized state vector

$$|\varphi(E_n,\lambda)\rangle = \left(\frac{n^{*3}}{2z^2R}\right)^{1/2} |\varphi_n(\lambda)\rangle \quad (3.15)$$

that in the limit $n\rightarrow\infty$ passes smoothly into the energy-normalized zero-energy continuum state $|\varphi(0,\lambda)\rangle$ [9]. In that limit the numerator on the right-hand side of Eq. (3.14) becomes $\langle\varphi(0,\lambda)|\tilde{\mathscr{V}}(\varepsilon)|\varphi(0,\lambda)\rangle$. With the assumption that this matrix element and its energy derivative are finite, it follows that the denominator in Eq. (3.14) goes to unity and we arrive at the relation

$$\frac{d\mu(\infty,\lambda)}{d\lambda} = -\langle \varphi(0,\lambda)|\tilde{\mathscr{V}}(\varepsilon)|\varphi(0,\lambda)\rangle. \quad (3.16)$$

Comparison with Eq. (3.8) shows that

$$\frac{d}{d\lambda}\left[\frac{1}{\pi}\delta(0,\lambda) - \mu(\infty,\lambda)\right] = 0. \quad (3.17)$$

After integrating this relation with respect to λ between zero and 1, and recalling the definitions of the phase shift and quantum defect at these limits, we find that

$$\delta(0) = \mu(\infty)\pi, \quad (3.18)$$

a relation that provides an absolute determination of the phase shift, as defined using standard scattering theory, and that contains within it the well-known result $\delta(0)(\mathrm{mod}\ \pi) = \mu(\infty)\pi$ of quantum-defect theory.

IV. DISCUSSION

It has long been understood that there are useful consequences arising from the fundamental connection that exists between low-energy scattering and bound-state dynamics. An absolute determination of the partial-wave phase shift at zero energy based on Levinson's theorem (relating the zero-energy phase shift in a given partial wave to the number of bound states of the same angular momentum) can, by extrapolation in the energy variable, be helpful in an analysis of low-energy scattering. Another aspect of this connection is the applicability of calculational methods of the Rayleigh-Ritz type as an aid in the variational determination of scattering parameters for energies below the ionization threshold. Interestingly, the minimum principle for the scattering length has provided a formal tool for the extension of Levinson's theorem to scattering by a compound system, with the effects of the Pauli principle properly accounted for [8]. A straightforward generalization of the result of Ref. [8] to electron scattering by positive ions is not possible owing to the existence of an infinite series of bound states of the electron-ion system converging at the continuum threshold. Moreover, such an absolute determination of the zero-energy phase shift must be consistent with Seaton's theorem [9] relating this phase, modulo π, to the quantum defect parameter evaluated at threshold. In the approach adopted here, a theorem of the Levinson-Seaton type has been derived through a formal conversion of the multiparticle Schrödinger equation into an equivalent one-body system defined by an energy-dependent, nonlocal effective potential from which the long-range attractive Coulomb tail has been separated off. It was then possible to arrive at the result, shown in Eq. (3.18), by suitable modification of a method used earlier in a treatment of the problem of scattering by a purely local one-body potential [10]. The effective potential is not unique; one can have different extensions off the energy shell leading, through a solution of the Lippmann-Schwinger integral equation, to the same physical scattering parameters. The particular choice made here (distinct from that obtained in the Feshbach formulation, a version that can be difficult to implement in practice) has the merit of allowing for a variational construction in which trial functions can be systematically improved with the aid of a minimum principle of the Rayleigh-Ritz type, applicable even in the presence of a Rydberg series accumulating at threshold. The validity of the minimum principle depends on the availability of trial target wave functions sufficiently accurate to give binding. Since these target functions need not be known exactly, the method is not restricted to scattering by hydrogenlike ions—the essential requirement is that breakup of a two-cluster scattering system into three or more subsystems be energetically forbidden. This variational approach can provide an effective supplement to existing calculational methods, allowing for the use of flexible trial functions to account for the strong, long-range multiparticle correlations that are often encountered in studies of scattering at low energies.

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