

Generalized Hartree-Fock method for electron-atom scattering

Leonard Rosenberg

Department of Physics, New York University, New York, New York 10003

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In the widely used Hartree-Fock procedure for atomic structure calculations, trial functions in the form of linear combinations of Slater determinants are constructed and the Rayleigh-Ritz minimum principle is applied to determine the best in that class. A generalization of this approach, applicable to low-energy electron-atom scattering, is developed here. The method is based on a unique decomposition of the scattering wave function into open- and closed-channel components, so chosen that an approximation to the closed-channel component may be obtained by adopting it as a trial function in a minimum principle, whose rigor can be maintained even when the target wave functions are imprecisely known. Given a closed-channel trial function, the full scattering function may be determined from the solution of an effective one-body Schrödinger equation. Alternatively, in a generalized Hartree-Fock approach, the minimum principle leads to coupled integrodifferential equations to be satisfied by the basis functions appearing in a Slater-determinant representation of the closed-channel wave function; it also provides a procedure for optimizing the choice of nonlinear parameters in a variational determination of these basis functions. Inclusion of additional Slater determinants in the closed-channel trial function allows for systematic improvement of that function, as well as the calculated scattering parameters, with the possibility of spurious singularities avoided. Electron-electron correlations can be important in accounting for long-range forces and resonances. These correlation effects can be included explicitly by suitable choice of one component of the closed-channel wave function; the remaining component may then be determined by the generalized Hartree-Fock procedure. As a simple test, the method is applied to s -wave scattering of positrons by hydrogen. [S1050-2947(97)01509-6]

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I. INTRODUCTION

Well established procedures exist for the calculation of electron-atom scattering parameters based on the use of Slater determinants to represent wave functions, for both the target and the full scattering system [1–3]. At the simplest level, a continuum projectile wave function is combined with the Hartree-Fock target wave function and is determined with the aid of the Kohn variational principle. In a more ambitious procedure [2] one attempts to account for virtual excitations of the target by adding to the open-channel component of the wave function a Slater determinant (or a sum of such determinants). Each single-particle function appearing in the antisymmetrized product is represented as a superposition of Slater orbitals, with the linear expansion coefficients then determined by applying the Kohn variational principle.

Here we propose an alternative procedure, one which stays closer to the original Hartree-Fock strategy, which is to find the “best” Slater determinant. This leads to a set of coupled integrodifferential equations for the single-particle wave functions which must be solved self-consistently. Experience gained in the solution of similar sets of equations appearing in the analogous bound-state problem should be helpful in this task. Specifically, we recall that the Rayleigh-Ritz minimum principle plays a useful role in determining the single-particle Hartree-Fock bound-state wave functions, represented as a superposition of Slater orbitals, by providing a criterion for making the optimum choice of nonlinear variational parameters appearing in these orbitals [4]. An analogous minimum principle is available for the scattering problem and we base our approach on this principle; it has

recently been extended to account for antisymmetrization explicitly and to include scattering of electrons by positive ions [5]. It is reasonable to expect that by optimizing the basis functions for the scattering problem at hand, rather than working with predetermined Hartree-Fock bound-state orbitals, better convergence properties can be attained. Since the minimum principle determines the best trial function in a given set, convergence is monotonic, the calculated phase shifts increasing steadily as the trial function is made more flexible. In particular, such calculations are free of the near-singularity difficulties that can arise (unless special measures are taken to avoid them [2]) in applications of the Kohn principle.

The scattering formalism which provides the basis for the minimum principle and for the development of the generalized Hartree-Fock method is reviewed in Sec. II. The use of Slater determinants to represent the closed-channel component of the wave function is described in Sec. III, along with an iterative procedure for generating approximations of steadily increasing accuracy. Modifications of the method designed to account explicitly for the effects of long-range polarization forces and of resonant interactions, within the context of the generalized Hartree-Fock approach, are presented in Sec. IV. An application of the method to positron-hydrogen scattering is described in Sec. V. Results are summarized in a concluding section.

II. SCATTERING FORMALISM

The essential limitation of the method to be described is that the scattering energy must lie below the ionization threshold. Additional restrictions are introduced here to sim-

ply the presentation. We confine the present discussion to the scattering of an electron by a target consisting of N electrons bound to a fixed nucleus of charge $Z|e|$, which in the LS coupling scheme has zero orbital angular momentum and spin S_T . Single-channel scattering is assumed, with the more general multichannel problem discussed in the Appendix. The target ground-state wave function χ_T , normalized to unity, is coupled to the spin function of the projectile to produce a function χ having well-defined total spin and spin projection. We use the notation

$$\chi_T(\bar{n}; S_T, M_T) = \chi_T(1, 2, \dots, n-1, n+1, \dots, N+1; S_T, M_T) \quad (2.1)$$

to denote the antisymmetrized target function, with the symbol j representing the space and spin coordinates of the j th particle, for the system from which the n th electron has been removed. The function $\chi(\bar{n}) = \chi(1, 2, \dots, n-1, n+1, \dots, N+1)$ represents the result of coupling the spin of the target with that of the n th electron; the resultant spin quantum numbers are suppressed in this notation. [For states with the same spin quantum numbers the normalization condition $\langle \chi(\bar{n}) | \chi(\bar{n}) \rangle = 1$ holds, with the understanding that integrations range over the spatial coordinates of the target and sums over *all* spins are taken.] The eigenvalue equation for the target in its ground state is

$$h(n) | \chi(\bar{n}) \rangle = \epsilon | \chi(\bar{n}) \rangle, \quad (2.2)$$

and the Schrödinger equation for the full scattering system is $(H-E)\Psi=0$, with the total energy E taken here to lie below the first excitation threshold. It will be convenient to decompose the Hamiltonian as

$$H = K(n) + V(n) + h(n), \quad (2.3a)$$

where $K(n)$ represents the sum of the kinetic energy of the n th electron and its monopole Coulomb interaction with the residual system, whose Hamiltonian is $h(n)$. This leaves $V(n)$ to represent the interaction, with the monopole Coulomb component removed, of the n th electron with the residual system; thus

$$V(1) = -\frac{Ne^2}{r_1} + \sum_{j \neq 1}^{N+1} \frac{e^2}{r_{1j}}. \quad (2.3b)$$

We look for the scattering wave function in the form

$$\Psi(1, 2, \dots, N+1) = \mathcal{A} \chi(\bar{1}) f(1) + M(1, 2, \dots, N+1), \quad (2.4)$$

with the residual antisymmetrizer defined, in terms of the operator P_{ij} that interchanges the space and spin coordinates of the pair ij , as

$$\mathcal{A} = 1 - \sum_{j=2}^{N+1} P_{1j}. \quad (2.5)$$

The proper antisymmetrization of the scattering function in Eq. (2.4) is verified using the relation $P_{1j} \chi(\bar{1}) f(1) = (-1)^j \chi(\bar{j}) f(j)$, with the closed-channel function M assumed to be completely antisymmetric.

Since the function M , which describes virtual excitations of the system, is asymptotically decaying one might expect that it satisfies an equation involving a modified Hamiltonian whose continuous spectrum lies above the scattering energy E . This is indeed the case, and it provides the basis for the introduction of a minimum principle applicable to the approximate evaluation of this function. The modified Hamiltonian is

$$\hat{H} = H - \sum_{n=1}^{N+1} W(\bar{n}) \quad (2.6a)$$

with

$$W(\bar{n}) = \sum_{M_T} \left(\frac{h(n) | \chi_T(\bar{n}; S_T, M_T) \rangle \langle \chi_T(\bar{n}; S_T, M_T) | h(n)}{\langle \chi_T(\bar{n}; S_T, M_T) | h(n) | \chi_T(\bar{n}; S_T, M_T) \rangle} \right). \quad (2.6b)$$

This form for $W(\bar{n})$ is simplified by application of the target eigenvalue equation. However, when χ_T is replaced by a trial function, as required in general, the form given above is to be employed. It has been shown that with this version of the modified Hamiltonian \hat{H} adopted, its continuous spectrum lies at an energy that approaches the target excitation threshold as the accuracy of the trial target wave function is increased, in which case, for trial functions of sufficient accuracy and for a range of energies E in the elastic scattering region, the operator $\hat{H} - E$ will be positive [6]. To simplify the following development of the formalism, the target function will be assumed to be exact.

We look for the function M as the solution of the inhomogeneous equation

$$(\hat{H} - E)M = -J, \quad (2.7)$$

where

$$J = \mathcal{A} \hat{V}(1) \chi(\bar{1}) f(1), \quad (2.8)$$

and

$$\hat{V}(1) = V(1) - \sum_{n \neq 1} W(\bar{n}). \quad (2.9)$$

With this choice the Schrödinger equation reduces, after a brief calculation, to

$$\mathcal{A} \left[E - \epsilon - K(1) - \sum_{n' \neq 1} W(\bar{n}') \right] \chi(\bar{1}) f(1) = \sum_{n=1}^{N+1} W(\bar{n}) M. \quad (2.10)$$

It will now be shown that this equation will be satisfied provided the relation

$$\begin{aligned} & [E - \epsilon - K(1)] \chi(\bar{1}) f(1) + W(\bar{1}) \sum_{n \neq 1} (-1)^n \chi(\bar{n}) f(n) \\ & = W(\bar{1}) M \end{aligned} \quad (2.11)$$

holds. This is accomplished by making $N-1$ copies of Eq. (2.11), obtained by applying the interchange operators $P_{12}, P_{13}, \dots, P_{1N}$ successively and making use of the anti-

symmetry property of the functions χ and M . In this way we obtain N equations of the form

$$(-1)^{n+1}[E - \epsilon - K(n)]\chi(\bar{n})f(n) + W(\bar{n}) \times \sum_{n' \neq n} (-1)^{n'} \chi(\bar{n}')f(n') = W(\bar{n})M. \quad (2.12)$$

It remains to show that by adding these equations the original equation (2.10) is regained. This is readily accomplished with the aid of the relations

$$\sum_{n=1}^{N+1} (-1)^{n+1}[E - \epsilon - K(n)]\chi(\bar{n})f(n) = \mathcal{A}[E - \epsilon - K(1)]\chi(\bar{1})f(1) \quad (2.13)$$

and

$$\sum_{n=1}^{N+1} W(\bar{n}) \sum_{n' \neq n} \chi(\bar{n}')f(n')(-1)^{n'} = -\mathcal{A} \sum_{n \neq 1} W(\bar{n})\chi(\bar{1})f(1). \quad (2.14)$$

With Eq. (2.11) thus established we project each side onto the target state $\langle \chi(\bar{1}) |$ and make use of the eigenvalue equation (2.2) and the relation $\langle \chi(\bar{1}) | W(\bar{1}) = \epsilon \langle \chi(\bar{1}) |$; in this way we obtain the equivalent single-particle wave equation

$$[K(1) - E + \epsilon]|f(1)\rangle + \epsilon \langle \chi(\bar{1}) | (\mathcal{A} - 1) | \chi(\bar{1}) \rangle |f(1)\rangle + \epsilon \langle \chi(\bar{1}) | M \rangle = 0. \quad (2.15)$$

An alternative version of this equation is often useful. We first note that from Eqs. (2.3a), (2.6a), and (2.9) we have

$$\hat{H} = \hat{h}(1) + K(1) + \hat{V}(1) \quad (2.16)$$

with $\hat{h}(1) = h(1) - W(\bar{1})$ and $\langle \chi(\bar{1}) | \hat{h}(1) = 0$. With these relations in mind we may evaluate the result of projecting both sides of Eq. (2.7) onto the state $\langle \chi(\bar{1}) |$; we find that $[E - K(1)]\langle \chi(\bar{1}) | M \rangle - \langle \chi(\bar{1}) | \hat{V}(1) | M \rangle = \langle \chi(\bar{1}) | J \rangle$. Solving formally for $\epsilon \langle \chi(\bar{1}) | M \rangle$ and then substituting of the resulting expression for into Eq. (2.15), we obtain the relation

$$[K(1) - E + \epsilon]|f(1)\rangle + \frac{\epsilon}{E - K(1)} \langle \chi(\bar{1}) | \mathcal{A} \hat{V}(1) + [E - K(1)](\mathcal{A} - 1) | \chi(\bar{1}) \rangle |f(1)\rangle + \frac{\epsilon}{E - K(1)} \langle \chi(\bar{1}) | \hat{V}(1) | M \rangle = 0. \quad (2.17)$$

Equations (2.7) and (2.17) must be solved self-consistently. The uniqueness of the solution of these self-consistency conditions, or rather their multichannel generalization, is established in the Appendix for the case in which the target wave function is of determinantal form. In an equivalent formulation of the theory a solution of Eq. (2.7), in terms of the negative-definite resolvent operator $\hat{G}(E) = (E - \hat{H})^{-1}$, may be combined with Eq. (2.16) to arrive at a

single-particle wave equation expressed in terms of an effective (or optical) potential [5,7]. Thus we introduce the formal solution $M = \hat{G}(E)J$ and define the propagator (with principal-value prescription understood in the treatment of the singularity)

$$\mathcal{G} = \frac{1}{E - \epsilon - K} \frac{\epsilon}{E - K}. \quad (2.18)$$

The wave function F is defined as the solution of $(K - E + \epsilon)F = 0$, and normalized on the energy scale. Equation (2.17) may then be reformulated as the integral equation

$$f = F + \mathcal{G}\mathcal{V}f. \quad (2.19)$$

The effective potential may now be written as $\mathcal{V} = \mathcal{V}^{(0)} + \mathcal{V}^{(1)}$ with

$$\mathcal{V}^{(0)} = \langle \chi(\bar{1}) | \{ \mathcal{A} \hat{V}(1) + [E - K(1)](\mathcal{A} - 1) \} | \chi(\bar{1}) \rangle \quad (2.20)$$

and

$$\mathcal{V}^{(1)} = \langle \chi(\bar{1}) | \hat{V}(1) \hat{G}(E) \mathcal{A} \hat{V}(1) | \chi(\bar{1}) \rangle. \quad (2.21)$$

A convenient starting point for the introduction of variational approximation methods is the resolvent identity

$$\hat{G} = \hat{G}_t + \hat{G}[(\hat{H} - E)\hat{G}_t + 1], \quad (2.22)$$

expressed here in terms of the trial resolvent \hat{G}_t . Equivalently, we have, after a single iteration

$$\hat{G} = \hat{G}_{\text{var}} + [(\hat{H} - E)\hat{G}_t + 1]^\dagger \hat{G}[(\hat{H} - E)\hat{G}_t + 1], \quad (2.23)$$

where the variational approximation to the resolvent is

$$\hat{G}_{\text{var}} = \hat{G}_t + \hat{G}_t[(\hat{H} - E)\hat{G}_t + 1]. \quad (2.24)$$

Since the error term in Eq. (2.23) is negative, these last two relations provide the basis for the use of a minimum principle in the evaluation of matrix elements of the resolvent.

A number of numerical methods are available for solving the equivalent one-body scattering problem defined by Eq. (2.19). A particularly convenient method is provided by the Kohn variational principle [8], an application of which is described in Sec. V.

III. SLATER-DETERMINANT FORM FOR TRIAL FUNCTIONS

The component of the scattering wave function that describes virtual excitations satisfies the inhomogeneous equation (2.7). Assuming temporarily that the function J is known, an approximate solution M_t may be obtained by writing $M_t = \hat{G}_t J$ and minimizing the functional

$$\mathcal{F} \equiv \langle J | \hat{G}_{\text{var}} | J \rangle = \langle M_t | \hat{H} - E | M_t \rangle + \langle J | M_t \rangle + \langle M_t | J \rangle. \quad (3.1)$$

One might choose, for example, a trial function of the form $M_t = \sum_i c_i \Phi_i$, where the functions Φ_i may be constructed as Slater determinants formed from a predetermined basis. With

the linear expansion coefficients c_i determined variationally one obtains the improved approximation $M_{\text{var}} = \hat{G}_{\text{var}} J$ with

$$\hat{G}_{\text{var}} = \sum_{i,j} |\Phi_i\rangle \langle \mathbf{d}^{-1} \rangle_{ij} \langle \Phi_j| \quad (3.2)$$

and $d_{ij} = \langle \Phi_i | E - \hat{H} | \Phi_j \rangle$. The minimum principle may be used to optimize the choice of nonlinear variational parameters in the basis functions, in analogy with standard treatments of the bound-state problem. Starting with a given trial function M_t , the approximation may be improved systematically by an iterative procedure in which the second-order error term, defined by the identity (2.23), is itself replaced by a variational approximation thus providing an approximation correct to *third* order.

Rather than introduce a predetermined set of basis functions one may, in the spirit of the standard Hartree-Fock approach to the bound-state problem, attempt to derive an optimum determinantal wave function by requiring that the functional (3.1) be minimized. Once such a function, or an approximation to it, has been obtained it may be adopted as the starting point for the above-mentioned iterative procedure in which improved approximations are obtained in a systematic way. Along with the obvious similarities with the Hartree-Fock method there are distinct differences, arising from the fact that here we look for solutions of an *inhomogeneous* differential equation. To bring out these differences in the clearest manner, we first consider the relatively simple problem of elastic electron-hydrogen scattering, and then electron-lithium scattering in a frozen-core model, as illustrations of the method. An extension required to account for the effect of the polarizability of the target is described in Sec. IV.

The hydrogenic target wave function is represented as

$$\chi(\bar{1}) = u(2) \xi_{\pm}(1,2), \quad (3.3)$$

where $u(2)$ is the spatial part of the hydrogenic ground-state wave function and $\xi_{\pm}(1,2)$ is the normalized spin function of the electron pair, the subscripts distinguishing between triplet (+) and singlet (-) states. The simplest choice of closed-channel wave function is a sum of determinantal functions based on two single-particle spatial states denoted by $|a\rangle$ and $|b\rangle$. In this approximation the full scattering wave function, in the form (2.4), is then

$$\Psi(1,2) = [u(2)f(1) \mp u(1)f(2) + a(2)b(1) \mp a(1)b(2)] \xi_{\pm}(1,2). \quad (3.4)$$

To write down the form taken by the functional (3.1) we define, following Eq. (2.6a),

$$\hat{H} = \hat{h}(1) + \hat{h}(2) + V(1,2), \quad (3.5)$$

with $V(1,2) = e^2/r_{12}$, $\hat{h}(i) = K(i) + v(i) - \epsilon |u(i)\rangle \langle u(i)|$, and $v(i) = -e^2/r_i$. [The spin sum in Eq. (2.6b) has been performed using closure.] The modified electron-target interaction, defined in Eq. (2.9), is here given by

$$\hat{V}(1) = v(1) + V(1,2) - \epsilon |u(1)\rangle \langle u(1)|. \quad (3.6)$$

In constructing matrix elements that appear in Eq. (3.1) we use the notation $\langle x|\hat{h}|y\rangle = \hat{h}_{xy}$, $\langle x|v|y\rangle = v_{xy}$, and

$$\langle w(1)|\langle x(2)|V(1,2)|y(1)\rangle|z(2)\rangle = V_{wx;yz}. \quad (3.7)$$

We then find that

$$\begin{aligned} \frac{1}{2} \langle M | \hat{H} - E | M \rangle &= \langle a|a\rangle \hat{h}_{bb} + \langle b|b\rangle \hat{h}_{aa} \mp (\langle a|b\rangle \hat{h}_{ba} \\ &+ \langle b|a\rangle \hat{h}_{ab}) - E (\langle a|a\rangle \langle b|b\rangle \mp \langle a|b\rangle \\ &\times \langle b|a\rangle) + V_{ab;ab} \mp V_{ab;ba}, \end{aligned} \quad (3.8a)$$

and

$$\begin{aligned} \frac{1}{2} \langle M | J | M \rangle &= \langle a|u\rangle v_{bf} \mp \langle b|u\rangle v_{af} + V_{ba;fu} \mp V_{ab;fu} - \epsilon \langle a|u\rangle \\ &\times \langle u|f\rangle \langle b|u\rangle (1 \mp 1), \end{aligned} \quad (3.8b)$$

with $\langle J | M \rangle = \langle M | J \rangle^*$.

In the Hartree-Fock procedure for bound states the Rayleigh-Ritz functional is minimized subject to an orthogonality constraint placed on the single-particle basis functions. Since we deal here with an inhomogeneous equation a normalization condition cannot be imposed. One might suppose that in the triplet case, where, for example, the addition to the function b of a multiple of a leaves the function M unchanged, it would be desirable to impose an orthogonality condition in order to simplify the numerical calculation [1]. In fact, the orthogonality property follows directly from the equations; there is no lack of uniqueness in the solutions as the following argument demonstrates.

We introduce the functional $\mathcal{F}' = \mathcal{F} - 2\langle b|a\rangle [E\langle a|b\rangle - \hat{h}_{ab}]$, that is, we subtract terms from \mathcal{F} that are proportional to $\langle b|a\rangle$, and require—the reason will soon be clear—that variations of \mathcal{F}' with respect to the vector $\langle a|$, with no constraints applied, should vanish. The resultant single-particle equation is, in the triplet state,

$$\begin{aligned} |a\rangle \hat{h}_{bb} + \langle b|b\rangle \hat{h}|a\rangle - |b\rangle \hat{h}_{ba} - E|a\rangle \langle b|b\rangle + V_{b;b}|a\rangle - V_{b;a}|b\rangle \\ + V_{b;f}|u\rangle - V_{b;u}|f\rangle + v_{bf}|u\rangle - v|f\rangle \langle b|u\rangle = 0, \end{aligned} \quad (3.9)$$

where $V_{x;y}(1) \equiv \langle x(2)|V(1,2)|y(2)\rangle$. When the state $\langle b|$ is projected onto each member of Eq. (3.9) we find that $\langle b|a\rangle [\hat{h}_{bb} - E\langle b|b\rangle] = 0$, the canceling of all other terms may be traced to the fact that one has effectively replaced a with b in the antisymmetrized product function $a(1)b(2) - a(2)b(1)$. Since E is not fixed we conclude that $\langle b|a\rangle$ must vanish, so that the orthogonality condition is satisfied automatically by functions a and b determined by Eq. (3.9). Now the equation obtained by varying \mathcal{F} with respect to $\langle a|$ differs from Eq. (3.9) in that the left-hand side contains the additional term $\langle b|a\rangle [E|b\rangle - \hat{h}|b\rangle]$ which vanishes for $\langle b|a\rangle = 0$. It follows that this latter equation will be satisfied by a solution of Eq. (3.9); thus the orthogonality of the functions a and b is a property of the solution that minimizes the *original* functional \mathcal{F} . It is not difficult to show that when the functions a and b are each represented by a linear superposition $\sum_{i=1}^m c_{i\alpha} \zeta_i$, $\alpha = a$ or b , of atomic orbitals ζ_i , the orthogonality property is passed on to the vectors formed from the linear expansion coefficients $c_{i\alpha}$. These coefficients are to be determined self-consistently, but now algebraically,

with the exponential parameters appearing in the atomic orbitals optimized with the aid of the minimum principle; this is in close analogy with similar procedures that have proved useful in the bound-state problem [4,9].

In the singlet state the equation corresponding to Eq. (3.9) takes the form

$$\begin{aligned} &|a\rangle\hat{h}_{bb} + \langle b|a\rangle\hat{h}|b\rangle + \langle b|b\rangle\hat{h}|a\rangle + |b\rangle\hat{h}_{ba} - E(|a\rangle\langle b|b\rangle \\ &+ |b\rangle\langle b|a\rangle) + V_{b;b}|a\rangle + V_{b;a}|b\rangle + V_{b;f}|u\rangle + V_{b;u}|f\rangle \\ &+ v_{bf}|u\rangle + v|f\rangle\langle b|u\rangle - 2\epsilon\langle b|u\rangle\langle u|f\rangle|u\rangle = 0; \quad (3.10) \end{aligned}$$

the proof of the orthogonality of the functions a and b does not apply in this case.

The procedure described above leading to Eq. (3.9) for the basis functions in the triplet state may be reformulated in an equivalent but more convenient manner. One omits from the functional \mathcal{F} terms containing the overlaps $\langle a|b\rangle$ as well as $\langle b|a\rangle$. The variation of this functional with respect to a is set equal to zero. The resultant equation must be modified since the vanishing of $\langle a|b\rangle$ does not imply that variations of $\langle a|b\rangle$ will vanish. The correct equation is obtained by including a term $\lambda|b\rangle$, with λ evaluated using the requirement that the resultant equation have the property seen in Eq. (3.9)—the left-hand member must be orthogonal to $|b\rangle$. This requires that $\lambda = -\hat{h}_{ba}$. In this formulation [10], the prescription is easily generalized to apply to multiparticle applications where it considerably simplifies the analysis. As an illustration we briefly consider the form of trial functions that may be used in a frozen-core model of electron-lithium scattering.

The antisymmetrized lithium-target trial wave function, corresponding to spin projection 1/2, is taken to be

$$\chi_T(\bar{1}; 1/2, 1/2) = \mathcal{N}(1 - P_{23} - P_{24})\chi_c(3,4)u(2)\alpha(2), \quad (3.11)$$

where \mathcal{N} is a normalization constant and $\alpha(2)$ is a spin-1/2 function with projection +1/2; the target state with projection -1/2 is obtained by replacing $\alpha(2)$ with $\beta(2)$. The antisymmetric heliumlike core is represented as

$$\chi_c(3,4) = c(3)c(4)\xi_-(3,4), \quad (3.12)$$

with $\langle c|c\rangle = 1$ and $\langle c|u\rangle = 0$. We now couple the projectile spin to that of the target to construct a triplet or singlet state according to

$$\chi(\bar{1}) = \mathcal{N}(1 - P_{23} - P_{24})\chi_c(3,4)u(2)\xi_{\pm}(1,2). \quad (3.13)$$

The approximate scattering wave function is of the form shown in Eq. (2.4). Consistent with the frozen-core model of the target, the closed-channel wave function is chosen as

$$M = \mathcal{A}(1 - P_{23} - P_{24})\chi_c(3,4)a(2)b(1)\xi_{\pm}(1,2), \quad (3.14)$$

with $\mathcal{A} = (1 - P_{12} - P_{13} - P_{14})$; the core state is fixed and the basis functions a and b are to be determined by minimizing the functional (3.1). The modified Hamiltonian is that shown in Eq. (2.6a), with the exact target function χ_T in Eq. (2.6b)

replaced by that corresponding to the frozen-core approximation Eq. (3.11). The function J has been defined in Eqs. (2.8) and (2.9) [11].

We observe that the argument given earlier for the electron-hydrogen system to the effect that the spatial functions a and b in the triplet state, as determined by Eq. (3.9), are orthogonal, is immediately generalized. The proof relies on the antisymmetry of the function M under interchange of a and b , a property satisfied by the triplet version of the form given in Eq. (3.14). It is easily verified that in both the triplet and singlet states the addition of an arbitrary multiple of the core function c to either of the functions a or b leaves M , as defined above, unchanged—the vanishing of the additional term is most simply viewed as a consequence of the exclusion of a third particle from a closed two-particle subshell. This property, rather than indicating a lack of uniqueness, provides the basis for a proof that the equations determining the functions a and b ensure that each are orthogonal to c . The argument is similar to the orthogonality proof used earlier for e^- -H scattering and alluded to just above. That is, one may evaluate the functional \mathcal{F} , Eq. (3.1), by ignoring overlaps of either of the functions a or b with c . This eliminates a large number of terms, thereby simplifying the calculation. After setting the variation of this functional with respect to a or b equal to zero, the correct equation is obtained by inserting a factor $(1 - |c\rangle\langle c|)$ before each term, ignoring overlaps of c with the functions a , b , and u .

We do not record here the analogs of Eqs. (3.9) and (3.10) for e^- -Li scattering since they are rather lengthy. Rather, we conclude this discussion with the remark that the expressions simplify considerably in the approximation that the spatial extent of the frozen-core function c is small enough to justify ignoring matrix elements connecting that function with the other bound state and scattering orbitals. The equations then take on the form obtained for scattering by H, but containing a correction in which the potential $v(1)$, the interaction of particle 1 with the Li nucleus, is replaced by the shielded potential

$$v_s(1) = -\frac{3e^2}{r_1} + \langle c(3)|\frac{2e^2}{r_{13}}|c(3)\rangle. \quad (3.20)$$

IV. LONG-RANGE FORCES AND RESONANCE EFFECTS

The calculational procedure outlined above must be modified in order to account explicitly for the effect, of particular importance at low energies, of long-range forces arising from the polarizability of the target. Specifically, a representation of the closed-channel wave function appearing in Eq. (2.4) as an antisymmetrized product of single-particle orbitals that decay asymptotically will be inappropriate—the long-range potential induces a power-law falloff. Inclusion of the effect of long-range forces is accomplished most directly with the aid of the variational treatment of the effective potential discussed at the conclusion of Sec. II. Thus with reference to Eqs. (2.21)–(2.23) we write $\mathcal{V}^{(1)} = \mathcal{V}_{\text{var}}^{(1)} + \Delta\mathcal{V}^{(1)}$ with $\mathcal{V}_{\text{var}}^{(1)}$ determined such that it provides the dominant contribution to the effective potential at great distances. It would then be appropriate to apply the generalized Hartree-Fock procedure

to the estimate of the error term $\Delta\mathcal{V}^{(1)}$; this is discussed further below.

We begin by introducing the Green's function $\hat{g}(1) \equiv [\epsilon - \hat{h}(1)]^{-1}$, where the modified target Hamiltonian was defined earlier as $\hat{h}(1) = h(1) - W(\bar{1})$. Note that \hat{g} is a negative operator since ϵ lies below the minimum eigenvalue of \hat{h} [12]. The (antisymmetrized) trial Green's function in the adiabatic approximation, in which target polarization is evaluated with the projectile taken to be at rest, is chosen (under the assumption that it acts on antisymmetrized states) as

$$\hat{G}_t = (N+1)^{-1} \mathcal{A} \hat{g}(1). \quad (4.1)$$

With this form introduced into Eq. (2.22), a variational approximation to the effective potential, Eq. (2.21), is obtained in the form $\mathcal{V}_{\text{var}}^{(1)} = \mathcal{V}^{(1,1)} + \mathcal{V}^{(1,2)}$. We find that

$$\mathcal{V}^{(1,1)} = (N+1)^{-1} \langle \chi(\bar{1}) | \hat{V}(1) \mathcal{A} \hat{g}(1) \mathcal{A} \hat{V}(1) | \chi(\bar{1}) \rangle. \quad (4.2)$$

The first-order correction is obtained with the aid of the relation

$$\begin{aligned} \Omega &\equiv (\hat{H} - E) \hat{G}_t + 1 \\ &= (N+1)^{-1} \mathcal{A} [K(1) - E + \epsilon + \hat{V}(1)] \hat{g}(1), \end{aligned} \quad (4.3)$$

where Eq. (2.16) and the definition (4.1) was used in the evaluation Ω ; we find that

$$\mathcal{V}^{(1,2)} = (N+1)^{-1} \langle \chi(\bar{1}) | \hat{V}(1) \mathcal{A} \hat{g}(1) \Omega \mathcal{A} \hat{V}(1) | \chi(\bar{1}) \rangle. \quad (4.4)$$

An estimate of the Green's function \hat{g} can be obtained by application of the minimum principle to the calculation of the electric multipole polarizability of the target, in analogy with the procedure discussed above in connection with Eqs. (3.1) and (3.2) [13]. It is not difficult to verify that the asymptotic form of the approximate effective potential $\mathcal{V}_{\text{var}}^{(1)} = \mathcal{V}^{(1,1)} + \mathcal{V}^{(1,2)}$ correctly reproduces the leading $1/r^4$ and $1/r^6$ terms that appear in the true effective potential for large values of the projectile-target separation. The coefficients of these terms [14] may be determined variationally from the calculation of \hat{g} .

A noteworthy feature of the present analysis of the long-range behavior of the effective potential is that the Pauli principle is accounted for, as is the presence of the monopole component of the Coulomb field. Moreover, the error in the adiabatic approximation leading to Eqs. (4.2)–(4.4) can be estimated in a systematic way. Thus in accordance with Eq. (2.23), the error $\Delta\mathcal{V}^{(1)} = \mathcal{V}^{(1)} - \mathcal{V}_{\text{var}}^{(1)}$ is given by the expression

$$\Delta\mathcal{V}^{(1)} = (N+1)^{-1} \langle \chi(\bar{1}) | \hat{V}(1) \mathcal{A} \Omega \hat{G}_t \Omega^\dagger \mathcal{A} \hat{V}(1) | \chi(\bar{1}) \rangle. \quad (4.5)$$

A variational estimate of the error, aided by the use of the minimum principle, may be obtained by application of the procedure described earlier in connection with Eqs. (3.1) and (3.2). Since we are here at the next level of iteration the function J is replaced by $J' = \Omega J$, with \hat{G}_t given by Eq. (4.1), and Eq. (3.1) is replaced by

$$\mathcal{F}' \equiv \langle J' | \hat{G}_{\text{var}} | J' \rangle = \langle M'_t | \hat{H} - E | M'_t \rangle + \langle J' | M'_t \rangle + \langle M'_t | J' \rangle. \quad (4.6)$$

Since the effects of the long-range polarization potential have been accounted for in the construction of the function J' , the generalized Hartree-Fock procedure may be applied to the evaluation of the closed-channel trial function M'_t . It is convenient to transform the functional \mathcal{F}' to an amplitude-independent form by writing $M'_t = c\Phi'$ and determining c variationally. This converts Eq. (4.6) to

$$\mathcal{F}' = \langle J' | \Phi' \rangle \frac{1}{\langle \Phi' | E - \hat{H} | \Phi' \rangle} \langle \Phi' | J' \rangle. \quad (4.7)$$

In this way we obtain an approximation to the component M' of the closed-channel wave function, with polarization effects included, of the form $M'_{\text{var}} = \hat{G}_{\text{var}} J'$ with

$$\hat{G}_{\text{var}} = |\Phi' \rangle \frac{1}{\langle \Phi' | E - \hat{H} | \Phi' \rangle} \langle \Phi' |. \quad (4.8)$$

This variational approximation to the resolvent may be combined with Eq. (4.5) to provide a variational approximation to the error in the effective potential, thus allowing for a smooth joining of the effects of long-range and short-range interactions in the scattering process.

Bound states of the modified Hamiltonian \hat{H} correspond to scattering resonances of the closed-channel type. It is frequently desirable to include the effect of such states explicitly, thereby simplifying the calculation of the background scattering. Suppose for simplicity that only one of these states exist, satisfying

$$\hat{H} |B\rangle = E_b |B\rangle, \quad (4.9)$$

with $E_b < E$. We look for the closed-channel wave function in the form

$$M = \alpha |B\rangle + M'', \quad (4.10)$$

where α is a parameter to be determined and M'' is required to satisfy

$$(\hat{H}_{\text{mod}} - E) |M''\rangle = -|J\rangle \quad (4.11)$$

with

$$\hat{H}_{\text{mod}} = \hat{H} - \frac{\hat{H} |B\rangle \langle B| \hat{H}}{\langle B | \hat{H} | B \rangle}. \quad (4.12)$$

For energies near or above the energy of the resonance, the minimum principle based on Eq. (3.1) is violated, but the resonant state has effectively been removed from the spectrum of \hat{H}_{mod} . While the bound-state wave function B will in most cases of interest be imprecisely known, the minimum principle applied to the approximate solution of Eq. (4.11) will be preserved provided the trial function used to approximate B in Eq. (4.12) is sufficiently accurate to give binding [15]. The generalized Hartree-Fock method, in the form de-

scribed in Sec. III, is applicable for the construction of the function M'' , with no impediments arising from the existence of the resonance.

To determine the coefficient α in Eq. (4.10) we combine the form given there for M with Eq. (2.7). Assuming for this purpose that the exact wave function B appears, and making use of its eigenvalue equation, we obtain

$$\alpha(E_b - E)|B\rangle = -E_b|B\rangle\langle B|M''\rangle. \quad (4.13)$$

Now projecting the ket $\langle B|$ onto both sides of Eq. (4.11) and employing the relation $\langle B|\hat{H}_{\text{mod}}=0$, satisfied when $\langle B|$ is exact, we find that $E\langle B|M''\rangle = \langle B|J\rangle$, and inserting the value of α thereby determined, we have

$$|M\rangle = \frac{E_b}{E} \frac{1}{E - E_b} |B\rangle\langle B|J\rangle + |M''\rangle. \quad (4.14)$$

Equivalently, with $M = \hat{G}J$, we have

$$\hat{G} = \frac{E_b}{E} \frac{1}{E - E_b} |B\rangle\langle B| + \hat{G}_{\text{mod}}, \quad (4.15)$$

with $\hat{G}_{\text{mod}} = (E - \hat{H}_{\text{mod}})^{-1}$. Referring back to Eq. (2.21) for one of the components of the effective potential, we may write $\mathcal{V}^{(1)} = \mathcal{V}^{(1,1)} + \mathcal{V}^{(1,2)}$ with

$$\mathcal{V}^{(1,1)} = \frac{E}{E_b} \langle \chi(\bar{1})|\hat{V}(1)|B\rangle \frac{1}{E - E_b} \langle B|\mathcal{A}\hat{V}(1)|\chi(\bar{1})\rangle, \quad (4.16)$$

representing the resonant contribution and

$$\mathcal{V}^{(1,2)} = \langle \chi(\bar{1})|\hat{V}\hat{G}_{\text{mod}}\mathcal{A}\hat{V}(1)|\chi(\bar{1})\rangle. \quad (4.17)$$

The minimum principle is applicable to the construction of the background contribution $\mathcal{V}^{(1,2)}$ to the effective potential.

V. AN ILLUSTRATIVE APPLICATION

In order to illustrate some aspects of the proposed calculational procedure in a simple context we consider elastic s -wave scattering of positrons by hydrogen [16]. It will be convenient to replace the integral equation (2.19) by the differential equation

$$(-\mathcal{G}^{-1} + \mathcal{V}^{(0)} + \mathcal{V}^{(1)})f = 0, \quad (5.1)$$

with the modified Green's function given by Eq. (2.18). The expression (2.20) for $\mathcal{V}^{(0)}$ reduces (atomic units are used in the following) to the static approximation

$$\mathcal{V}^{(0)}(r_1) = e^{-2r_1}(r_1^{-1} + 1), \quad (5.2)$$

where we have set $\hat{V}(1) = V(1) = r_1^{-1} - r_{12}^{-1}$ and $\mathcal{A} = 1$. The appropriate version of the Kohn variational principle [8],

$$\tan \delta_{\text{var}} = \tan \delta_t - \pi \langle f_t | -\mathcal{G}^{-1} + \mathcal{V}^{(0)} + \mathcal{V}^{(1)} | f_t \rangle, \quad (5.3)$$

is adopted to provide an approximation for the phase shift given a specific choice of the effective potential $\mathcal{V}^{(1)}$. Such a calculation generates, in addition, a (nonvariational) approximation to the wave function f for use in the next phase of the

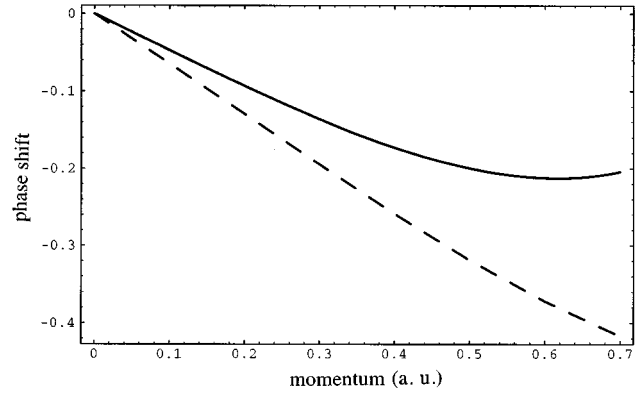


FIG. 1. s -wave phase shift plotted as a function of the momentum of the incident positron. The dashed curve is obtained using the static approximation for the effective potential. The solid curve shows the phase shift with closed-channel contributions to the effective potential included.

self-consistency procedure in which an improved approximation to $\mathcal{V}^{(1)}$ is determined. With the Green's function $\hat{G}(E)$ appearing in Eq. (2.21) replaced by a single-term version of the variational approximation (3.2) we have

$$\langle f_t | \mathcal{V}^{(1)} | f_t \rangle = \langle J_t | \Phi \rangle \frac{1}{\langle \Phi | E - \hat{H} | \Phi \rangle} \langle \Phi | J_t \rangle. \quad (5.4)$$

Here \hat{H} is the modified three-particle Hamiltonian in which the hydrogenic target Hamiltonian h is replaced by $h - \epsilon|u\rangle\langle u|$, a form in which the ground-state component has been subtracted off. The function J_t is given by Eq. (2.8) with the exact solution f replaced by f_t . A simple trial function

$$f_t(r) = \left(\frac{2}{\pi k} \right)^{1/2} (\sin kr + A(1 - e^{-\alpha r}) \cos kr + Bre^{-2r}), \quad (5.5)$$

with $E = k^2/2$, containing two linear parameters and a single exponential parameter to be varied, was employed and appeared to give a level of accuracy adequate for our present purposes in all cases considered.

To start the self-consistency search we ignored $\mathcal{V}^{(1)}$ in Eq. (5.3) and obtained a variational solution of the "static" problem, leading to phase shifts represented in Fig. 1 by the dashed curve for a range of energies extending just below the threshold for positronium formation. These phases lie below the conventionally defined static phase shifts since the operator

$$-\mathcal{G}^{-1} = (K - E + \epsilon) + \frac{(K - E + \epsilon)^2}{|\epsilon|} \quad (5.6)$$

contains an additional repulsive term, as required in the formulation of the minimum principle for the effective potential. The presence of higher-order derivatives in this additional term causes no difficulty, either in the derivation of the variational principle or in its implementation.

For the trial function Φ appearing in Eq. (5.4) the simplest product form

$$\Phi(r_1, r_2) = \exp(-\beta r_1 - \gamma r_2) \quad (5.7)$$

was chosen, with exponential parameters determined by minimization of the expression on the right in Eq. (5.4). At each stage, updated values were employed for the variational parameters appearing in the trial function (5.5); only a few iterations were required to achieve self-consistency. The phase shifts determined in this way are shown as the solid curve in Fig. 1. Polarization of the target by the low-energy positron, when fully accounted for, has a strongly attractive effect not included in the present model, which is based on product wave functions having no explicit dependence on the electron-positron separation r_{12} . It is was therefore to be expected at the outset that the phases obtained here will differ markedly from the exact values [17]. (Effectively, we are working with a model in which the positron-electron interaction $1/r_{12}$ is replaced by $1/r_{>}$.) The calculation serves to demonstrate the applicability of the method, based on the minimum principle and self-consistency, in a simple, non-trivial case.

VI. SUMMARY

While minimum principles for scattering have been known for many years, applications have been limited to relatively simple few-body systems for which the target ground-state wave function is known. The version of the minimum principle reviewed here in Sec. II is applicable to a wider class of scattering systems. The use of determinantal trial wave functions is a practical necessity in applications to multielectron systems, and it is natural to seek the optimum choice of such functions with the aid of the minimum principle. The Hartree-Fock method for bound states provides a model for such an approach. An outline of a generalized Hartree-Fock procedure was developed in Sec. III, with particular attention paid to those features, such as the uniqueness and orthogonality properties of the single-particle wave functions, that differ in the scattering and bound-state formulations. This was described in the context of simple (hydrogenlike targets) in order to illustrate these features in the clearest way. In its general form the method does not depend on any specific choice of target wave function, provided that it is sufficiently accurate in the sense described [5,6]. (The target function may be fixed at the outset and when, as will frequently be the case, a Hartree-Fock solution for this function is chosen, self-consistency between the orbitals in the target function and the closed-channel wave function is not required.) The formal and practical advantages gained by expressing the theory in terms an effective (or optical) potential was emphasized. In particular, the treatment of long-range forces associated with the polarizability of the target, and of resonances associated with closed-channel bound states, is carried out most conveniently in using the effective-potential formalism. The modifications of the calculational procedure required to account for target polarization and resonance effects were taken up in Sec. IV. The procedure was seen to work effectively in a first test, an application to positron-hydrogen scattering described in Sec. V. Methods described here can provide the basis for systematic, large-scale numerical treatments of electron-atom scattering, comparable in scope and accuracy to the widely used Hartree-

Fock procedure, and (with significant exceptions discussed here) sharing many of its features.

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APPENDIX

In standard applications of close-coupling theory, with the target wave function approximated by a Slater determinant, orthogonality conditions must be imposed on the projectile orbital to fix it uniquely [1]. The tighter constraints built into the present approach obviate the need for the imposition of additional orthogonality constraints. We confirm this here by demonstrating the uniqueness of the solution of the multichannel version of the self-consistency problem formulated in Sec. II for the case in which the target is treated in Hartree-Fock approximation. We begin by summarizing the multichannel generalization of the formalism developed in Sec. II. The scattering wave function corresponding to an incident channel with index v is represented as

$$\Psi_v(1, 2, \dots, N+1) = \mathcal{A} \sum_{\gamma=1}^p \chi_{\gamma}(\bar{1}) f_{\gamma v}(1) + M_v(1, 2, \dots, N+1). \quad (A1)$$

Here $\chi_{\gamma} f_{\gamma v}$ is 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. The closed-channel wave function is taken to be the solution of an equation of the form (2.7) where the operator $W(\bar{n})$ in Eq. (2.6) is here replaced by a sum of such terms, one for each open channel. The scattering problem is then defined by the coupled equations

$$(\hat{H} - E)M_v = -\mathcal{A} \sum_{\gamma} \hat{V}(1) \chi_{\gamma}(\bar{1}) f_{\gamma v}(1), \quad (A2)$$

$$[K(1) - E + \epsilon_{\alpha}] |f_{\alpha v}(1)\rangle + \epsilon_{\alpha} \langle \chi_{\alpha}(\bar{1}) | \times \sum_{\gamma} (\mathcal{A} - 1) | \chi_{\gamma}(\bar{1}) \rangle |f_{\gamma v}(1)\rangle + \epsilon_{\alpha} \langle \chi_{\gamma} | M_v \rangle = 0. \quad (A3)$$

To test uniqueness we suppose that a different set of solutions

$$f'_{\gamma v} = f_{\gamma v} + \Delta f_{\gamma v}, \quad M'_v = M_v + \Delta M_v \quad (A4)$$

exists, satisfying equations of the form (A2) and (A3). To leave Ψ_v unchanged we require that $\Delta M_v = -\mathcal{A} \sum_{\gamma} \chi_{\gamma} \Delta f_{\gamma v}$. According to Eq. (A2), this function must satisfy the relation

$$(\hat{H} - E) \Delta M_v = -\mathcal{A} \sum_{\gamma} \hat{V} \chi_{\gamma} \Delta f_{\gamma v} \quad (A5)$$

which may be reduced to the form

$$\mathcal{A} \sum_{\gamma} \chi_{\gamma}(\bar{1}) [K(1) - E] \Delta f_{\gamma v}(1) = 0. \quad (\text{A6})$$

A general solution of this equation is provided by the form $\Delta f_{\gamma v} = [E - K(1)]^{-1} \phi$, where ϕ is an arbitrary linear combination of the orbitals that appear in the target Slater determinant. [The left-hand side of Eq. (A6) is then recognized as an N -electron determinantal wave function which vanishes identically.] The desired uniqueness property, namely $\Delta f_{\gamma v} = 0$ and $\Delta M_v = 0$, is established by the observation that $\phi = 0$. Thus with $f_{\gamma v}$ and M_v replaced by $\Delta f_{\gamma v}$ and ΔM_v , respectively, in Eq. (A3) this equation becomes

$$\begin{aligned} & -\phi(1) + \epsilon_{\alpha} [E - K(1)]^{-1} \phi(1) \\ & + \epsilon_{\alpha} \sum_{\gamma} \langle \chi_{\alpha}(\bar{1}) | (\mathcal{A} - 1) | \chi_{\gamma}(\bar{1}) \rangle [E - K(1)]^{-1} \phi(1) \\ & - \epsilon_{\alpha} \langle \chi_{\alpha}(\bar{1}) | \mathcal{A} \sum_{\gamma} | \chi_{\gamma}(\bar{1}) \rangle [E - K(1)]^{-1} \phi(1) = 0. \end{aligned} \quad (\text{A7})$$

Combining terms and making use of the orthonormality property $\langle \chi_{\alpha}(\bar{1}) | \chi_{\gamma}(\bar{1}) \rangle = \delta_{\alpha\gamma}$ of the target wave functions, we observe that all terms cancel but the first, which implies that $\phi = 0$ and that the solution is unique.

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