# Minimum principle for Dirac scattering lengths

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A minimum principle for the nonrelativistic scattering length was derived some years ago under the assumption that only a finite number of discrete states exist below the scattering threshold. The variational bound is applicable even when the bound-state wave functions are imprecisely known—they need only be accurate enough to give binding in a Rayleigh-Ritz calculation. The method is generalized here to apply to potential scattering described by the Dirac equation. An apparent difficulty associated with the existence of a continuum of negative-energy states, that is, the problem of "variational collapse," is removed through the inclusion of second-order terms in the variational expression involving matrix elements of the square of the Dirac Hamiltonian. In the course of the derivation a relativistic version of the Hylleraas-Undheim theorem is developed. Applications of this theorem are described that provide a sufficient condition for the existence of a given number of bound states, lower bounds on the energy eigenvalues, and a systematic procedure for improving the accuracy of trial bound-state wave functions. A very simple model calculation was performed to illustrate the minimum property and the stability of the numerical procedure.

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## I. INTRODUCTION

Recent efforts in the development of a relativistic many-body theory of atomic structure and scattering have focused attention on the problem of finding numerical solutions of the one-body Dirac equation—such solutions enter into the construction of basis states [1]. Variational methods for determining approximate solutions of the Dirac equation will suffer from instabilities unless the existence of the negative-energy continuum branch of the spectrum is properly accounted for. Several methods have been suggested for removing the variational collapse problem [2–7]. For example, a relativistic version of the Hylleraas-Undheim theorem [8]—a generalization of the Rayleigh-Ritz method to excited states—was derived for a Dirac electron in a Coulomb potential [7]. An extension of this theorem to a wide class of short range potentials is obtained below, in Sec. III, in the course of a derivation of a minimum principle for the Dirac scattering length. There are several motivations for treating the zero-energy scattering problem relativistically. First, it may lead to improvements in techniques for constructing basis states and the Green's function for the Dirac equation. This would be of use in many-electron perturbation calculations. The present treatment provides a theoretical basis for developing such improvements. Secondly, since minimum principles have played such an important role in nonrelativistic bound-state and low-energy scattering problems, the availability of relativistic extensions would be of methodological interest. The result obtained here gives evidence that the variational collapse problem associated with the negative-energy Dirac sea can be removed in scattering as well as bound-state calculations. Finally, the simple and restricted theory described below may prove useful in later generalizations to higher energies and to a consistent relativistic treatment of both the projectile and the complex target. More specifically, a low-energy electron incident on a heavy neutral atom will be prevented by the Pauli principle from penetrating into the region close to the nucleus [9], but if the outer electrons have been stripped off such penetration will occur and the electron will be accelerated to high speeds; relativistic corrections may then be significant. An extension of the present potential-scattering theory to one applicable to scattering from a compound target, and to energies above the continuum threshold, would make use of techniques developed for the analogous nonrelativistic problem [10,11].

## II. VARIATIONAL FORMULATION

We consider the scattering of a Dirac particle of mass $m$ in the field of a short range, central potential $V(r)$. Specifically, we require that $rV(r)\to 0$ as $r\to\infty$ to guarantee the validity of the asymptotic boundary conditions stated below. After removal of angular and spin coordinates the Dirac equation reduces to a set of two coupled equations for the radial wave functions [12,13]. In units with $\hbar=c=1$, and with the energy of the incident particle taken to be $m$, these equations may be written in the form $(H-m)u=0$, where $m$ in this equation is understood to be a multiple of the unit $2\times 2$ matrix and

$$H=\begin{bmatrix} V+m & -\dfrac{d}{dr}-\dfrac{1}{r} \\ \dfrac{d}{dr}-\dfrac{1}{r} & V-m \end{bmatrix},\quad u(r)=\begin{bmatrix} u_1(r) \\ u_2(r) \end{bmatrix}. \tag{2.1}$$

The Dirac quantum number $\kappa$ appearing in the radial equations appropriate to arbitrary energies [12] has been taken to be $-1$, corresponding to $l=0$ and $j=\frac{1}{2}$. It will be convenient to take the scattering wave function to be

 

dimensionless, in which case the asymptotic solutions have the form

$$u_1(r)\to m(r-A)\ ,$$
$$u_2(r)\to\frac{A}{2r}\ ,\quad r\to\infty\ . \tag{2.2}$$

The scattering length $A$ is related to the phase shift $\delta$ (for $\kappa=-1$) and momentum $p$ according to

$$A=-\lim_{p\to 0}\tan\delta/p\ . \tag{2.3}$$

The boundary conditions at the origin are $u_1(0)=u_2(0)=0$ [13].

As a first step in deriving a minimum principle for the scattering length we introduce trial functions $u_{1t}(r)$ and $u_{2t}(r)$ satisfying boundary conditions of the form (2.2) but with $A$ replaced by a trial parameter $A_t$. The useful identity [14]

$$A=A_t+(2/m)\int_0^\infty u^\dagger(r)(H-m)u_t(r)dr \tag{2.4}$$

is readily verified by allowing the Hamiltonian to operate to the left, making use of the Dirac equation satisfied by the adjoint wave function, and evaluating the surface terms at the origin and at infinity with the aid of the boundary conditions. A variational principle is obtained by replacing the exact adjoint solution appearing on the right-hand side of Eq. (2.4) with an appropriate trial function. In the analogous nonrelativistic problem [10] the variational principle is actually a minimum principle if the potential does not support any bound states. However, minimization of the relativistic expression leads to variational collapse owing to the existence of a continuum of negative-energy states lying below the scattering energy $m$. We shall now demonstrate how this difficulty is removed through the addition of a correction term, formally of second order, to the variational expression obtained by the method just mentioned, that is, by the substitution of $u_t^\dagger$ for $u^\dagger$ in the identity (2.4). Another source of instability, arising from the existence of bound states, will be treated in Sec. III; here we assume that no bound states exist.

We proceed by displaying the explicit form for the error term in the variational expression. This is readily accomplished through the introduction of the Green's function $G(r,r')$ satisfying

$$(H-m)G(r,r')=-\delta(r'-r)\ , \tag{2.5}$$

where it is understood that the $\delta$ function on the right multiplies a unit $2\times 2$ matrix. In terms of this function the exact scattering solution is given formally as

$$u(r)=u_t(r)+\int_0^\infty G(r,r')(H'-m)u_t(r')dr'\ . \tag{2.6}$$

The Green's function may be represented as an expansion in a complete set of $s_{1/2}$ eigenfunctions satisfying $(H-E_n)\phi_n=0$; we write the expansion as

$$G(r,r')=\mathbf{S}_n\phi_n(r)(m-E_n)^{-1}\phi_n^\dagger(r')\ . \tag{2.7}$$

A generalized sum over all states, both bound and continuum, is implied here. More explicitly, with continuum states normalized as

$$\int_0^\infty\phi_{E'}^\dagger(r)\phi_E(r)dr=\delta(E'-E)\ , \tag{2.8}$$

the completeness relation takes the form

$$\begin{aligned}\mathbf{S}_n\phi_n(r')\phi_n^\dagger(r)\equiv&\sum_{n=1}^{N}\phi_n(r')\phi_n^\dagger(r)\\&+\left[\int_{-\infty}^{-m}+\int_m^\infty\right]\phi_E(r')\phi_E^\dagger(r)dE\\=&\,\delta(r'-r)\ .\end{aligned} \tag{2.9}$$

(The function $\phi_E$ with $E=m$ is identified with the scattering solution $u$ of particular interest here.) Combining the adjoint of Eq. (2.6) with Eq. (2.4) and making use of the reciprocity relation $G^\dagger(r,r')=G(r',r)$ which is implied by the representation (2.7), we arrive at the variational identity

$$\begin{aligned}A=A_t+(2/m)\Big\{&\int_0^\infty u_t^\dagger(r)(H-m)u_t(r)dr\\&+\int_0^\infty\int_0^\infty[(H'-m)u_t(r')]^\dagger G(r',r)\\&\times[(H-m)u_t(r)]dr'dr\Big\}\ .\end{aligned} \tag{2.10}$$

Owing to the appearance of negative-energy states in the eignfunction expansion of the Green's function, the second-order error term in Eq. (2.10) is not positive definite. However, these negative-energy states can be effectively "subtracted out" by the following simple device. We write

$$G(r,r')=\bar{G}(r,r')+\frac{1}{2m}\delta(r-r')\ , \tag{2.11}$$

where

$$\bar{G}(r,r')=\mathbf{S}_n\phi_n(r)\left[\frac{1}{m-E_n}-\frac{1}{2m}\right]\phi_n^\dagger(r')\ . \tag{2.12}$$

The quantity contained in large parentheses, namely,

$$w(E_n)\equiv\frac{1}{2m}\left[\frac{E_n+m}{m-E_n}\right]\ , \tag{2.13}$$

is negative provided the energy eigenvalue lies outside the gap between $m$ and $-m$, that is, provided no bound states exist. (This simple property plays a key role in all that follows.) Under the assumption that there are no bound states, a variational bound on the error term is obtained by discarding the negative contribution given by the diagonal matrix element of $\bar{G}$. In this way we arrive at the minimum principle $A\le A^{(0)}$, where

$$A^{(0)}=A_t+\frac{2}{m}\int_0^\infty u_t^\dagger(r)(\bar{H}-m)u_t(r)dr\ . \tag{2.14a}$$

Having introduced the modified Hamiltonian

$$\bar{H}\equiv H+\frac{1}{2m}(H-m)^2=\frac{1}{2m}(H^2+m^2) \tag{2.14b}$$

we are able to put the minimum principle in a form similar to that taken in the nonrelativistic case [10]. That it should be possible to do so is understandable since the modified Hamiltonian has a spectrum that is bounded from below; the negative-energy continuum of $H$ has been mapped onto the domain extending from $m$ to infinity and the discrete eigenenergies of $\bar{H}$ lie in the domain between $m/2$ and $m$. It is clear at this stage that the analysis could have been formulated from the outset in terms of the modified Hamiltonian, an observation that can be of heuristic value in setting up a correspondence between the treatments based on the Schrödinger and Dirac equations. We note that the square of the Hamiltonian appearing in Eq. (2.14b) is a second-order differential operator whose appearance causes no special difficulties in numerical evaluation of the variational approximation [15].

## III. MINIMUM PRINCIPLE ALLOWING FOR BOUND STATES

We assume here that a single bound state exists, the wave function satisfying $(H-E_1)\phi_1(r)=0$, along with the normalization condition

$$\int_0^\infty \phi_1^\dagger(r)\phi_1(r)dr \equiv \langle \phi_1|\phi_1\rangle = 1 \ . \tag{3.1}$$

(Here and in the following we simplify notation by adopting the Dirac inner product.) Let us first assume that the bound-state wave function is known precisely. Given an arbitrarily chosen trial scattering function $u_t(r)$, it is reasonable to suppose that an improved trial function $u_{tt}$ would result from the orthogonalization

$$u_{tt}(r)=u_t(r)-\phi_1(r)\langle \phi_1|u_t\rangle \ . \tag{3.2}$$

The replacement of $u_t$ with $u_{tt}$ in the functional given in Eq. (2.14a) leads to the variational approximation

$$A \cong A^{(0)}+\left[1-\left[\frac{E_1}{m}\right]^2\right]\langle \phi_1|u_t\rangle^2 \ , \tag{3.3}$$

where no orthogonality constraint is placed on $u_t(r)$. It is easily verified that this expression constitutes a valid minimum principle. Thus we return to the identity (2.10) and expand the Green's function as

$$G(r,r')=\mathbf{S}'_n\phi_n(r)w(E_n)\phi_n^\dagger(r') +\phi_1(r)w(E_1)\phi_1^\dagger(r')+\frac{1}{2m}\delta(r-r') \ , \tag{3.4}$$

where $w(E_n)$ was defined in Eq. (2.13) and where the prime on the generalized sum indicates that the bound-state contribution is omitted. With this omission the function $w(E_n)$ appearing in the sum is negative. Removal of the first term on the right in Eq. (3.4) leads, when the remainder is combined with Eq. (2.10), to the expression appearing on the right-hand side of Eq. (3.3), whose error has now been shown to be negative.

A very simple test of the minimum principle (3.3) was performed by choosing a square-well potential that supports a single bound state, and a trial scattering function of minimal complexity consistent with the boundary conditions. (Further details are given in the Appendix.) With the second term on the right-hand side of Eq. (3.3) omitted the numerical results obtained are quite useless; the bound is violated and the calculated scattering length is completely unstable with respect to variation of the exponential parameter in the trial function. Inclusion of the positive correction term rectifies the situation; the bound is preserved and the results are stable and surprisingly accurate. Evidently, imposition of the orthogonality condition not only provides a bound but, by introducing the correct nodal structure, also results in a significant improvement in the trial function.

The above discussion suggests that when the bound-state function is imprecisely known an improved trial scattering function could be constructed in the form

$$u_{tt}(r)=u_t(r)+b\phi_{1t}(r) \ , \tag{3.5}$$

where $\phi_{1t}(r)$ is a trial bound-state wave function and $b$ is a parameter to be determined variationally. That is, we replace $u_t$ with $u_{tt}$ in the functional given in Eq. (2.14a) and require that the expression be stationary with respect to variations in the linear parameter $b$. This procedure leads to the approximation

$$A^{(1)}=A^{(0)}+\frac{2}{m}\frac{\langle \phi_{1t}|(\bar{H}-m)|u_t\rangle^2}{\langle \phi_{1t}|(m-\bar{H}|\phi_{1t}\rangle} \ , \tag{3.6}$$

with $\bar{H}$ defined as in Eq. (2.14b). This approximation for the scattering length reduces, as it must, to that shown in Eq. (3.3) when the trial bound-state function is exact. It will now be demonstrated that the functional $A^{(1)}$ just defined represents a minimum principle for the scattering length provided that the parameter $d=\langle \phi_{1t}|(m-\bar{H})|\phi_{1t}\rangle$ is positive. This positivity requirement will be seen to represent a sufficient condition for the existence of a bound state; one may say that the condition $d>0$ implies that the trial bound-state function is accurate enough to give binding. We shall, in addition, obtain a maximum principle for the bound-state energy [16]. These results will be generalized later to the case where an arbitrary, but finite, number of bound states exist.

To begin, we seek an analog of the nonrelativistic Rayleigh-Ritz method to provide an aid in the construction and systematic improvement of a trial bound-state wave function. Let $\xi(r)$ be an admissible, normalized trial function. (Formally, an admissible trial function in a variational calculation is one that can be expanded in a complete set of eigenfunctions of the Hamiltonian; no attempt is made here to provide a more rigorous characterization.) Recalling that the modified Green's function $\bar{G}$, Eq. (2.12), is negative if no bound states exist, we see that there is at least one bound state is $\langle \xi|\bar{G}|\xi\rangle>0$. The maximum value of this expectation value is $w(E_1)$, and this inequality provides a lower bound on $E_1$; the eigenvalues are assumed to be ordered according to $m>E_1>E_2>\cdots>E_n>-m$. To put this inequality in a useful form we adopt a procedure used in Ref. [6] and write

$$|\xi\rangle = \frac{(m-H)|\phi_{1t}\rangle}{\langle\phi_{1t}|(H-m)^2|\phi_{1t}\rangle^{1/2}} . \tag{3.7}$$

The maximum principle for the highest bound-state energy is then expressed as

$$E_1 \geq m - \frac{\langle\phi_{1t}|(H-m)^2|\phi_{1t}\rangle}{\langle\phi_{1t}|(m-H)|\phi_{1t}\rangle} . \tag{3.8}$$

These results may be generalized with the aid of the Hylleraas-Undheim theorem [8]. Thus we may suppose that a matrix representation of the operator $\bar{G}$ is constructed using as basis a set $\{\xi_n\}$ of $M$ normalized, linearly independent functions. Raising the dimension of the matrix to $M+1$ raises the eigenvalues in such a way that the new set interlaces those of the original matrix. In particular, if an $N\times N$ matrix of $\bar{G}$ has been constructed that is positive (that is, each eigenvalue $\lambda_n$, or equivalently, each principal minor, is positive) we may conclude that there are at least $N$ bound states and that

$$w(E_1)\geq\lambda_1\geq w(E_2)\geq\cdots\geq w(E_N)\geq\lambda_N \tag{3.9}$$

are valid inequalities. A variational lower bound on each energy eigenvalue, put in practical form by transformation of the basis functions as indicated in Eq. (3.7), is derived from the inequalities (3.9). The functions $\phi_{nt}$ obtained from this procedure can be useful in applications requiring a basis set that effectively spans the spectrum of solutions of the Dirac equation. (While the scattering theory discussed here is not valid for potentials with a Coulomb tail, this restriction does not apply to the use of the Hylleraas-Undheim theorem for bound-state calculations.)

Returning now to the scattering problem, we assume that one (and only one) bound state exists and that a trial function $\xi(r)$ has been found that gives a positive expectation value for $\bar{G}$. It follows from the preceding discussion that a $2\times 2$ matrix of $\bar{G}$ formed from the functions $\xi(r)$ and $\psi(r)$ (they need not be orthogonal) must have a negative determinant, that is

$$\langle\psi|\bar{G}|\psi\rangle \leq \frac{\langle\psi|\bar{G}|\xi\rangle\langle\xi|\bar{G}|\psi\rangle}{\langle\xi|\bar{G}|\xi\rangle} . \tag{3.10}$$

An upper bound on the scattering length is obtained by inserting the decomposition of the Green's function shown in Eq. (2.11) into the identity (2.10), with $\bar{G}$ replaced by its upper bound, as determined by Eq. (3.10). With $\xi(r)$ chosen as in Eq. (3.7) and with $\psi$ taken to be $(H-m)u_t$, the minimum principle for the scattering length, in the form shown in Eq. (3.6), is confirmed. To complete the demonstration we observe that the condition $\langle\xi|\bar{G}|\xi\rangle>0$ is equivalent to the requirement that $d=\langle\phi_{1t}|(m-\bar{H})|\phi_{1t}\rangle$ be positive.

Extension of the preceding analysis to the case where $N$ bound states exist is straightforward and we merely state the results. We assume that a set of $N$ linearly independent trial functions $\{\xi_i\}$ has been found such that the matrix $d$, with elements $d_{ij}=\langle\xi_i|\bar{G}|\xi_j\rangle$, is positive. Application of the Hylleraas-Undheim theorem leads to a generalization of Eq. (3.10) which may be stated in the form of an operator inequality, namely, that the modified Green's function

$$\bar{G} - \sum_{i=1}^{N}\sum_{j=1}^{N} \bar{G}|\xi_i\rangle(d^{-1})_{ij}\langle\xi_j|\bar{G}$$

is negative. One has effectively "subtracted out" not only the continuum of negative-energy states but the set of $N$ discrete states as well. Combining this result with the identity (2.10) for the scattering length and the definition (2.11), we are led immediately to the generalized version of the minimum principle. To put this prescription in practical form we express each of the functions $\xi_i$ in terms of functions $\phi_{it}$—these are the functions that are constructed in an actual calculation—as

$$\xi_i = \frac{(m-H)|\phi_{it}\rangle}{\langle\phi_{it}|(H-m)^2|\phi_{it}\rangle^{1/2}} . \tag{3.11}$$

While it is unnecessary in practice, we assume that the matrix $d$ has been explicitly diagonalized, so that the statement of the minimum principle can be given in its simplest form, which adheres closely to that derived earlier, in Eq. (3.6) for $N=1$. One finds that

$$A \leq A_t + \frac{2}{m}\langle u_t|(\bar{H}-m)|u_t\rangle + \frac{2}{m}\sum_{i=1}^{N}\frac{\langle\phi_{it}|(\bar{H}-m)|u_t\rangle^2}{\langle\phi_{it}|(m-\bar{H})|\phi_{it}\rangle} . \tag{3.12}$$

An equivalent formulation may be established, in analogy with the earlier analysis that started with Eq. (3.5). Thus we consider a trial scattering function

$$u_{tt}(r) = u_t(r) + \sum_{i=1}^{N} b_i\phi_{it}(r) , \tag{3.13}$$

where the trial bound-state functions $\phi_{it}$ are sufficiently accurate to give binding to $N$ states (that is, each of the lower bounds that they generate lies in the gap between $-m$ and $m$). We now replace $u_t$ with $u_{tt}$ in the functional given in Eq. (2.14) and require that the expression be stationary with respect to variations in the linear parameters $b_i$. This procedure leads to a more general form of the minimum principle since the diagonalization requirement that appears in the version stated in Eq. (3.12) has not been imposed. These results are closely analogous to versions of the minimum principle derived some time ago for nonrelativistic scattering [10]. As in the nonrelativistic case, the requirement that the number of bound states be known may impose a limitation on the applicability of the method. Information obtained from experiment can sometimes be useful in determining the number of bound states. Sufficiently accurate variational calculations will generate the correct number of states, though one cannot rule out the possibility that some will be missed, particularly if they are very weakly bound.

## IV. VARIATIONAL PRINCIPLE FOR WAVE FUNCTIONS

The approximate bound-state wave functions required in the implementation of the minimum principle for the scattering length can be improved systematically using a

variational procedure, the stability of which is guaranteed by a subsidiary minimum principle. Since the procedure provides an illustration of the utility of some of the techniques described above, and should find applications in other contexts, we now present a brief outline of the method. Suppose that a single bound state $|\phi_1\rangle$ exists and that an accurate evaluation of the matrix element $S=\langle\psi|\phi_1\rangle$ is sought, with $\psi$ a known function. Let $\phi_{1t}$ be a trial function sufficiently accurate to give binding (in the sense defined earlier). We assume that the error in this trial function is a quantity that may be considered to be of first order and we look for a correction term that removes the first-order error. This will provide us with a variational approximation $\phi_{1v}$ for the wave function and hence a variational approximation $S_v=\langle\psi|\phi_{1v}\rangle$ for the overlap. As discussed in detail in connection with the analogous nonrelativistic problem [17], numerical instabilities may occur (arising from the use of an inexact bound-state wave function and manifesting themselves in the form of small energy denominators) in the course of the evaluation of the first-order correction term. A procedure for avoiding these difficulties with the introduction of a subsidiary minimum principle was developed [17]. A straightforward extension of that method to the relativistic case is not possible owing to the existence of the negative-energy continuum, an additional potential source of instability. We now show how the minimum principle, and hence the numerical stability of the calculational procedure, may be preserved.

Generalizing the form of the modified Hamiltonian introduced earlier in Eq. (2.14b), we define

$$\bar{H}(E)=H+\frac{(H-E)^2}{E+m}\ , \tag{4.1}$$

with $-m<E<m$, and observe that if $H$ has no discrete eigenvalues below $E$ then the operator $\bar{H}(E)-E$ is positive. (The negative-energy branch of the continuum has been mapped onto the positive-energy branch; as will be seen, this will provide the basis for the subsidiary minimum principle.) The eigenvalue equation for $|\phi_1\rangle$ may be taken to be

$$[\bar{H}(E)-E]|\phi_1\rangle=0\ . \tag{4.2}$$

A variational approximation to the solution of this equation is given formally by

$$|\phi_{1v}\rangle=|\phi_{1t}\rangle+G^q(E_{1v})\bar{H}(E_{1v})|\phi_{1t}\rangle\ . \tag{4.3}$$

Here $E_{1v}$ is a variational approximation to the energy and $G^q$ satisfies the resolvent equation

$$q[E-\bar{H}(E)]qG^q(E)=1\ , \tag{4.4}$$

with $q=1-|\phi_{1t}\rangle\langle\phi_{1t}|$. This improved approximation for the wave function leads to a variational approximation for the overlap in the form

$$S_v=\langle\psi|\phi_{1t}\rangle+\langle L|\bar{H}(E_{1v})|\phi_{1t}\rangle\ , \tag{4.5}$$

where $L$ satisfies the inhomogeneous equation

$$q[E_{1v}-\bar{H}(E_{1v})]q|L\rangle=q|\psi\rangle\ . \tag{4.6}$$

There remains the task of finding a suitable approximation scheme for determining the auxiliary function $L$, free of numerical instabilities that could arise by virtue of the approximate nature of the trial bound-state function and the existence of the negative-energy continuum. We now show that by virtue of our choice of modified Hamiltonian, these difficulties may be avoided. Thus let the approximate eigenvalue $E_{1v}$ be chosen to be a variational *lower* bound to the true energy—the bound given in Eq. (3.8) would be a convenient and appropriate choice. Since $H$ has no discrete eigenvalues below $E_{1v}$, it follows (see above) that the minimum expectation value of $\bar{H}(E_{1v})$ lies above $E_{1v}$. The same must hold for the minimum expectation value of $q\bar{H}(E_{1v})q$ since the presence of the projection operator introduces an additional constraint. It may be concluded that the resolvent $G^q(E_{1v})$ is negative. A minimum principle for the resolvent is then available for constructing a suitable trial function to be used, in Eq. (4.5), for the evaluation of the overlap. Specifically, we consider the matrix element $M=\langle\psi|G^q(E_{1v})|\psi\rangle$ and observe that it may be expressed as the sum of a variational approximation and a second-order error term [in analogy with the variational identity for the scattering length introduced in Eq. (2.10)]. The identity takes the form

$$M=\langle\psi|L_t\rangle+\langle L_t|\psi\rangle+\langle L_t|[\bar{H}(E_{1v})-E_{1v}]|L_t\rangle$$
$$+\langle J|G^q(E_{1v})|J\rangle\ , \tag{4.7}$$

where

$$|J\rangle=q|\psi\rangle+q[\bar{H}(E_{1v})-E_{1v}]q|L_t\rangle\ , \tag{4.8}$$

and where $|L_t\rangle$ is an approximate solution of Eq. (4.6). Since the error term in Eq. (4.7) is negative, minimization of the variational approximation for $M$ represents a well-defined, stable, procedure for determining the trial function $L_t$ to be used as an approximation to $L$ in Eq. (4.5).

## V. DISCUSSION

The effectiveness of variational methods in the treatment of nonrelativistic bound-state and scattering problems suggests that relativistic extensions would be useful. Progress in this direction has been made during the past few years in the development of variational procedures of the Rayleigh-Ritz type for a Dirac particle bound in a potential well. It has been demonstrated here that rather similar techniques can be applied to the scattering problem. We have focused our attention on the evaluation of the scattering length since in this case a minimum principle can be derived and this allows us to confirm unambiguously that the variational collapse problem has in fact been solved. In the course of the analysis we have introduced methods that should be useful in calculating bound-state energies and wave functions. A variational principle for bound-state wave functions was derived, along with a subsidiary minimum principle for the construction of auxiliary trial functions (these play the familiar role of Lagrange multipliers) that appear in the variational functional. Very similar methods are applicable to

the solution of the inhomogeneous equations of perturbation theory, that is, to the evaluation of the Dirac Green's function.

One may speculate about the utility of minimum principles in relativistic treatments of electron-atom scattering. In hole theory, projection operators appear which eliminate negative-energy continuum branches from the spectrum of the Hamiltonian. The problem is then (at least formally) analogous to that of nonrelativistic scattering by a compound target, in which case a minimum principle for the effective potential, valid over a restricted range of energies above the continuum threshold, is available [11]. Relativistic versions might be useful for electron scattering by highly charged ions, even in the low-energy domain. The existence of an infinite series of Feshbach resonances would at first appear to pose a serious obstacle to such a development. Fortunately, the accumulation point of that series lies at the threshold of an *excited* state of the target. For a scattering energy $E$ below that level there is only a finite number of resonances (bound-state poles of the effective potential) that must be subtracted out to preserve the minimum principle, and methods discussed here for subtracting out bound states should be useful in this context. Of course, there are many other difficulties, both formal and practical, that must be overcome before such a calculational program can be implemented.

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## APPENDIX

As a partial test of the minimum principle for the scattering length a square-well potential was chosen, of range $a$ and strength $-V_0$, and a calculation was performed using trial functions of the very simple form

$$u_{1t}=mr-mA_t(1-e^{-\alpha r/a}) ,$$
$$u_{2t}=\frac{A_t}{2r}(1-e^{-\beta r/a})^2 . \tag{A1}$$

An exact solution shows that with the dimensionless range parameter $R=ma$ fixed at the value 1.5, the first bound state appears for $U\equiv V_0/m=0.522$. With this dimensionless potential-strength parameter taken to be 0.3, a variational calculation based on the functional shown in Eq. (2.14) provides the bound $A<-0.835a$, to be compared to the exact value $-1.020a$. The accuracy improves for weaker potentials and, as would be expected, grows increasingly poor as the critical value is approached from below, but in all cases the bound is satisfied. With $U$ taken to lie above 0.522, results obtained using the functional given in Eq. (2.14) are unstable with respect to variation of the exponential parameters. Such behavior is to be expected since Eq. (2.14) is not a valid minimum principle when a bound state exists, unless that state is built into the trial function as in Eq. (3.2) or (3.5); this is not the case for the function (A1), as indicated by the absence of nodes. Since the bound-state eigenvalue problem is solvable, the version of the minimum principle given in Eq. (3.3) was adopted, with $U=0.8$, a value for which a single bound state exists. With the exponential parameter $\beta$ fixed at unity, and with $\alpha$ varied between 1 and 3, the upper bound obtained is accurate to 10%; the best result for the scattering length, obtained for $\alpha=1.5$, was $2.108a$, the exact value being $2.004a$.

[1] G. W. F. Drake and S. P. Goldman, Adv. At. Mol. Opt. Phys. **25**, 393 (1988).
[2] H. Wallmeier and W. Kutzelnigg, Chem. Phys. Lett. **78**, 341 (1981); W. Kutzelnigg, Int. J. Quantum Chem. **25**, 107 (1984).
[3] W. Baylis and S. J. Peel, Phys. Rev. A **28**, 2552 (1983).
[4] L. Rosenberg and L. Spruch, Phys. Rev. A **34**, 1720 (1986).
[5] J. D. Talman, Phys. Rev. Lett. **57**, 1091 (1986).
[6] R. N. Hill and C. Krauthauser, Phys. Rev. Lett. **72**, 2151 (1994).
[7] G. W. F. Drake and S. P. Goldman, Phys. Rev. A **23**, 2093 (1981); S. P. Goldman, *ibid.* **31**, 3541 (1985).
[8] E. A. Hylleraas and B. Undheim, Z. Phys. **65**, 759 (1930).
[9] L. Spruch, Phys. Rev. Lett. **16**, 1137 (1966).
[10] L. Rosenberg, L. Spruch, and T. F. O'Malley, Phys. Rev. **118**, 184 (1960).
[11] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **134**, B1911 (1964).
[12] M. E. Rose, *Relativistic Electron Theory* (Wiley, New York, 1961).
[13] Recall that for a Dirac particle in a central potential the wave function has the form

$$\psi=\begin{pmatrix} g(r)\chi_\kappa^\mu \\ if(r)\chi_{-\kappa}^\mu \end{pmatrix} ,$$

where $\chi_\kappa^\mu$ is a spin-angle function and $\mu$ and $\kappa$ are angular momentum quantum numbers (see Ref. [12], p. 159). The radial wave functions of interest here are $u_1=rg$ and $u_2=rf$. We restrict our attention to potentials for which $rV(r)$ is finite for $r\to 0$, in which case $u_1(0)$ and $u_2(0)$ are both zero. This is seen from the explicit solution for a potential that is Coulombic at the origin (although $g$ and $f$ are singular in that case) and less directly (see Ref. [12], p. 241) for potentials that are bounded there. For completeness we mention that only electron scattering (energy $=+m$) is considered here. The equations that determine the charge conjugate radial functions $f^c$ and $g^c$ appropriate to a description of positrons are obtained from those

for $f$ and $g$ by changing the sign of the potential (see Ref. [12], p. 160).

[14] This represents a relativistic version of an identity introduced by T. Kato, Prog. Theor. Phys. (Kyoto) **6**, 295 (1950).

[15] Several treatments of the variational collapse problem in Dirac bound-state calculations involve the square of the Hamiltonian; see Refs. [2,3,6].

[16] Alternative methods for obtaining bounds on Dirac energy eigenvalues are described in Refs. [2,3,6,7].

[17] E. Gerjuoy, L. Rosenberg, and L. Spruch, J. Math. Phys. **16**, 455 (1975).