Extremum principles for relativistic atomic structure and scattering: Two-electron ions

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The time-independent Hamiltonian version of QED provides a foundation for a relativistic description of atomic structure and scattering, with virtual-pair effects treated in a consistent manner. Since the spectrum of the Hamiltonian is bounded from below, the problem of "variational collapse," associated with the existence of negative-energy solutions of the Dirac equation, does not arise. For the same reason, extremum principles of the Rayleigh-Ritz type may be applied. These features are illustrated here in the context of a system consisting of two electrons in an external Coulomb field. An effective Hamiltonian describing this system is constructed in a ladder approximation that accounts for the virtual creation and annihilation of electron-positron pairs. It is shown that this pair contribution to the effective Hamiltonian satisfies a maximum principle and that, consequently, a minimax principle is available for the approximate evaluation of the binding energy of the heliumlike ion. The relation between the present treatment of virtual-pair effects and that based on the Bethe-Salpeter equation in the ladder approximation is clarified.

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I. INTRODUCTION

Relativistic effects can be significant in the analysis of heavy atoms. The theory of such effects is often formulated by setting up a multielectron generalization of the Dirac equation. The potential difficulties of such an approach, associated with the appearance of negative-energy solutions, has been discussed in detail in the context of bound-state calculations [1,2]. It is clear that similar difficulties arise, in principle, in the scattering problem. Indeed, the difficulty is compounded since the possibility of the creation of a virtual pair having a combined energy anywhere in the continuum implies that intermediate states in the scattering process will appear with such a range of energies. This will introduce spurious branch cuts in the scattering amplitude leading, for example, to incorrect behavior near reaction thresholds.

It is to be expected [1,2] that the problems mentioned above do not arise in a QED formulation (in which negative-energy electrons are reinterpreted as positive-energy positrons). Here we shall verify explicitly, in the context of a particular model allowing for virtual-pair creation, that variational collapse is avoided in the QED formulation through the natural appearance of projection operators. It will be shown that an infinite subset of contributions to the effective Hamiltonian arising from sequences of pair-creation and pair-annihilation processes may be summed in closed form and evaluated approximately with the aid of an extremum principle of the Rayleigh-Ritz type.

The starting point of our analysis is a relativistic version of the resolvent-operator formulation of time-independent many-body perturbation theory [3]. To illustrate the application of this theory in a relatively simple context we develop, in Sec. II, a formal expression for the effective Hamiltonian for a two-electron ion. Radiative corrections are ignored here; presumably they may be treated perturbatively once the wave equation containing the effects of the dominant instantaneous Coulomb interactions has been solved. (This will be possible provided that a proper treatment of radiative corrections can be given, surmounting the problem of renormalization that remains in the noncovariant Hamiltonian formulation.) An explicit approximation for the effective Hamiltonian is determined, in Sec. III, that allows for a class of virtual-pair effects consistent with a generalized ladder approximation of the type introduced some time ago [4] in the context of the two-body Bethe-Salpeter equation. It is shown that this effective Hamiltonian may be constructed variationally, with the aid of a maximum principle. The use of a minimax principle for the evaluation of bound-state energies, analogous to that introduced previously for the one-electron Dirac equation [5], is then described. Results are summarized briefly in Sec. IV.

II. EFFECTIVE HAMILTONIAN

The resolvent-operator formalism provides a convenient basis for the analysis of time-independent bound-state and scattering problems. Following the procedure outlined previously [3] we introduce the resolvent,

$$R(z)=(z-H)^{-1} . \tag{2.1}$$

The Hamiltonian H is defined in terms of the matter-field operator,

$$\psi(\mathbf{x})=\sum_{n}^{(+)} A_n u_n(\mathbf{x})+\sum_{m}^{(-)} B_m^{\dagger} v_m(\mathbf{x}) , \tag{2.2}$$

where A_n and B_m are electron and positron annihilation operators with the property that their action on the vacuum state is given by

$$A_n|0\rangle=B_m|0\rangle=0 . \tag{2.3}$$

The anticommutation relations are

$$\{A_n, A_n^\dagger\}=\delta_{nn'}\ , \quad \{B_m, B_m^\dagger\}=\delta_{mm'}\ , \tag{2.4}$$

with all other anticommutators vanishing. The spinors u_n and v_m satisfy

$$h(\mathbf{x})u_n(\mathbf{x})=\varepsilon_n u_n(\mathbf{x})\ , \quad \varepsilon_n>0 \tag{2.5a}$$

and

$$h(\mathbf{x})v_m(\mathbf{x})=\varepsilon_m v_m(\mathbf{x})\ , \quad \varepsilon_m<0 \tag{2.5b}$$

where, with $\hbar=c=1$,

$$h(\mathbf{x})=\boldsymbol{\alpha}\cdot(-i\nabla)+\beta m+V_{\text{ext}}(\mathbf{x})=0\ . \tag{2.5c}$$

The external potential V_{ext} is taken here to be the attractive electron-nucleus Coulomb interaction.

With the neglect of transverse-photon effects the Hamiltonian is just the sum $H=H_0+H_C$, where H_0, when put into normal-ordered form, becomes

$$H_0=\sum_n^{(+)}\varepsilon_n A_n^\dagger A_n+\sum_m^{(-)}|\varepsilon_m|B_m^\dagger B_m\ , \tag{2.6}$$

and the (instantaneous) Coulomb interaction is

$$H_C=\tfrac{1}{2}\int\psi^\dagger(\mathbf{x})\psi(\mathbf{x})\frac{e^2}{4\pi|\mathbf{x}-\mathbf{x}'|}\psi^\dagger(\mathbf{x}')\psi(\mathbf{x}')d^3x\,d^3x'\ . \tag{2.7}$$

(Effects of the exchange of virtual transverse photons between electrons can be taken into account in an approximate manner by adding the Breit operator to the above Coulomb interaction [1]; this will not be indicated explicitly here.)

We consider matrix elements of the resolvent of the form $\langle\beta|R(z)|\alpha\rangle$. Here $|\alpha\rangle$ and $|\beta\rangle$ are eigenstates of H_0 corresponding to a pair of electrons in the presence of the external field of the nucleus (but unperturbed by self-energy interactions [6]) with positive-energy eigenvalues $E_{0\alpha}$ and $E_{0\beta}$, respectively. A perturbation expansion of the matrix element of the resolvent may be obtained from an iterative solution of the integral equation,

$$R(z)=R_0(z)+R_0(z)H_CR(z)\ , \tag{2.8}$$

where $R_0(z)=(z-H_0)^{-1}$. Terms in the expansion may be represented diagrammatically in the usual way. According to the Hugenholtz factorization theorem [7] the matrix element $\langle\beta|R(z)|\alpha\rangle$ may be expressed as the convolution [8] of $\langle\beta|\hat{R}(z)|\alpha\rangle$, defined as the sum of all connected diagrams, and $\langle 0|R(z)|0\rangle$, representing the sum of all disconnected vacuum-to-vacuum transitions. (Figure 1 provides an example of a fifth-order disconnected diagram consisting of a second-order vacuum component and a connected third-order scattering component.) The factorization property is useful since it allows us to focus our attention on the connected contributions, ignoring the (in general divergent) vacuum graphs.

We now define the "two-electron irreducible" amplitude,

$$F_{\beta\alpha}(z)=\langle\beta|[H_C+H_CR_0(z)H_C+\cdots]'|\alpha\rangle\ , \tag{2.9}$$

where the prime on the bracket enclosing the sum indicates that only connected diagrams are included in the perturbation expansion and no terms with two-electron intermediate states are retained. Since the general term in the expansion of $\langle\beta|\hat{R}(z)|\alpha\rangle$ is obtained by connecting the irreducible components with two-electron propagators we may write

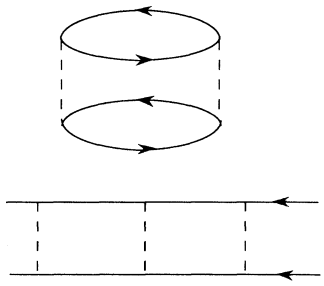


FIG. 1. Disconnected diagram containing a vacuum-to-vacuum component of second order, representing the virtual creation and subsequent annihilation of two electron-positron pairs, and a connected component contributing to scattering in third order. The Coulomb interaction is represented by a dashed line and solid lines represent electron or positron propagation in the Coulomb field of the nucleus.

$$\langle\beta|\hat{R}(z)|\alpha\rangle=\delta_{\beta\alpha}(z-E_{0\alpha})^{-1}+(z-E_{0\beta})^{-1}\times\sum_\gamma F_{\beta\gamma}(z)\langle\gamma|\hat{R}(z)|\alpha\rangle\ , \tag{2.10}$$

where we have used the relation $R_0(z)|\alpha\rangle=(z-E_{0\alpha})^{-1}|\alpha\rangle$, and where the sum is over two-electron intermediate states.

By converting Eq. (2.10) to configuration space we may deduce the form of the effective Hamiltonian and from that the configuration-space wave equation that describes the bound-state structure and scattering dynamics of physical interest. Toward this end we introduce the ket,

$$|\mathbf{x}_1\mathbf{x}_2\rangle=\frac{1}{\sqrt{2}}\sum_{n_1}^{(+)}\sum_{n_2}^{(+)}u_{n_1}^\dagger(\mathbf{x}_1)u_{n_2}^\dagger(\mathbf{x}_2)A_{n_1}^\dagger A_{n_2}^\dagger|0\rangle\ , \tag{2.11}$$

describing a pair of positive-energy electrons at well-defined positions. The matrix that brings about the transformation to the coordinate representation is

$$\langle\mathbf{x}_1\mathbf{x}_2|n_1n_2\rangle=\frac{1}{\sqrt{2}}[u_{n_1}(\mathbf{x}_1)u_{n_2}(\mathbf{x}_2)-u_{n_1}(\mathbf{x}_2)u_{n_2}(\mathbf{x}_1)]\ . \tag{2.12}$$

The eigenstates of the system may be determined from the residues of the poles in the resolvent operator, as described in Ref. [3]. That formalism is readily adapted to the two-electron system studied here, and rather than repeat the analysis we simply provide the result; with the aid of the resolvent equation (2.10) we obtain a wave equation of the form,

$$[h_1(\mathbf{x}_1)+h_2(\mathbf{x}_2)]\Psi(\mathbf{x}_1,\mathbf{x}_2) + \int d^3y_1 d^3y_2 M(\mathbf{x}_1,\mathbf{x}_2;\mathbf{y}_1,\mathbf{y}_2;E)\Psi(\mathbf{y}_1,\mathbf{y}_2) = E\Psi(\mathbf{x}_1,\mathbf{x}_2) . \quad (2.13)$$

The effective potential is identified as the coordinate representation of the two-electron irreducible amplitude, that is,

$$M(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';E\rangle = \langle \mathbf{x}_1\mathbf{x}_2|[H_C + H_C R_0(E) H_C + \cdots]'|\mathbf{x}_1'\mathbf{x}_2'\rangle . \quad (2.14)$$

The restriction of the wave function to the two-electron subspace is expressed in terms of projection operators as

$$\int d^3y_1 d^3y_2 L_1^{(+)}(\mathbf{x}_1,\mathbf{y}_1) L_2^{(+)}(\mathbf{x}_2,\mathbf{y}_2)\Psi(\mathbf{y}_1,\mathbf{y}_2) = \Psi(\mathbf{x}_1,\mathbf{x}_2) , \quad (2.15)$$

with

$$L^{(+)}(\mathbf{x},\mathbf{x}') = \sum_n^{(+)} u_n(\mathbf{x}) u_n^\dagger(\mathbf{x}') . \quad (2.16)$$

Since the effective potential is energy-dependent the eigenvalue equation (2.13) for bound states must be determined self-consistently, a feature familiar from standard Brillouin-Wigner perturbation theory. The scattering problem is simpler in the sense that the energy is fixed in advance. The effective potential, to first order in the Coulomb interaction and with a self-energy contribution omitted [6], is

$$M^{(1)}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2';E\rangle = \int d^3y_1 d^3y_2 \langle \mathbf{x}_1\mathbf{x}_2|\mathbf{y}_1\mathbf{y}_2\rangle \times \frac{e^2}{4\pi|\mathbf{y}_1-\mathbf{y}_2|}\langle \mathbf{y}_1\mathbf{y}_2|\mathbf{x}_1'\mathbf{x}_2'\rangle . \quad (2.17)$$

Note that

$$\langle \mathbf{x}_1\mathbf{x}_2|\mathbf{y}_1\mathbf{y}_2\rangle = L_1^{(+)}(\mathbf{x}_1,\mathbf{y}_1) L_2^{(+)}(\mathbf{x}_2,\mathbf{y}_2) \quad (2.18)$$

in the space of antisymmetric wave functions.

III. LADDER APPROXIMATION

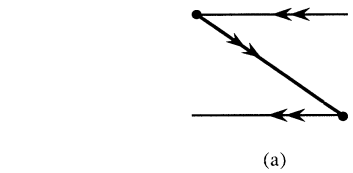
A. Diagram summation procedure

The wave equation (2.13) has the structure $(H_0+M)\Psi=E\Psi$. It will be convenient to rearrange this to read $(H_+ + Z)\Psi = E\Psi$, with $H_+ = H_0 + M^{(1)}$ representing the two-electron Hamiltonian obtained by neglecting virtual-pair effects and with $Z = M - M^{(1)}$. The resolvent associated with the "no-pair" Hamiltonian is denoted as R_+. We also introduce eigenfunctions $\Phi_\alpha^\pm$ of H_+, satisfying either outgoing-wave $(+)$ or incoming-wave $(-)$ boundary conditions at infinity, along with the corresponding eigenvalues E_α. We shall not enter at this time into a thorough discussion of the scattering theory appropriate to the relativistic system under consideration, which would include a precise specification of the boundary conditions and a formal definition of the transition amplitude $T_{\beta\alpha}$. Rather, we simply adopt from such a theory the result of use to us here, which is the distorted-wave Born expansion [9],

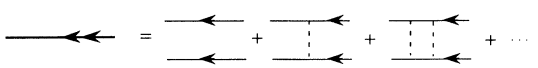
$$T_{\beta\alpha} = T_{\beta\alpha}^{\text{no pair}} + (\Phi_\beta^{(-)}, [Z + ZR_+Z + \cdots]\Phi_\alpha^{(+)}) \quad (3.1)$$

of the T matrix. If the first term on the right-hand side, the T matrix in the no-pair approximation, is expanded in powers of the interelectronic Coulomb potential a series is generated the terms of which may be represented by ladder diagrams of the type pictured in Fig. 2(b). We look for an approximation for the very complicated effective potential Z in the form of a generalized ladder approximation that includes an arbitrary number of interactions in which two electron-positron pairs are created and are subsequently annihilated. The simplest term of this type, involving a single creation-annihilation sequence, is shown in Fig. 2(a); the propagation of the two-particle system under the influence of their mutual Coulomb interaction and the field of the nucleus is pictured in Fig. 2(b). We denote the contribution to the effective potential shown in Fig. 2(a), of second order in the creation-annihilation interaction, as $Z^{(2)}$. Two of the diagrams contributing to $Z^{(4)}$ are shown in Fig. 3. Not shown there are the remaining three diagrams required to provide all possible orderings of creation and annihilation vertices consistent with the ladder approximation in fourth order. Remarkably, the ladder diagrams representing the terms in the expansion of Z, along with those obtained from the iterative construction of the transition amplitude given in Eq. (3.1), can be summed formally to all orders, as will now be demonstrated. This will lead us to a very much simplified form for the effective potential that will be analyzed further, with the aid of variational techniques, in Sec. III C.

The amplitude represented in Fig. 2(a) is determined by



(a)



(b)

FIG. 2. Diagram (a) is a schematic representation of the contribution to the transition amplitude arising from the virtual creation of two electron-positron pairs and their subsequent annihilation. The line with two arrow heads pointing to the left represents the propagation of a pair of electrons subject to their mutual Coulomb interaction and the Coulomb field of the nucleus. This propagator can be pictured as a sum of ladder graphs, as indicated in diagram (b). The diagonal line in (a) represents the propagator, in the ladder approximation, for a pair of positrons.

summing over intermediate states consisting of two electron pairs and a positron pair, each pair under the influence of their mutual Coulomb interaction and the external Coulomb field of the nucleus. (Interactions between particles in different pairs are excluded in the ladder approximation.) The propagation of each pair is described by a resolvent operator that may be expanded in terms of the appropriate eigenfunctions. The two-electron eigenfunctions Φ_α of H_+ have been introduced earlier. There is a corresponding configuration-space Hamiltonian H_- describing the two positrons whose eigenfunctions and eigenvalues we denote as Θ_κ and E_κ, respectively, with $E_\kappa > 0$. [We adopt the convention that two-electron states are labeled by the indices $\alpha,\beta,\gamma,\ldots$, and the indices $\kappa,\lambda,\mu,\ldots$, label two-positrons states. In addition, we temporarily drop the superscripts $(+)$ and $(-)$ that distinguish between the different boundary conditions satisfied by the continuum eigenfunctions.] The explicit form taken by H_- is determined (by examination of the ladder approximation for the positron-pair propagator) to be

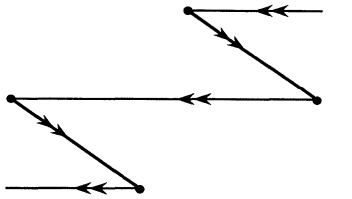
$$H_-(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = -[h_1(\mathbf{x}_1)+h_2(\mathbf{x}_2)]L^{(-)}(\mathbf{x}_1,\mathbf{x}_1')L^{(-)}(\mathbf{x}_2,\mathbf{x}_2') + \int d^3y_1 d^3y_2 L^{(-)}(\mathbf{x}_1,\mathbf{y}_1)L^{(-)}(\mathbf{x}_2,\mathbf{y}_2)V_C(\mathbf{y}_1,\mathbf{y}_2)L^{(-)}(\mathbf{y}_1,\mathbf{x}_1')L^{(-)}(\mathbf{y}_2,\mathbf{x}_2') \; . \tag{3.2}$$

Here $V_C(\mathbf{x}_1,\mathbf{x}_2)$ is an abbreviation for the Coulomb potential $e^2/4\pi|\mathbf{x}_1-\mathbf{x}_2|$ and

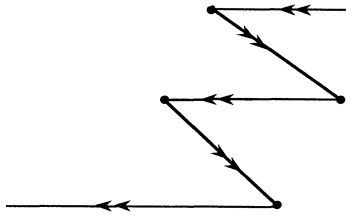
$$L^{(-)}(\mathbf{x},\mathbf{x}') = \sum_m^{(-)} v_m(\mathbf{x})v_m^\dagger(\mathbf{x}') \tag{3.3}$$

is the projection operator onto negative-energy solutions of the Dirac equation (2.5b). The contribution to the transition amplitude corresponding to diagram 2(a) may be written as

$$[\Phi_\beta, Z^{(2)}(E)\Phi_\alpha] = -\sum_\kappa \tilde{\Gamma}_{\beta\kappa}[E-(E_\beta+E_\alpha+E_\kappa)]^{-1}\Gamma_{\kappa\alpha} \; , \tag{3.4}$$



(a)



(b)

FIG. 3. Diagrams (a) and (b) each represent contributions to the transition amplitude of fourth order in the interaction that creates or annihilates two electron-positron pairs. Not shown are the three additional diagrams that complete the set of fourth-order contributions with all possible orderings (along the horizontal direction in the diagram) of creation and annihilation vertices.

where

$$\Gamma_{\kappa\alpha} = \int d^3x_1 d^3x_2 \Theta_\kappa^\dagger(\mathbf{x}_1,\mathbf{x}_2)V_C(\mathbf{x}_1,\mathbf{x}_2)\Phi_\alpha(\mathbf{x}_1,\mathbf{x}_2) \tag{3.5}$$

represents the vertex for the annihilation of an electron-positron pair and $\tilde{\Gamma}_{\beta\kappa}=\Gamma^*_{\kappa\beta}$ represents the creation vertex. [The dagger in Eq. (3.5) denotes the adjoint of a sixteen component spinor.] Since we are calculating the physical scattering amplitude we shall impose the on-shell condition $E=E_\beta=E_\alpha$ in each order; this leads to important simplifications. For example, in summing the five ladder diagrams that constitute the fourth-order contribution to the on-shell scattering amplitude we may combine energy denominators to arrive at the relatively simple form,

$$(\Phi_\beta, Z^{(4)}\Phi_\alpha)+(\Phi_\beta, Z^{(2)}R_+Z^{(2)}\Phi_\alpha) = \sum_\gamma\sum_\kappa\sum_\lambda \tilde{\Gamma}_{\beta\lambda}[E+E_\lambda]^{-1}\Gamma_{\lambda\gamma}[E-E_\gamma]^{-1} \times \tilde{\Gamma}_{\gamma\kappa}[E+E_\kappa]^{-1}\Gamma_{\kappa\alpha} \; . \tag{3.6}$$

This expression, along with the on-shell version of Eq. (3.4), suggests (the proof is given below) that the expansion (3.1) of the scattering amplitude is equivalent to one of the same form, but with Z replaced by the much simpler potential Z_{eff} [the on-shell version of $Z^{(2)}$], where

$$(\Phi_\beta, Z_{\text{eff}}\Phi_\alpha) = \sum_\kappa \tilde{\Gamma}_{\beta\kappa}[E+E_\kappa]^{-1}\Gamma_{\kappa\alpha} \; . \tag{3.7}$$

The sum over states in this expression can be evaluated implicitly with the introduction of the Green's function,

$$G(E) \equiv (E+H_-)^{-1} \; . \tag{3.8}$$

This leads to the representation

$$Z_{\text{eff}}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{y}_1,\mathbf{y}_2;E) = V_C(\mathbf{x}_1,\mathbf{x}_2)G(\mathbf{x}_1,\mathbf{x}_2;\mathbf{y}_1,\mathbf{y}_2;E) \times V_C(\mathbf{y}_1,\mathbf{y}_2) \; . \tag{3.9}$$

The suggestion just advanced concerning the form of the effective potential implies that in calculating the *on-shell* scattering amplitude in the ladder approximation we may assume an effective Hamiltonian,

$$H_{\text{eff}}=H_{+}+Z_{\text{eff}} , \tag{3.10}$$

with Z_{eff} given by Eq. (3.9). This latter expression is very similar to the form of the effective Hamiltonian for a single Dirac electron in a static potential [10,5], an observation that may in fact be used to provide a simple (if somewhat indirect) justification of the result shown in Eq. (3.9). Thus let us consider the Born expansion of the one-electron scattering amplitude in a hole-theoretic formulation in which the field operator is expanded in a basis of free-particle solutions of the Dirac equation. This problem was analyzed [10] as a pedagogic exercise; the form of the effective potential that emerges from the calculation is known in advance to be that derived much more directly, without the use of field theory, from the first-quantized Dirac equation. That calculation becomes relevant to our present concerns, however, when we realize that the diagram-summation procedure which led to the expression for the effective potential in the one-electron problem may be adopted, formally, to carry out the verification of Eq. (3.9). For example, the algebra that led to Eq. (3.6), involving the regrouping of the set of all terms contributing to the scattering amplitude in fourth order, is identical to that encountered, in the corresponding order, in the one-electron problem. The vertex functions are different but the energy denominators are the same, and that allows us to put the two calculations in one-to-one correspondence. In general, the terms in the expansion are of the same form, order-by-order, with different meanings given to the vertex functions in the two cases. In this way the justification of Eq. (3.9) is achieved.

B. Salpeter equation

It is of interest to observe that an alternative derivation of the effective Hamiltonian shown in Eq. (3.10) follows from the Salpeter equation [4], or rather its external-field version, obtained by imposing the ladder approximation on the Bethe-Salpeter equation for the two-electron system in the presence of the nuclear Coulomb field. In the present notation, the external-field Salpeter equation is of the form,

$$[E-h_1-h_2]|\Psi\rangle=[L_{+}-L_{-}]V_C|\Psi\rangle . \tag{3.11}$$

We have introduced the simplified notation $L_{+}(\mathbf{x}_1\mathbf{x}_2,\mathbf{y}_1\mathbf{y}_2)=L_1^{(+)}(\mathbf{x}_1,\mathbf{y}_1)L_2^{(+)}(\mathbf{x}_2,\mathbf{y}_2)$, along with an analogous definition of L_{-}. We write $\Psi=\Psi_{+}+\Psi_{-}$, where (with integration variables suppressed) $L_{+}\Psi=\Psi_{+}$ and $L_{-}\Psi=\Psi_{-}$. With the aid of the projection operators we may decompose the equation (3.11) for Ψ into two coupled equations for the components Ψ_{+} and Ψ_{-}. Then Ψ_{-} may be eliminated, in the standard way [11]. This leaves us with an equation for Ψ_{+} alone. The result is

$$\begin{aligned}[E-h_1-h_2-L_{+}V_CL_{+}]|\Psi_{+}\rangle \\ =L_{+}V_CL_{-}[E-h_1-h_2 \\ +L_{-}V_CL_{-}]^{-1}L_{-}V_C|\Psi_{+}\rangle .\end{aligned} \tag{3.12}$$

The effective potential appearing on the right-hand side is just that defined above in Eq. (3.9). In this way we have established a correspondence between the covariant Bethe-Salpeter approach and that based on the use of a time-independent Hamiltonian formulation. This latter method may be more tractable for the study of multielectron systems.

C. Extremum principles

With the expression (3.10) now established, we next turn our attention to the problem of setting up an approximation procedure—specifically, one based on a maximum principle—for the construction of the effective potential $Z_{\text{eff}}=V_CG(E)V_C$. Here we make use of an approach developed previously [5] in the context of the one-electron Dirac equation. The physics of the present problem is quite different since it is based on hole theory, but the mathematical procedure is essentially identical to that described in Ref. [5]. The essential point is that the operator $E+H_{-}$ is positive definite in the space of functions W_{-} satisfying $L_{-}W_{-}=W_{-}$. This is the case since the potential V_C in Eq. (3.2) is positive as is the operator $-(h_1+h_2)L_{-}$. (In the scattering problem, which we consider first, the energy parameter E takes on a specified positive value. Bound states are considered below.) It follows [5] that the Green's function $G(E)$ defined in Eq. (3.8) may be approximated with the aid of a maximum principle. Thus with $G^t(E)$ representing a trial Green's function satisfying $L_{-}G^t=G^tL_{-}=G^t$, we have the identity

$$G=G^t+G[1-(E+H_{-})G^t] . \tag{3.13}$$

We now replace G on the right-hand side by $G^t+\Delta G$ to obtain

$$G=G^v+\Delta G(E+H_{-})\Delta G , \tag{3.14}$$

where

$$G^v=G^t+G^t[1-(E+H_{-})G^t] \tag{3.15}$$

is a variational approximation whose error, according to Eq. (3.14), is positive. Consequently, the choice of the variational parameters in the trial Green's function may be optimized by maximizing a diagonal expectation value of the variational approximation,

$$(Z_{\text{eff}})^v=V_CG^v(E)V_C , \tag{3.16}$$

of the effective potential. To put this prescription in more specific terms, consider the separable approximation $G^t=c|W_{-}^t\rangle\langle W_{-}^t|$ and let the variational parameter c be determined by requiring that the expression (3.15) be stationary with respect to variations in this parameter. This leads to the form

$$(Z_{\text{eff}})^v=V_C|W_{-}^t\rangle\frac{1}{\langle W_{-}^t|(E+H_{-})|W_{-}^t\rangle}\langle W_{-}^t|V_C . \tag{3.17}$$

One may be guided by the maximum principle in the choice of the trial function W_{-}^t.

To satisfy the requirement that the function W_{-}^t lie in

the negative-energy subspace one may adopt the form

$$W^t_-(\mathbf{x}_1,\mathbf{x}_2)=\sum_{i=1}^{N}\sum_{j=1}^{N}a_{ij}w_i(\mathbf{x}_1)w_j(\mathbf{x}_2)\ . \tag{3.18}$$

The set of negative-energy basis functions $\{w_i\}$ may be constructed with the aid of the generalized Hylleraas-Undheim theorem [12], which has been shown [13] to be valid for the one-electron Dirac equation when the external potential is of the Coulomb form. In this procedure one diagonalizes the Hamiltonian $h(\mathbf{x})$ in a $2N$-dimensional space. The $2N$ eigenvalues split into N positive and N negative eigenvalues. The positive eigenvalues behave exactly as if the Dirac Hamiltonian were a positive-definite operator. The N negative eigenvalues all lie below $-mc^2$ and move progressively toward $-mc^2$ as the basis dimension is increased. The eigenfunctions associated with these negative eigenvalues may be taken to constitute the basis $\{w_i\}$ from which the trial function W^t_- is formed. There is in addition the positive-energy constraint, of the form $L_+\Psi_+=\Psi_+$, that must be imposed on the scattering wave function. One method for eliminating the constraint, through a transformation to a set of reduced equations of the Schrödinger-Pauli form, was discussed in Ref. [1].

We have thus far focused our attention on the scattering problem. The effective Hamiltonian may also be used to determine bound states. The maximum principle for the effective potential may be combined with the standard Rayleigh-Ritz minimum principle for the energy eigenvalues; the minimax principle that emerges from these considerations may be formulated, in parallel with the analysis given in Ref. [5], as follows. Let E represent the ground-state energy determined by the equation $H_{\text{eff}}(E)W_+=EW_+$. A trial ground-state energy E^t is chosen, and its value is fixed in the initial stage of the process leading to a variational approximation to the ground-state energy. (As will be seen later, one may ultimately have to perform iterations to improve the estimate of the energy.) The variational approximation for the energy is taken to be

$$\begin{aligned}E^v=&\langle W^t_+|H_+|W^t_+\rangle+\langle W^t_+|V_C|W^t_-\rangle\\&+\langle W^t_-|V_C|W^t_+\rangle-\langle W^t_-|H_-+E^t|W^t_-\rangle\ ,\end{aligned} \tag{3.19}$$

where W^t_+ and W^t_- are trial functions satisfying $L_+W^t_+=W^t_+$ and $L_-W^t_-=W^t_-$, respectively. These trial functions are to be determined with the aid of the minimax procedure. Thus for a given choice of W^t_+ and E^t the variational parameters contained in W^t_- are determined by maximizing the energy E^v. The maximum value is achieved when W^t_- is an exact solution of

$$L_-(H_-+E^t)|W^t_-\rangle=L_-V_C|W^t_+\rangle\ . \tag{3.20}$$

Note that were it possible to satisfy Eq. (3.20) exactly, thereby making available a solution that may be represented formally as $W^t_-=G(E^t)V_CW^t_+$, Eq. (3.19) would reduce to the Rayleigh-Ritz estimate,

$$E^v=\langle W^t_+|H_{\text{eff}}(E^t)|W^t_+\rangle\ . \tag{3.21}$$

In practice, with the parameters in W^t_- determined by the maximization process, and with E^t still fixed, the optimum choice of the variational parameters in W^t_+ is that which minimizes E^v. If necessary one would repeat the process with different choices for E^t and search for a more self-consistent solution. If it were possible to make a complete search for the optimum choice of trial functions the minimax value thus obtained would coincide with the ground-state energy of $H_{\text{eff}}(E^t)$. The above analysis may be extended to the variational determination of excited-state energies, as discussed in Appendix B of Ref. [5] for the analogous treatment of the one-body Dirac equation.

We remark, finally, that since Z_{eff} in Eq. (3.10) is a positive operator its presence can only raise the energy eigenvalues above those determined by the Hamiltonian H_+. It follows that an exact determination of the energy levels of H_+ provides rigorous (nonvariational) lower bounds on the eigenvalues of H_{eff}.

IV. SUMMARY

The time-independent Hamiltonian formulation of QED provides a general basis for the analysis of relativistic effects in atomic bound-state and scattering problems. In the presence of strong interparticle Coulomb interactions nonperturbative methods are required and in many cases the Hamiltonian approach will provide the most effective calculational procedure. The version of this formulation outlined here, leading to the construction of effective Hamiltonians in configuration space, is an extension of that described in Refs. [1] and [2]. The effects of virtual-pair creation has been included here in a particular model, the ladder approximation for a two-electron ion, and the infinite series of terms generated by this approximation have been summed. The resultant expression for the effective potential is of the form that allows for the use of a maximum principle as an aid in its evaluation. Since the spectrum of the effective Hamiltonian is bounded from below (no variational collapse difficulties arise) it has been possible to formulate a minimax procedure for the approximate determination of binding energies. This provides a hole-theoretic generalization of the development of extremum principles in the analysis of the one-electron Dirac equation [5].

The configuration-space wave equation derived here in the ladder approximation represents an external-field version of that obtained some time ago [4] from the Bethe-Salpeter equation. It is noteworthy that while the summation of ladder diagrams is more difficult using noncovariant propagators—the Feynman procedure allows one to sum many diagrams corresponding to different time ordering in a very efficient manner—it has been possible to perform the sum in the model considered here. The possibility of carrying out such sums for a wider class of problems, combined with the calculational benefits of the Hamiltonian method, suggests that this method deserves further consideration in the search for a practical, and very generally applicable, basis for the study of relativis-

tic multielectron systems.

It may be appropriate, in conclusion, to take note of some earlier work concerned with relativistic effects in high-Z atoms which has some overlap with the subject addressed here, though not with its methodology. Consideration of virtual-pair effects is central to the analysis of the decay of the unstable neutral vacuum in supercritical fields [14,15]. Extensive theoretical studies of this process, taking into account the dynamic effect of the motion of the pair of heavy ions which momentarily coalesce to form the superheavy nucleus, have been performed [16]. With regard to the study of two-electron ions, it should be mentioned that relativistic bound-state calculations for such systems have been carried out in the no-pair approximation using many-body perturbation theory [17]. The high accuracy of these calculations compares with that obtained from a nonrelativistic variational treatment with QED corrections included perturbatively [18]. The multiconfiguration Fock-Dirac procedure also provides satisfactory results in may cases of interest [19–21]; a version of that method has recently been applied to a high-Z two-electron system as part of an investigation of parity-violation effects in atoms [22]. There has clearly been a great deal of progress made in the relativistic treatment of heliumlike ions. A search for alternative formulations that allow for the systematic improvement of calculational accuracy, with relativistic correlation and virtual-pair effects included, would still appear to be worthwhile.

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[1] J. Sucher, Phys. Rev. A **22**, 358 (1980).
[2] M. H. Mittleman, Phys. Rev. A **5**, 2395 (1972); **24**, 1167 (1981).
[3] L. Rosenberg, Phys. Rev. A **39**, 4377 (1989).
[4] E. E. Salpeter, Phys. Rev. **87**, 328 (1952).
[5] L. Rosenberg and L. Spruch, Phys. Rev. A **34**, 1720 (1986).
[6] The Coulomb interaction H_C introduces a self-energy contribution that is ignored here. It must eventually be combined with a corresponnding transverse-photon term, the sum then put in covariant form so that it may be subjected to standard renormalization procedures.
[7] N. M. Hugenholtz, Physica **23**, 481 (1957).
[8] The convoluton of two functions, say, $f(z)$ and $g(z)$, is defined as the integral $(2\pi i)^{-1}\int_c d\zeta f(z-\zeta)g(\zeta)$, where c is a counterclockwise contour enclosing the singularities of $g(z)$ on the real axis.
[9] The development of such an expansion in the context of the nonrelativistic scattering problem may be found in A. Messiah, *Quantum Mechanics* (Wiley, New York, 1966), p. 822. The relativistic version is obtained from a similar analysis.
[10] J. Sucher, Int. J. Quantum Chem. **25**, 3 (1984).
[11] Projection operators for the construction of effective potentials have been used in the treatment of resonant nuclear reactions by H. Feshbach, Ann. Phys. (N.Y.) **5**, 357 (1958).
[12] E. A. Hylleraas and B. Undheim, Z. Phys. **65**, 759 (1930).
[13] S. P. Goldman, Phys. Rev. A **31**, 3541 (1985).
[14] J. Rafelski, B. Müller, and W. Greiner, Nucl. Phys. B **68**, 585 (1974); L. Fulcher and A. Klein, Phys. Rev. D **8**, 2455 (1973).
[15] J. Reinhardt, B. Müller, and W. Greiner, Phys. Rev. A **24**, 103 (1981).
[16] W. Greiner, B. Müller, and J. Rafelski, *Quantum Electrodynamics of Strong Fields* (Springer-Verlag, Berlin, 1985).
[17] W. R. Johnson and J. Saperstein, Phys. Rev. A **46**, R2197 (1992).
[18] G. W. F. Drake, Can. J. Phys. **66**, 586 (1988).
[19] J. Hata and I. P. Grant, J. Phys. B **16**, 523 (1983); **17**, 931 (1984).
[20] P. Indelicato, O. Gorceix, and J. P. Desclaux, J. Phys. B **20**, 651 (1987).
[21] C. D. Lin, W. R. Johnson, and A. Dalgarno, Phys. Rev. A **15**, 154 (1977).
[22] A. Schöfer, G. Soff, P. Indelicato, B. Müller, and W. Greiner, Phys. Rev. A **41**, 4659 (1990).