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MINIMUM PRINCIPLE FOR THE DIRAC HAMILTONIAN: EXAMPLE OF THE COULOMB POTENTIAL*

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ABSTRACT

A minimum principle is established for the radial Dirac Hamiltonian for any potential. This principle uses an r-dependent unitary transformation to decouple the equations for the large and small components of the radial wavefunction; the transformed equation maps to an ordinary Sturm-Liouville equation whose minimum principle ensures convergence of the eigenvalues from above. As a concrete and typical example of the application of the principle, basis sets are developed for the Coulomb potential; these sets may be built out of any complete sequence of functions. The positive matrix eigenvalues converge from above to the exact bound-state eigenvalues, the negative eigenvalues converge from below to $-mc^2$, and the wavefunctions corresponding to positive eigenvalues converge in mean-square to the exact bound-state wavefunctions. For the Coulomb potential only, bases of relativistic Sturmian functions are found in which the matrix eigenvalue problem is banded instead of full, and can be solved quickly and stably on a computer even for as many as 4800 basis vectors. An analytic formula is given which expresses the eigenvalues and eigenvectors in terms of the Pollaczek polynomials and their zeros. A simple recursion is presented that will evaluate in any Sturmian basis the matrix elements involved in the emission and absorption of radiation.

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INTRODUCTION

The radial Dirac Hamiltonian has often been diagonalized in a finite basis, in order to sum numerically over intermediate states. The Hamiltonian for the Coulomb potential has been diagonalized in a variety of Slater bases [1] with noninteger leading powers, by Goldman and Drake [2], by Goldman [3], and by Drake [4], in order to calculate two-photon decay rates in one- and two-electron high-Z ions. Even in these bases, and for so simple a potential, a numerical eigenstate can be found that is physically meaningless, or a genuine eigenstate can be lost from the numerical spectrum. In more complicated bases and for other potentials, numerical eigenstates can be found which are physically sensible but whose numerical eigenvalues lie below the true eigenvalues. Reviews of the empirical prescriptions used to circumvent such problems may be found in reference 5. Only for the Coulomb potential, and for one particular Slater basis, have the numerical eigenvalues been proved, by Goldman [6, 7], even to be correctly bounded; our paper represents a generalization of his seminal work.

For the Coulomb potential we find that the use of all of Drake's and Goldman's Slater bases can be justified by a minimum principle for the radial Dirac Hamiltonian. This principle ensures, for any potential whatever, both the convergence from above of the positive eigenvalues, and the convergence in mean-square of the corresponding wavefunctions. This principle uses any of a infinite set of r-dependent unitary transformations to decouple the large and small components of the radial Dirac equation; the transformed equation maps to an ordinary Sturm-Liouville equation, whose familiar minimum principle provides the bounds on the eigenvalues and the convergence of the wavefunctions. We prove that this principle applies to any regular Dirac equation in a finite interval; to show that it applies to

at least one singular Dirac equation in an infinite interval, we apply it to the radial Dirac equation for the Coulomb potential. For this potential there are two particularly simple unitary transformations, for each of which the related Sturm-Liouville equation is just the radial Schrödinger equation for the Coulomb potential. To each transformation there corresponds a basis; for each basis it is shown when and why a meaningless eigenvector is found or a genuine one is lost, and how the basis can be repaired. The positive variational eigenvalues are proved to converge strictly from above to the exact eigenvalues, and the corresponding wavefunctions to converge in mean-square to the exact bound-state wavefunctions. The functions used in the bases may have any variation near the origin, may have discontinuous second derivatives, and may contain a set of nonlinear parameters that may be tuned to optimize the representation; we can thus apply to the Coulomb potential, and implicitly to any potential whatever, the full variational methods of Rayleigh and of Ritz [8].

Some results apply to the Coulomb potential only. All the Slater bases used by Goldman and by Drake are special cases of one or the other of our two bases, and we thus justify their use. A relativistic Sturmian basis [1] is found in which the matrix eigenvalue problem is banded instead of full; this matrix problem can be solved quickly and stably in $\sim N^2$ computer operations, instead of the usual $\sim N^3$, even for 4800 basis vectors. An analytic formula is found that expresses the matrix eigenvalues and eigenfunctions of this basis, and also of the bases of Drake and of Goldman, in terms of the Pollaczek polynomials and their zeros. A simple recursion is presented that can evaluate in any Sturmian basis the matrix elements involved in the emission and absorption of radiation.

The beginning of this paper deals with our first simple basis for the Coulomb potential; the middle deals with the second; and the end deals with our general

minimum principle. Section I reviews our conventions for the Dirac equation and a known correspondence between the Dirac and Schrödinger Coulomb problems. Section II begins our actual work and for our first basis lists our five principal theorems about the convergence of the eigenvalues and eigenfunctions; these theorems are proved in Sec. III. Section IV develops a relativistic Sturmian basis in which the matrix eigenvalue problem is banded, and Sec. V shows how to write the eigenvalues and eigenvectors in that basis analytically in terms of the Pollaczek polynomials and their zeros. Section VI introduces and develops our second simple basis, and Sec. VII presents the recursion that evaluates matrix elements in any Sturmian basis. Finally, in Sec. VIII we develop the minimum principle that applies to any potential whatever, prove that is works for any regular Dirac problem on a finite interval, and building on our success with the Coulomb potential, make some general remarks about the application of the minimum principle to any Dirac problem on an infinite interval. The paper is written so that section VIII can be read independently of the rest.

I. REVIEW OF UNITS AND CONVENTIONS

The symbol $\langle f \rangle$ is a shorthand for $\int_0^\infty f(r)\,dr$. The symbol (a,b) denotes the open interval $a < r < b$; the symbol $[a,b]$ denotes the closed interval $a \leq r \leq b$; and the symbol $[a,b)$ denotes the interval $a \leq r < b$. We adopt atomic units, $\hbar = m = e = 1$, and for the Dirac equation we adapt the conventions of Goldman [6], [9]. The Dirac equation for an electron in the Coulomb potential of a charge $Z > 0$ is $H\Psi = E\Psi$, where

$$H = \vec{\alpha}\cdot\vec{p} + \beta - \frac{Z\alpha^2}{r}\,. \tag{1.1}$$

Here $\vec{\alpha}$ and β are the usual 4×4 Dirac matrices. The solutions Ψ may be written as

$$\Psi = \begin{pmatrix} i\,\dfrac{g(r)}{r}\,\Omega_{jlm} \\ \\ -\dfrac{f(r)}{r}\,\Omega_{j\tilde{l}m} \end{pmatrix}, \tag{1.2}$$

where $g(r)$ and $f(r)$ are the large and small radial functions, and the functions Ω are two-component spherical spinors. The large and small functions satisfy the coupled equations $H(r)\psi = \epsilon\psi$,

$$\begin{pmatrix} \left(1-\dfrac{\alpha^2 Z}{r}\right) & \alpha\left(\dfrac{\kappa}{r}-\dfrac{d}{dr}\right) \\ \\ \alpha\left(\dfrac{\kappa}{r}+\dfrac{d}{dr}\right) & -\left(1+\dfrac{\alpha^2 Z}{r}\right) \end{pmatrix} \begin{pmatrix} g(r) \\ f(r) \end{pmatrix} = \epsilon \begin{pmatrix} g(r) \\ f(r) \end{pmatrix}, \tag{1.3}$$

where $\epsilon = \alpha^2 E$, and where κ is the Dirac quantum number, $\kappa = \pm(j+\frac{1}{2})$ for upper component angular momentum $l = j \pm \frac{1}{2}$ and lower component angular momentum $\tilde{l} = j \mp \frac{1}{2}$. Two new functions ϕ and θ, and a two-component function Φ, may be defined by a unitary transformation [10] of the functions f and g:

$$\Phi(r) \equiv \begin{pmatrix} \phi(r) \\ \theta(r) \end{pmatrix} \equiv \begin{pmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{pmatrix} \begin{pmatrix} g(r) \\ f(r) \end{pmatrix}. \tag{1.4}$$

Here φ may be in general a function of r. We seek a transformation that will reduce the upper-left element of the matrix in Eq. (1.3) to a constant. There are two simple solutions that have φ itself constant: $\sin 2\varphi = \alpha Z/\kappa$, with $\cos 2\varphi = -\gamma/\kappa$; and $\sin 2\varphi = \alpha Z/\kappa$, with $\cos 2\varphi = +\gamma/\kappa$. The parameter γ is defined by $\gamma = \sqrt{\kappa^2 - (Z\alpha)^2}$. To each solution there corresponds a simple way to construct variational states. Picking the first solution, Eq. (1.3) transforms to $h\Phi = \epsilon\Phi$, where the matrix operator $h(\kappa)$ is defined by

$$\begin{pmatrix} -\gamma/\kappa & -\alpha\left(\dfrac{Z}{\kappa}+\dfrac{\gamma}{r}+\dfrac{d}{dr}\right) \\ \\ -\alpha\left(\dfrac{Z}{\kappa}+\dfrac{\gamma}{r}-\dfrac{d}{dr}\right) & +\gamma/\kappa - 2\dfrac{\alpha^2 Z}{r} \end{pmatrix} \equiv \begin{pmatrix} \eta(\kappa) & B(\kappa) \\ B^\dagger(\kappa) & -\eta(\kappa)+A \end{pmatrix}. \tag{1.5}$$

The operators $B(\kappa)$ and $B^\dagger(\kappa)$, so defined [9], are Hermitian conjugates, because $\langle f_1 B(\kappa) f_2\rangle = \langle f_2 B^\dagger(\kappa) f_1\rangle$, if $[f_1 f_2]_0^\infty = 0$. The eigenvalues of $h(\kappa)$ for which $\epsilon \neq \eta(\kappa)$ fall into two continua, with $\epsilon < -1$ or $\epsilon > 1$, or into the discrete set

$$\epsilon_p = \left[1 + \left(\frac{(Z\alpha)^2}{\gamma + p}\right)\right]^{-1/2} , \tag{1.6}$$

where the index p runs $p = 1, 2, \ldots$. There are two normalized solutions with $\epsilon = \eta(\kappa)$. We label these as Φ_0 for $\kappa < 0$, and as Φ_f for $\kappa > 0$. Both have lower component functions θ that are zero. The upper component functions ϕ_0 and ϕ_f are respectively

$$\begin{aligned} \phi_0(r) &= \left[\left(\frac{2Z}{|\kappa|}\right)^{-(1+2\gamma)} \Gamma(1+2\gamma)\right]^{-1/2} r^{+\gamma} \exp\{-Zr/|\kappa|\} , \quad \kappa < 0 , \\ \phi_f(r) &= \left[\left(\frac{2Z}{|\kappa|}\right)^{-(1-2\gamma)} \Gamma(1-2\gamma)\right]^{-1/2} r^{-\gamma} \exp\{-Zr/|\kappa|\} , \quad \kappa > 0 . \end{aligned} \tag{1.7}$$

The second solution Φ_f is normalizable only for $\gamma < 1/2$. It is excluded from the spectrum of states, however, on the physical grounds that for it alone is the expectation value of the potential energy infinite. We thus recover the familiar result that the bound-state eigenvalues are given by Eq. (1.6), where the index p runs 0, 1, ... for $\kappa < 0$, but runs 1, 2, ... for $\kappa > 0$.

Except for Φ_0 and Φ_f, all other solutions of $h\Phi = \epsilon\Phi$ have $\theta(r) \neq 0$, eigenvalues $\epsilon \neq \eta(\kappa)$, and have components which satisfy the differential equations

$$\phi(r) = \frac{1}{\epsilon - \eta(\kappa)} B(\kappa)\, \theta(r) ,$$

$$\left[-\frac{d^2}{dr^2} + \frac{\gamma(\gamma+1)}{r^2} - \frac{2Z\epsilon}{r} - \frac{\epsilon^2 - 1}{\alpha^2}\right] \theta(r) = 0 . \tag{1.8a,b}$$

For bound states we impose the normalization $\langle \phi^2 + \theta^2 \rangle = 1$. We note that the solutions $\theta(r)$ of Eq. (1.8b) are proportional to the solutions $\theta_S(r)$ of the differential equation

$$\left[-\frac{d^2}{dr^2} + \frac{\gamma(\gamma+1)}{r^2} - \frac{2Z'}{r} \right] \theta_S(r) = 2E\, \theta_S(r) \ , \tag{1.9}$$

if one makes the correspondences $Z' = Z\epsilon$ and $(\epsilon^2 - 1)/\alpha^2 = 2E$. Equation (1.9) is the familiar eigenvalue equation for the radial Schrödinger Hamiltonian, for an electron in the Coulomb potential of a charge Z' (which may be positive or negative), and for an artificial noninteger angular momentum equal to γ. That the only bound states of Eq. (1.9) occur for $Z' > 0$ and for eigenvalues E_p given by

$$E_p(Z') = -\frac{Z'^2}{2(\gamma+p)^2} \ , \qquad p = 1, 2, \ldots \ , \tag{1.10}$$

at once establishes, for example, that the bound states of Eq. (1.8b) must have eigenvalues ϵ_p given by Eq. (1.6). Equation (1.8b), and the equivalence of the Dirac and Schrödinger Coulomb equations, were probably first obtained by Martin and Glauber [11]. We will use the equivalence to establish a minimum principle for the operator $h(\kappa)$.

II. THEOREMS ON BOUNDS AND CONVERGENCE

The following five theorems summarize, for the operator $h(\kappa)$ and therefore for our first basis, the principal results of our study of both bounds and completeness for variational eigenstates for the Dirac Coulomb Hamiltonian. Parallel theorems for the second basis are described in Sec. VI.

Theorem 1. *Eigenvalue bounds*

Let $\{w\}$ be a set of N linearly independent functions. Let the functions w and dw/dr and w/r be absolutely continuous on $[0,\infty)$. For all n,m let the integrals

$$\begin{aligned} &\left\langle \frac{d^2w_n}{dr^2}\, w_m \right\rangle , \qquad \left\langle \frac{dw_n}{dr}\, w_m \right\rangle , \qquad \left\langle w_n w_m \right\rangle , \\ &\left\langle \frac{dw_n}{dr}\, \frac{dw_m}{dr} \right\rangle , \qquad \left\langle \frac{w_n w_m}{r} \right\rangle , \\ &\left\langle \frac{dw_n}{dr}\, \frac{w_m}{r} \right\rangle , \\ &\left\langle \frac{w_n w_m}{r^2} \right\rangle , \end{aligned} \tag{2.1}$$

exist, and let the (absolutely continuous) functions $w_n w_m/r$ and $w_n(dw_m/dr)$ vanish at the origin. Define the basis of $2N$ two-component functions $\{Q(\kappa)\}$ by $Q_n \equiv (B(\kappa)w_n, 0)$ for $n = 1,\ldots,\ N$, and $Q_{N+n} \equiv (0, w_n)$ for $n = 1,\ldots,\ N$. Diagonalizing $h(\kappa)\Phi = \epsilon\Phi$ in the basis $\{Q(\kappa)\}$ produces N positive and N negative eigenvalues. For $\kappa < 0$ the eigenvectors are all normal to the exact state Φ_0. For either sign of κ the eigenvalues obey proper variational bounds, in that the negative eigenvalues lie below -1, and the p^{th} positive eigenvalue lies above the corresponding exact bound-state eigenvalue ϵ_p, for $p = 1,\ 2,\ \ldots$. The upper and lower components ϕ and θ of the eigenfunctions are connected by the differential equation (3.5).

Theorem 2. *Equivalence of problems with opposite signs of* κ

Compare the results of diagonalizing, for each sign of κ, the operator $h(\kappa)$ in the base $Q(\kappa)$. The N eigenvalues are the same, and the lower component functions θ of eigenvectors corresponding to equal eigenvalues are proportional. The constant of proportionality is given by Eq. (3.9).

Theorem 3. *Completeness of the representation*

Suppose that, in addition to satisfying the assumptions of Theorem 1, the set of functions $\{w\}$ is complete. Then for $\kappa > 0$, the set $\{Q(\kappa)\}$ is a complete set of two-component functions, while for $\kappa < 0$, the set $\{Q(\kappa) \oplus \Phi_0\}$ is a complete set. As $N \to \infty$, the matrix eigenfunctions Φ that have positive eigenvalues converge in mean-square to the corresponding bound-state eigenfunctions. The positive eigenvalues converge monotonically from above to the exact eigenvalues ϵ_p, and the negative eigenvalues converge monotonically from below to -1.

Theorem 4. *Harmless expansion of the basis set*

To any base $\{Q(\kappa)\}$ made of functions $\{w\}$ which satisfy the requirements of Theorem 1, add a number m of new basis vectors of the form $(f_j(r), 0)$, for $j = 1, \ldots, m$. Let the $N + m$ functions $\{f_m, B(\kappa)w_n\}$ be linearly independent. Then the original $2N$ eigenvalues and eigenfunctions of the basis $\{Q\}$ are unchanged, and there are m new eigenfunctions of the form $(F_j, 0)$, for $j = 1, \ldots, m$. The functions F_j are linear combinations of the functions $f_j(r) - \sum_{n=1}^{N} \langle f_j | B(\kappa)w_n \rangle B(\kappa)w_n(r)$. The new eigenvectors may be distinguished from the old both by their common eigenvalue η and by their vanishing lower component function θ.

Theorem 5. *Variational representation of* Φ_0

Suppose that, corresponding to a sequence of functions w_n, of which the first N always satisfy the assumptions of Theorems 1 and 3, there can be found a sequence of functions u_n, such that the first $N+1$ functions u span both the first N functions

$B(\kappa)w$ and the first N functions $B(-\kappa)w$. Then $h(\kappa)$ and $h(-\kappa)$ may both be diagonalized in the common basis of $2N+1$ functions $\{P\}$, where $P_n \equiv (u_n, 0)$ for $n = 1, \ldots, N+1$, and $P_{n+N+1} \equiv (0, w_n)$ for $n = 1, \ldots, N$. According to Theorem 4, of the $2N+1$ eigenvalues and eigenvectors, $2N$ are identical to those from a diagonalization of h in the basis Q. For $\kappa < 0$, provided $\langle u_1 | \phi_0 \rangle \neq 0$, the one extra numerical eigenfunction and eigenvalue so introduced may be used to complete the basis, instead of the exact eigenfunction Φ_0 and its eigenvalue ϵ_0. For $\kappa > 0$, the extra numerical eigenfunction so introduced is not needed to complete the basis, does not converge as $N \to \infty$, and cannot be assigned a meaning.

III. PROOFS OF BOUNDS AND CONVERGENCE

Let $\{w\}$ be a set of N linearly independent functions satisfying the requirements of Theorem 1. Then for either sign of κ, the integrals $\langle B(\kappa)w_n | B(\kappa)w_m \rangle$ and $\langle w_n B^\dagger(\kappa) B(\kappa) w_m \rangle$ exist, and a justifiable integration by parts shows that they are equal. Indeed the conditions on the functions w in Theorem 1 have been chosen mostly to ensure that these integrals will exist and be equal. Consider diagonalizing $h(\kappa)$ in the basis of $2N$ vectors $\{Q(\kappa)\}$, where $Q_n \equiv \big(B(\kappa)w_n, 0\big)$ for $n = 1, \ldots, N$; and $Q_{n+N} \equiv \big(0, w_n\big)$ for $n = 1, \ldots, N$. The integral $\big\langle Q_n h(\kappa) Q_m \big\rangle$ always exists; the bases used for opposite signs of κ are different because $B(\kappa) \neq B(-\kappa)$. We note that the solution to the differential equation $B(\kappa)f = 0$ is the function $f(r) = r^{-\gamma} e^{-Zr/\kappa}$. For neither sign of κ does $\langle f^2/r \rangle$ exist (the function f is square integrable, however, if $\gamma < 1/2$), so we exclude the function f from the set $\{w\}$. The linear independence of the functions $\{w\}$ then ensures the linear independence of the set of functions $\{B(\kappa)w\}$. The allowed class of functions $\{w\}$ is quite broad; it may include, for example, functions

for which the second derivative is only piecewise continuous, as well as functions which do not vary near the origin like $r^{\gamma+1}$ as do all the exact eigenfunctions θ. For $\kappa < 0$, the functions Q are all normal (because $B^\dagger(\kappa)\phi_0 = 0$ for $\kappa < 0$) to the eigenstate Φ_0, which lacks a corresponding state with $\kappa > 0$ that is degenerate in energy.

In the basis $\{Q\}$, the upper and lower functions ϕ and θ of the eigenstates $\Phi = (\phi, \theta)$ may be expanded in terms of two N-component vectors x_1 and x_2 as

$$\phi = \sum_{j=1}^{N} (x_1)_j \; B(\kappa) w_j \; , \qquad \text{and} \qquad \theta = \sum_{j=1}^{N} (x_2)_j \; w_j \; . \tag{3.1}$$

The eigenvalue equation $h(\kappa)\Phi = \epsilon\Phi$ in the basis $\{Q\}$ is equivalent both to the matrix equation

$$\begin{pmatrix} \eta M & M \\ M & A \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \epsilon \begin{pmatrix} M & 0 \\ 0 & U \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \; , \tag{3.2}$$

and to the pair of separate equations

$$\begin{aligned} \eta M x_1 + M x_2 &= \epsilon M x_1 \; , \\ M x_1 + (-\eta U + A)\; x_2 &= \epsilon U x_2 \; , \end{aligned} \tag{3.3a,b}$$

where $M_{nm} = \langle B(\kappa) w_n | B(\kappa) w_m \rangle$, $A_{nm} = \langle w_n | A | w_m \rangle$, and $U_{nm} = \langle w_n | w_m \rangle$. The matrix M is the overlap matrix of N independent functions Bw, and so is positive definite. Therefore, if $MX = 0$ for some vector X, then $X = 0$. At least one of the vectors x_1 and x_2 must be nonzero in a valid solution to Eq. (3.2). Equation (3.3b) shows that $x_2 \neq 0$, and then Eq. (3.3a) that $x_1 \neq 0$ and $\epsilon \neq \eta$. Therefore, the vectors x_1 and x_2 are proportional,

$$x_1 = \frac{x_2}{\epsilon - \eta} \; , \tag{3.4}$$

and from Eq. (3.1) one finds that the variational wavefunctions satisfy the differential equation

$$\phi = \left[\frac{1}{\epsilon - \eta(\kappa)}\right] B(\kappa)\,\theta \ , \tag{3.5}$$

which is analogous to Eq. (1.8a) for the exact states. Eliminating x_1 in Eq. (3.3b), using Eq. (3.5), we find that x_2 satisfies a matrix equation analogous to Eq. (1.8b):

$$\sum_{m=1}^{N} \left\langle w_n \left| -\frac{d^2}{dr^2} + \frac{\gamma(\gamma+1)}{r^2} + \frac{1-\epsilon^2}{\alpha^2} - \frac{2Z\epsilon}{r} \right| w_m \right\rangle [x_2]_m = 0 \ . \tag{3.6}$$

This equation does not depend on the sign of κ, and one can work backward from Eq. (3.6) to construct the matrix eigenvalue equation, Eq. (3.2), for either sign. Therefore, the variational states with opposite signs of κ have equal eigenvalues, and have, except for normalization, the same lower component functions $\theta(r)$. That the exact eigenvalues and eigenfunctions have these properties too is evident from an examination of Eq. (1.8b), which like Eq. (3.6) is independent of the sign of κ. A proof that in a Slater basis the eigenvalues and eigenfunctions must have these properties was presented by Goldman [6], but the proof is incomplete [12].

The constant of proportionality between θ_κ and $\theta_{-\kappa}$ depends on their common eigenvalue ϵ and may be calculated, following Goldman [6], as follows. The eigenvalue equation $\langle \Phi h(\kappa) \Phi \rangle = \epsilon \langle \Phi | \Phi \rangle$, expressed in terms of the upper and lower components ϕ and θ, is equivalent to the pair of equations

$$\begin{aligned} \big(\eta(\kappa) - \epsilon\big)\langle \phi | \phi \rangle + \langle \phi | B(\kappa)\,\theta \rangle &= 0 \ , \\ \langle \theta | B(\kappa) \phi \rangle - \epsilon \langle \theta | \theta \rangle + \langle \theta A\, \theta \rangle &= 0 \ . \end{aligned} \tag{3.7}$$

Using Eq. (3.5) and the normalization condition $\langle \phi^2 + \theta^2 \rangle = 1$ to eliminate ϕ, we find that

$$\epsilon = \frac{\eta(\kappa) + 2\alpha^2 Z \left\langle \theta_\kappa^2 / r \right\rangle}{1 - 2 \left\langle \theta_\kappa^2 \right\rangle} \ , \tag{3.8}$$

from which it follows that

$$\theta_{-\kappa}(r) = \pm \left[\frac{\epsilon + \eta(\kappa)}{\epsilon - \eta(\kappa)}\right]^{1/2} \theta_\kappa(r) \ . \tag{3.9}$$

The factor under the square root is greater than zero. This follows from the integrals $\langle \theta_\kappa^2 \rangle$ and $\langle \theta_\kappa^2 / r \rangle$ being both greater than zero, or independently from the bounds on the eigenvalues ϵ that we shall prove shortly. The overall sign in Eq. (3.9) may be set by convention.

Compare now the two different matrix eigenvalue problems

$$\sum_{m=1}^{N} \left\langle w_n \left| -\frac{d^2}{dr^2} + \frac{\gamma(\gamma+1)}{r^2} - \frac{2Z\epsilon}{r} \right| w_m \right\rangle [x_2]_m = \left(\frac{\epsilon^2 - 1}{\alpha^2}\right) \sum_{m=1}^{N} \langle w_n | w_m \rangle \, [x_2]_m \ ,$$

$$\sum_{m=1}^{N} \left\langle w_n \left| -\frac{d^2}{dr^2} + \frac{\gamma(\gamma+1)}{r^2} - \frac{2Z'}{r} \right| w_m \right\rangle [x]_m = 2E \sum_{m=1}^{N} \langle w_n | w_m \rangle \, [x]_m \ . \tag{3.10a, b}$$

The first equation is Eq. (3.6) rewritten; the second is an ordinary eigenvalue problem in the same basis $\{w\}$ for N vectors x and eigenvalues E for the radial Schrödinger Hamiltonian of Eq. (1.9). Plainly there exists a solution x_2, ϵ, to the first, if and only if there exists a solution x, E, to the second, with $x = x_2$ and the correspondences

$$Z' = Z\epsilon \ , \qquad \text{and} \qquad \frac{\epsilon^2 - 1}{\alpha^2} = 2E \ . \tag{3.11a, b}$$

We desire to have the eigenvalues of Eq. (3.10b) bound by the exact eigenvalues—and for the eigenfunctions to converge in mean-square to the exact eigenfunctions—of the Schrödinger Coulomb problem, Eq. (1.9). It is both sufficient and necessary [13] that the integrals $\langle w_n w_m / r^2 \rangle$ and $\langle w_n \, d^2 w_m / dr^2 \rangle$ and $\langle \bar{w}_n w_m \rangle$ exist for all n, m (which conditions incidentally imply that the functions w_n vanish at zero and at infinity). For $Z' < 0$, the eigenvalues

E are therefore greater than zero. For $Z' > 0$, if the eigenvalues E are indexed 1, 2, ..., in order of increasing energy, then the p^{th} eigenvalue is greater than or equal to E_p, for $p = 1, 2, \ldots$. The correspondence in Eq. (3.11) shows that all negative eigenvalues ϵ of Eq. (3.10a) are less than -1. To show that the p^{th} positive eigenvalue of Eq. (3.10a) is greater than or equal to ϵ_p, we use the following graphical argument.

The N eigenvalues of Eq. (3.10b), considered as functions of Z', define N continuous curves with continuous first derivatives on the interval $-\infty < Z' < \infty$. Label these curves as $E^{(j)}(Z')$, for $j = 1, \ldots, N$. Because the matrix of $-d^2/dr^2 + \gamma(\gamma+1)/r^2$ is positive definite, when $Z' = 0$ the eigenvalues of (3.10b) are all greater than zero. The curves $E^{(j)}(Z')$ have asymptotes that are straight lines through the origin; for large $|Z'|$ these asymptotes are approached from above. The correspondence in Eq. (3.11) requires that the values of E and Z' for which there are eigenvalues ϵ are those for which the curves $E^{(j)}(Z')$ intercept the parabola $E(Z') \equiv (Z'^2 - Z^2)/(2Z\alpha)^2$. Because this parabola is negative for $Z' = 0$ and is concave up, it must cross each of the N curves $E^{(j)}(Z')$ at least twice. But a Hermitian matrix eigenvalue problem like Eq. (3.2) must have $2N$ linearly independent eigenvectors with precisely $2N$ corresponding eigenvalues, so the parabola must cross each of the curves just twice, once for $Z' > 0$ and once for $Z' < 0$. The correspondence in Eq. (3.11) shows then that there are then N positive and N negative eigenvalues ϵ.

The matrix of $-1/r$ is negative definite. Each eigenvalue of a Hermitian matrix decreases when a negative definite Hermitian matrix is added [14], and so each of the functions $E^{(j)}(Z')$ is a strictly decreasing function of Z'. Now suppose that one found p positive eigenvalues of Eq. (3.10a) all less than the exact bound-state eigenvalue ϵ_p, with $\epsilon^{(1)} \leq \epsilon^{(2)} \leq \ldots \leq \epsilon^{(p)} < \epsilon_p$. The correspondence

in Eq. (3.11b) requires that all the eigenvalues E be less than E_p, and the correspondence in Eq. (3.11a) that the values of Z' assigned to the eigenvalues be less than or equal to the value $Z'(\epsilon^{(p)})$ assigned to $\epsilon^{(p)}$. But all the curves $E^{(j)}(Z')$ are strictly decreasing functions of Z', and so for $Z' = Z'(\epsilon^{(p)})$ there must be p eigenvalues of Eq. (3.10b) all less than E_p. That would violate the eigenvalue bounds for the Schrödinger problem, and so the p^{th} eigenvalue of Eq. (3.10a) must always lie above the corresponding exact eigenvalue ϵ_p [15].

The inclusion theorem [16] of the theory of matrix diagonalization requires that if an $M \times M$ Hermitian matrix is augmented with a new row and column to become of dimension $(M+1) \times (M+1)$, then the set of new eigenvalues $\{\lambda\}$ interleaves with the set of the old eigenvalues $\{\Lambda\}$, so that the eigenvalues may be put in the order $\lambda_1 \leq \Lambda_1 \leq \lambda_2 \leq \Lambda_2 \ldots \leq \Lambda_M \leq \lambda_{M+1}$. Because there are always an equal number of positive and negative eigenvalues ϵ, if a new function w is added to $\{Q\}$, and so two new rows and columns added to the matrix equation in Eq. (3.2), the p^{th} positive eigenvalue cannot increase and the p^{th} negative eigenvalue cannot decrease.

Now suppose the set of functions $\{w\}$ is complete, so for any function $f(r)$ square-integrable on $[0, \infty)$, an expansion in terms of a set of coefficients a_n can be found, so that

$$\lim_{N\to\infty} \int_0^\infty \left[f(r) - \sum_{n=1}^{N} a_n w_n(r) \right]^2 dr = 0 \,. \tag{3.12}$$

For $\kappa > 0$ the set of two-component functions $\{Q(\kappa)\}$ is complete. For $\kappa < 0$ the set becomes complete if augmented (before or after the matrix diagonalization) with the eigenfunction Φ_0. As the size of the basis is increased, and so as the curve $E^{(j=p)}(Z')$ descends ever closer to the curve $E_p(Z')$, the p^{th} positive eigenvalue must limit to its lower bound, ϵ_p. We prove this formally as follows. The exact

eigenvalue ϵ_p corresponds to the crossing for $Z' > 0$ of the decreasing parabola $E_p(Z')$ and the increasing parabola $E(Z')$. This crossing occurs at the special value of Z' equal to $Z'_p \equiv Z\epsilon_p$. Because the p^{th} eigenvalue ϵ is always greater than or equal to ϵ_p, and never increases as N is increased, the values of Z' corresponding to the crossing points are always greater than or equal to Z'_p, and never increase. Label the values of Z' at the successive crossing points as $Z'_c(N)$. Pick a value N_0. Because the p^{th} eigenvalue never increases, the correspondence in Eq. (3.11a) shows that if $N > N_0$, then $Z'_p \leq Z'_c(N) \leq Z'_c(N_0)$. Let $E(p, Z')$ denote the p^{th} eigenvalue [17] of Eq. (3.10b) as a function of Z'. The convergence of the Schrödinger problem, Eq. (3.10b), guarantees that, corresponding to some number $\delta > 0$, we can find $N_1 \geq N_0$, so that if $N > N_1$, then $0 \leq E(p, Z') - E_p(Z') < \delta$ for all Z' in the interval $[Z'_p, Z'_c(N_0)]$. From the formulæ for the two parabolas $E(Z')$ and $E_p(Z')$, for all $N > N_1$ we can show that $0 \leq Z'_c(N) - Z'_p < \delta/C$, where $C > 0$ is the constant $C \equiv (dE/dZ' - dE_p/dZ')|_{Z'=Z'_p} = Z'_p/Z\alpha^2 + Z'_p/(\gamma + p)^2$. The bound on $Z'(N)$ translates via Eq. (3.11a) to the bound $0 \leq \epsilon - \epsilon_p < \delta/CZ$ for all $N > N_1$. Because δ is arbitrary, Z'_c and ϵ converge monotonically from above to Z'_p and ϵ_p, respectively. That the negative eigenvalues ϵ converge monotonically to -1 from below, and that the values of Z' converge monotonically from below to $-Z$, can be proved without a graphical argument. We need only the correspondence in Eq. (3.11), and the fact that the eigenvalues E of Eq. (3.10b) for $Z' < 0$ converge monotonically from above to zero.

We now establish the convergence in mean-square of those matrix eigenfunctions with positive eigenvalues to the exact bound-state wavefunctions. Unfortunately this is not guaranteed merely by convergence of each eigenvalue to ϵ_p [18], and our proof is somewhat long. We need to define some new notation; consider now $Z' > 0$ only. Let the exact Schrödinger eigenfunction of the bound state

that corresponds to the eigenvalue E_p be $\theta_S(r, Z')$, where $\langle \theta_S^2(r, Z') \rangle = 1$. The Schrödinger matrix problem in Eq. (3.10b) has a p^{th} eigenvalue, which has a corresponding approximate wavefunction, $\theta_{SM}(r, Z')$, normalized so $\langle \theta_{SM}^2(Z') \rangle = 1$. As N increases, $\theta_{SM}(r, Z')$ converges in mean-square to $\theta_S(r, Z')$. Let the upper and lower components of the exact Dirac eigenfunction of the bound state that corresponds to ϵ_p be $\phi_D(r)$ and $\theta_D(r)$, with $\langle \phi_D^2 + \theta_D^2 \rangle = 1$. The Dirac matrix problem in Eq. (3.10a) has a p^{th} positive eigenvalue, which has a corresponding eigenfunction with upper and lower components ϕ_{DM} and θ_{DM}, with $\langle \phi_{DM}^2 + \theta_{DM}^2 \rangle = 1$. We define too the scaled functions $\tilde{\theta}_D \equiv \theta_D / \langle \theta_D^2 \rangle^{1/2}$ and $\tilde{\theta}_{DM} \equiv \theta_{DM} / \langle \theta_{DM}^2 \rangle^{1/2}$.

Consider the integral

$$\int_0^\infty \left[\theta_S(r, Z') - \theta_S(r, Z'_p) \right]^2 dr \ . \tag{3.13}$$

The integral exists because $\theta_S(r, Z')$ is square integrable. For $Z' = Z'_p$ the integral vanishes. Now corresponding to an arbitrary value $\delta > 0$, pick an increment $\Delta Z' > 0$, so that for all Z' in the interval $[Z'_p, Z'_p + \Delta Z']$ we have

$$\int_0^\infty \left[\theta_S(r, Z') - \theta_S(r, Z'_p) \right]^2 dr < \frac{\delta}{4} \ . \tag{3.14}$$

Because $Z'_c(N)$ converges to Z'_p as N increases, there exists some value N_2 such that if $N > N_2$, then $0 \leq Z'_c(N) - Z'_p \leq \Delta Z'$. Because the eigenfunctions of the Schrödinger problem, Eq. (3.10b), converge in mean-square to the exact Schrödinger wavefunctions, there exists a value $N_3 \geq N_2$, so that for all $N > N_3$ and for all Z' in the interval $[Z'_p, Z'_p + \Delta Z']$, we have

$$\int \left[\theta_{SM}(Z', r) - \theta_S(Z', r) \right]^2 dr < \frac{\delta}{4} \ . \tag{3.15}$$

The correspondences between Eqs. (1.8b) and (1.9), and between Eqs. (3.10a) and (3.10b), show respectively that $\tilde{\theta}_D(r) = \theta_S(r, Z'_p)$, and $\tilde{\theta}_{DM}(r) = \theta_{SM}\big(r, Z'_c(N)\big)$. Therefore for all $N > N_3$, we have

$$\begin{aligned}
&\int_0^\infty \left[\tilde{\theta}_{DM} - \tilde{\theta}_D\right]^2 dr \\
&\qquad = \int_0^\infty \left[\theta_{SM}\big(Z'_c(N)\big) - \theta_S\big(Z'_c(N)\big) + \theta_S\big(Z'_c(N)\big) - \theta_{SM}(Z'_p)\right]^2 dr \\
&\qquad \le 2\int_0^\infty \left[\theta_{SM}\big(Z'_c(N)\big) - \theta_S(Z'_p)\right]^2 dr + 2\int_0^\infty \left[\theta_S(Z'_c(N)) - \theta_{SM}(Z'_p)\right]^2 dr \\
&\qquad < \delta\ .
\end{aligned} \tag{3.16}$$

As N goes to infinity, $\tilde{\theta}_{DM}$ converges in mean-square to $\tilde{\theta}_D$. Therefore, except for overall normalization, the lower component function θ_{DM} from the matrix diagonalization converges in mean-square to the lower component function θ_D of the exact bound-state wavefunction.

Consider now the normalization. We no longer need to refer to the eigenvalues and eigenfunctions of the Schrödinger problem, Eq. (3.10b), or to the values of $Z'_c(N)$, and so we can simplify our notation. Label as ϵ_n, for $n = N - p + 1 = 1, 2, \ldots$, those eigenvalues that limit to the value ϵ_p as N is increased. Label the upper and lower components of the corresponding eigenfunctions as $\phi_n(r)$ and $\theta_n(r)$. These are normalized so that $\left\langle \phi_n^2 + \theta_n^2 \right\rangle = 1$. Let the symbol "$\to$" denote a limit as N, and therefore n, goes to infinity. Label the upper and lower components of the exact eigenstate corresponding to ϵ_p as $\phi(r)$ and $\theta(r)$. These are normalized so that $\left\langle \phi^2 + \theta^2 \right\rangle = 1$. Also define $\tilde{\theta}_n \equiv \theta_n / \left\langle \theta_n^2 \right\rangle^{1/2}$ and $\tilde{\theta} \equiv \theta / \left\langle \theta^2 \right\rangle^{1/2}$. In terms of our earlier notation, $\theta = \theta_D$, and $\tilde{\theta} = \tilde{\theta}_D$, and $\theta_n = \theta_{DM}\big(r, Z'_c(n + p - 1)\big)$,

and $\tilde{\theta}_n = \tilde{\theta}_{DM}(r, Z_c'(n+p-1))$. We need the following four properties of the function $\tilde{\theta}(r)$, which follow readily from an examination of the exact formulæ for all the bound-state functions θ: $\tilde{\theta}(r)$ is continuous on $[0,\infty)$; and $\tilde{\theta}(r)$ is square-integrable; and $\tilde{\theta}^2/r$ has a Riemann integral on the interval $[0,a]$, for $a > 0$; and $\langle(\tilde{\theta}/r)^2\rangle$ exists.

The convergence in mean-square proved in (3.16) can now be written as $\langle(\tilde{\theta}_n - \tilde{\theta})^2\rangle \to 0$. We need to establish a few other limits, in particular the following set:

$$\begin{aligned} \left\langle(\tilde{\theta}_n - \tilde{\theta})^2\right\rangle &\to 0\ ; \qquad \left\langle(\tilde{\theta}_n - \tilde{\theta})^2/r\right\rangle \to 0\ ; \\ \left\langle\tilde{\theta}_n\tilde{\theta} - \tilde{\theta}^2\right\rangle &\to 0\ ; \qquad \left\langle\tilde{\theta}_n\tilde{\theta}/r - \tilde{\theta}^2/r\right\rangle \to 0\ ; \\ \left\langle\tilde{\theta}_n^2 - \tilde{\theta}^2\right\rangle &\to 0\ ; \qquad \left\langle\tilde{\theta}_n^2/r - \tilde{\theta}^2/r\right\rangle \to 0\ . \end{aligned} \tag{3.17}$$

Because $\tilde{\theta}_n$ and $\tilde{\theta}$ are square-integrable, we can apply the Schwartz inequality to show that

$$\left\langle(\tilde{\theta}_n - \tilde{\theta})\tilde{\theta}\right\rangle^2 \le \left\langle(\tilde{\theta}_n - \tilde{\theta})^2\right\rangle \cdot \left\langle\tilde{\theta}^2\right\rangle\ , \tag{3.18}$$

and so $\langle\tilde{\theta}_n\tilde{\theta}\rangle \to \langle\tilde{\theta}^2\rangle$. Expanding $\langle(\tilde{\theta}_n - \tilde{\theta})^2\rangle$ into $\langle\tilde{\theta}_n^2\rangle - 2\langle\tilde{\theta}_n\tilde{\theta}\rangle + \langle\tilde{\theta}^2\rangle$ shows that $\langle\tilde{\theta}_n^2\rangle \to \langle\tilde{\theta}^2\rangle$. Next, because $\tilde{\theta}_n$ and $\tilde{\theta}/r$ are square-integrable, we can apply the Schwartz inequality to show that

$$\left\langle\ (\tilde{\theta}_n - \tilde{\theta})\ \tilde{\theta}/r\right\rangle^2\ \le\ \left\langle\ (\tilde{\theta}_n - \tilde{\theta})^2\ \right\rangle\left\langle\ (\tilde{\theta}/r)^2\ \right\rangle\ , \tag{3.19}$$

and so $\langle\tilde{\theta}_n\tilde{\theta}/r\rangle \to \langle\tilde{\theta}^2/r\rangle$.

Finally, we show that $\langle\tilde{\theta}_n^2/r\rangle \to \langle\tilde{\theta}^2/r\rangle$, thus establishing both remaining limits in (3.17). Compute the difference

$$\left\langle\tilde{\theta}_n^2/r - \tilde{\theta}^2/r\right\rangle = \int_0^a \left(\tilde{\theta}_n^2/r - \tilde{\theta}^2/r\right)\,dr\ + \int_a^\infty \left(\tilde{\theta}_n^2/r - \tilde{\theta}^2/r\right)\,dr\ , \tag{3.20}$$

where the integral has been divided into two pieces at a convenient point $a > 0$. The second integral converges to zero because it is smaller in magnitude than $a^{-1}\langle\tilde{\theta}_n^2 - \tilde{\theta}^2\rangle$, and the latter integral converges to zero. To prove the vanishing of the first integral, we apply the following theorem [19]: if (1) a sequence of functions f_n converges to a function f everywhere on a finite, closed interval $[a, b]$, and if (2) the functions f_n and (3) the function f have Riemann integrals on $[a, b]$, then the Riemann integral over $[a, b]$ of f_n converges to the Riemann integral of f. We need to prove that the three assumptions of this theorem are satisfied, if $f_n = \tilde{\theta}_n^2/r$ and if $f = \tilde{\theta}^2/r$.

Because $\tilde{\theta}_n$ converges in mean-square to $\tilde{\theta}$, and because $\tilde{\theta}_n$ and $\tilde{\theta}$ are both continuous, $\tilde{\theta}_n(r)$ converges to $\tilde{\theta}(r)$ for all r in $[0, a]$, though this convergence is not necessarily uniform [20]. Therefore $\tilde{\theta}_n^2(r)/r \to \tilde{\theta}^2/r$, except perhaps at the origin. But $\tilde{\theta}_n^2/r$ is a linear combination of the functions $w_n w_m/r$, all of which vanish at the origin, and $\tilde{\theta}^2/r$ also vanishes there. Therefore $\tilde{\theta}_n^2(r)/r \to \tilde{\theta}^2/r$ for all r in closed interval $[0, a]$. So the first assumption about f_n is satisfied. Again, $\tilde{\theta}_n^2/r$ is a linear combination of the functions $w_n w_m/r$, all of which are absolutely continuous, so $\tilde{\theta}_n^2/r$ is absolutely continuous. It is therefore continuous on the closed interval $[0, a]$, and continuity of a function on a closed interval is sufficient [21] for the function to have a Riemann integral over the interval. Therefore, $f_n = \tilde{\theta}_n^2/r$ has a Riemann integral over [0,a], and the second assumption about f_n is satisfied. Finally, we know $f = \tilde{\theta}^2/r$ has a Riemann integral on $[0, a]$, so the last assumption is satisfied. Therefore all the limits in Eq. (3.17) hold.

Construct now the lower component functions $\theta_n = A_n^{-1}\tilde{\theta}_n$ and $\theta = A^{-1}\tilde{\theta}$ by evaluating the normalizing constants A_n and A, which are given by

$$A_n^2 = \int_0^\infty \left[\frac{B(\kappa)\tilde{\theta}_n}{\epsilon_n - \eta}\right]^2 + \tilde{\theta}_n^2\, dr\ , \qquad \text{and} \qquad A^2 = \int_0^\infty \left[\frac{B(\kappa)\tilde{\theta}}{\epsilon_p - \eta}\right]^2 + \tilde{\theta}^2\, dr\ . \tag{3.21}$$

Here Eqs. (3.5) and (1.8a) have respectively been used to express the functions ϕ_n and ϕ in terms of θ_n and θ, and hence in terms of $\tilde{\theta}_n$ and $\tilde{\theta}$. The function θ_n converges in mean-square to θ if and only if $A_n \to A$. Expanding the operator $B(\kappa)$, and using the eigenvalue equations (3.10a) and (1.8b) to eliminate derivatives, yields

$$\left(\frac{\epsilon_n - \eta}{\alpha}\right)^2 A_n^2 = \left[\frac{Z^2}{\kappa^2} - \left(\frac{1-\epsilon_n^2}{\alpha^2}\right) + 1\right] \int_0^\infty \tilde{\theta}_n^2 \, dr + 2Z\left[\epsilon_n + \frac{\gamma}{\kappa}\right] \int_0^\infty \tilde{\theta}_n^2/r \, dr \; ;$$

$$\left(\frac{\epsilon_p - \eta}{\alpha}\right)^2 A^2 = \left[\frac{Z^2}{\kappa^2} - \left(\frac{1-\epsilon_p^2}{\alpha^2}\right) + 1\right] \int_0^\infty \tilde{\theta}^2 \, dr + 2Z\left[\epsilon_p + \frac{\gamma}{\kappa}\right] \int_0^\infty \tilde{\theta}^2/r \, dr \; . \tag{3.22}$$

For large n, we have that ϵ_n limits to ϵ_p, and that the limits in Eq. (3.17) all hold. Therefore A_n limits to A, and θ_n converges in mean-square to θ. Consider next the convergence in mean-square of the upper components,

$$\int_0^\infty (\phi_n - \phi)^2 \, dr = \int_0^\infty \left(\frac{B\theta_n}{\epsilon_n - \eta} - \frac{B\theta}{\epsilon_p - \eta}\right)^2 dr \to \left(\frac{1}{\epsilon_p - \eta}\right)^2 \int_0^\infty (B\theta_n - B\theta)^2 \, dr$$

$$\to \left(\frac{\alpha}{\epsilon_p - \eta}\right)^2 \left[\left(\frac{1-\epsilon_p^2}{\alpha^2} + \frac{Z^2}{\kappa^2}\right) \int_0^\infty (\theta_n - \theta)^2 \, dr + 2Z\left(\epsilon_p + \frac{\gamma}{\kappa}\right) \int_0^\infty (\theta_n - \theta)^2/r \, dr\right] . \tag{3.23}$$

The differential equation (1.8b) and integration by parts have been used to eliminate terms in $d^2\theta/dr^2$. The remaining integrals vanish as n goes to infinity, so the upper components converge in mean-square as well. That the upper components converge properly is somewhat unexpected. The upper component is related to the lower by $\phi \propto B\theta$, and the operator B contains a derivative. The convergence in mean-square of a sequence of functions f_n to a function f does not usually imply that the sequence of functions df_n/dr converges in mean-square to df/dr.

We have shown that the two-component wavefunction Φ_n converges in mean-square to the exact bound-state wavefunction Φ. Stronger forms of convergence might be proved for specific sets of functions $\{w\}$, but convergence in mean-square is sufficient for many purposes. For example, if $f_{1,n}$ converges in mean-square to f_1, and if $f_{2,n}$ converges in mean-square to f_2, and if F is a function of r such that $\langle f_{1,n}F^2f_{1,n}\rangle$ and $\langle f_{2,n}F^2f_{2,n}\rangle$ exist for all n, then as $n,m\to\infty$ we have that $\langle f_{1,n}Ff_{2,m}\rangle \to \langle f_1Ff_2\rangle$. Convergence in mean-square appears to be sufficient for the evaluation of radial matrix elements.

We now establish some miscellaneous properties of the variational solutions. If the eigenvectors x_2 are split into two sets, corresponding to positive and negative eigenvalues, then the vectors in each set are linearly independent, a result established for a Slater basis by Goldman [6]. For, if $f(r)$ is any function with $\langle f^2\rangle = 1$, and if $\Phi = \big(f(r),0\big)$, then $\langle \Phi h\Phi\rangle = \eta$. Denote as Φ^+ the normalized eigenfunctions that have positive eigenvalues ϵ^+. If the lower component vectors x_2^+ corresponding to these eigenfunctions were linearly dependent, then there would exist a two-component function $\Phi' = \sum c_j\Phi_j^+$, with coefficients c_j with $\sum_j c_j^2 = 1$, such that Φ' has a lower component $0'(r)$ that is identically zero. But then

$$\eta = \langle \Phi' h\Phi'\rangle = \sum_j c_j^2\epsilon_j^+ > \epsilon_1 > \eta\ , \tag{3.24}$$

which is impossible. Therefore, the vectors x_2^+ are linearly independent. A similar argument shows that the lower component vectors x_2^- with negative eigenvalues are linearly independent.

By expanding the basis $\{Q\}$, we can construct a representation of Φ_0, as well as the other states; Goldman [6] was the first to prove this possible, though only for one special set of functions $\{w\}$. Suppose to a set of $2N$ basis vectors Q we add m extra linearly independent vectors of the form $\big(f(r),0\big)$, where the functions f

are square-integrable. Assume that the new vectors are normal to the old vectors and to each other, so that $\langle f|Bw_n\rangle = 0$ for $n = 1, \ldots, N$, and that $\langle f_i|f_j\rangle = 0$ for $i \neq j$. Now h does not couple the new vectors to the old, so $2N$ of the $2N+m$ eigenvectors and eigenvalues are just the $2N$ eigenvectors and eigenvalues found in the basis Q. The m new eigenvectors are linear combinations of the m new basis vectors. Indeed, provided that the $N+m$ functions $f_1, \ldots, f_m; Bw_1, \ldots, Bw_N$ are merely linearly independent, the $2N$ original eigenvectors will be unchanged. The new eigenvectors will have the form $(F, 0)$, where the functions F are linear combinations of the m functions $f_j(r) - \sum_{n=1}^{N} \langle f_j|Bw_n\rangle\, Bw_n(r)$. The new eigenvectors can be distinguished easily from the old, both by the vanishing of their lower component function θ, and by their common eigenvalue η.

Now suppose we find, for $n = 1, 2, \ldots$, a sequence of functions u_n, corresponding to the sequence of functions w_n, such that for any $N \geq 0$, the first $N+1$ functions u_n span the N functions $B(\kappa)w_n$. For each N there is one function f_N, a linear combination of the first $N+1$ functions u_n, not spanned. Consider diagonalizing h in the basis of $2N+1$ functions P, where $P_n \equiv (u_n, 0)$ for $n = 1, \ldots, N+1$, and $P_{n+N+1} \equiv (0, w_{n+N+1})$ for $n = 1, \ldots, N$. We find the same $2N$ eigenvectors and eigenvalues as from a diagonalization in the basis Q, plus one extra eigenfunction $(f_N, 0)$, with $\langle f_N^2\rangle = 1$ and with eigenvalue $\eta(\kappa)$. If the set of functions $\{w_n\}$ is complete, then u_1 like any square-integrable function has a unique expansion, which converges in mean-square to u_1, of the form $u_1 = a_0\phi_0 + \sum_{n=1}^{\infty} a_n B(\kappa)w_n$. The effect of the matrix diagonalization is to force the extra function f_N to be normal to each of the functions Bw_n, for $n = 1, \ldots, N$, so that $f_N \propto a_0\phi_0 + \sum_{n=N+1}^{\infty} a_n B(\kappa)w_n$, while scaling f_N to preserve the normalization $\langle f_N^2\rangle = 1$. Therefore as N goes to infinity, f_N converges

in mean-square to ϕ_0, and the extra two-component function converges in mean-square to Φ_0. We need only assume that the function u_1 is not accidentally normal to the function ϕ_0. Curiously, the eigenvalue obtained from the matrix diagonalization gives no sign of the convergence of this eigenfunction to Φ_0, because that eigenvalue is locked for all N at the value $\eta(\kappa)$ (which for $\kappa < 0$ is accidentally equal to ϵ_0). Therefore, for $\kappa < 0$, we are free to complete the set of $2N$ eigenfunctions and eigenvalues with either the exact eigenfunction Φ_0 and its eigenvalue ϵ_0, or with the approximate eigenfunction $(f_N, 0)$ and its eigenvalue.

Consider diagonalizing $h(\kappa)$, when instead $\kappa > 0$, in the basis P. When $\kappa > 0$, the function u_1 has an expansion, which converges in mean-square to u_1, of the form $u_1 = \sum_{n=1}^{\infty} b_n B(\kappa) w_n$. The extra eigenfunction is still of the form $(f_N, 0)$, where now $f_N \propto \sum_{n=N+1}^{\infty} b_n B(\kappa) w_n$, and f_N is scaled so $\langle f_N^2 \rangle = 1$. The sequence of functions f_1, f_2, ..., doesn't converge as N is increased (not even to $f_N(r) = 0$, because then the $2N + 1$ basis vectors P are then not, as has been assumed, linearly independent for large N); and when $\kappa > 0$, no extra eigenfunction is needed to complete the basis. While the extra eigenfunction introduced by using the basis P instead of the basis Q is meaningless, it can easily be discarded after the diagonalization, as it is marked both by its eigenvalue $\eta(\kappa)$ and by its vanishing lower component.

Now suppose we find a sequence of functions u_n so that the first $N+1$ functions span the N functions $B(\kappa)w_n$, for both signs of κ. Then we can diagonalize $h(\kappa)$ for both signs of κ in the same basis P and get sensible results, provided that we remember that for $\kappa > 0$ the extra eigenfunction is meaningless, and that for $\kappa < 0$ the extra eigenfunction may serve to complete the basis of $2N$ functions instead of the exact eigenfunction Φ_0.

We have shown how to establish a variational basis for the Dirac Coulomb Hamiltonian using virtually any complete set of functions $\{w\}$, augmented when $\kappa < 0$ with the exact wavefunction Φ_0 or with an approximation to it. The functions $\{w\}$ may be functions not only of r, but also of a set of arbitrary nonlinear parameters that may be tuned to optimize the representation of the wavefunctions—for example, by minimizing the smallest positive eigenvalue ϵ. Thus the complete method of Rayleigh and Ritz [8], so useful for the Schrödinger Coulomb Hamiltonian, may be applied to the Dirac Coulomb Hamiltonian. We emphasize that it is not necessary (though it may speed convergence) for the basis functions $\{w\}$ to vary near the origin as $r^{\gamma+1}$ as do all the exact lower components θ, or for the functions $\{w\}$ to have continuous second derivatives when $r > 0$.

We conjecture that we may obtain a useful representation of the eigenstates of an electron bound in the potential of a nucleus of finite size by treating the difference between the potentials of the finite and of the point nucleus as a small perturbation. We may also directly diagonalize the Hamiltonian for the potential of the finite nucleus, instead of the Hamiltonian for the pure Coulomb potential, provided we use a basis of type Q for $\kappa > 0$ and of type P for $\kappa < 0$. The essential point is to avoid using for $\kappa > 0$ a basis of type P, and so to avoid mixing a meaningless eigenfunction $(f_N, 0)$ with the other $2N$ eigenfunctions. Whether the positive eigenvalues for the new potential will lie above the exact bound-state eigenvalues is unknown. (The positive eigenvalues will indeed lie above, if we use instead the minimum principle developed in Sec. VIII.)

IV. RELATIVISTIC STURMIAN BASES

Any set of basis functions of the form $w_n \sim r^{\gamma+1}\ e^{-\lambda r}\ L_{n-1}^{2\gamma+1+p}\ (2\lambda r)$, for $n = 1, \ldots, N$, where L_μ^ν is a Laguerre polynomial [22], p a positive integer,

and λ a number greater than zero, yields in the eigenvalue equation, Eq. (3.2), narrow-band matrices M, A, and U. This follows readily from the recursion and orthogonality relations of the Laguerre polynomials [22]. The most narrow appear for $p = 0$, and we find the following relativistic generalization of the well-known Sturmian functions [1] :

$$\xi_n(r,\gamma,z) = \left[\frac{1}{2}\frac{(n-1)!}{\Gamma(2\gamma+1+n)}\right]^{1/2} \left(\frac{2zr}{\gamma+1}\right)^{\gamma+1} e^{-zr/(\gamma+1)}\, L_{n-1}^{2\gamma+1}\left(\frac{2zr}{\gamma+1}\right). \quad (4.1)$$

The relativistic Sturmian functions ξ are the solutions to the differential equation

$$\left[-\frac{d^2}{dr^2} + \frac{\gamma(\gamma+1)}{r^2} - \frac{2z}{r}\zeta_n + \frac{z^2}{(\gamma+1)^2}\right]\xi_n = 0\ , \quad (4.2)$$

with eigenvalues $\zeta_n = (\gamma+n)/(\gamma+1)$, and normalization $\langle \xi_n | 2/r | \xi_m \rangle = \delta_{nm}$. The overlap matrix is tridiagonal, with

$$\langle \xi_n | \xi_m \rangle \equiv T_{nm} = \frac{\gamma+1}{4z} \begin{cases} 2(n+\gamma)\ , & n = m\ , \\ -[p(p+2\gamma+1)]^{1/2}\ , & |n-m| = 1\ , \quad p = \min(n,m)\ , \\ 0\ , & |n-m| > 1\ . \end{cases} \quad (4.3)$$

For a proof of the completeness of the functions ξ see Szegö [23]; for their connection to the conventional Sturmian functions see Appendix A.

The functions ξ make the matrices M, A, and U in Eq. (3.2) tridiagonal. However, it is possible to simplify that equation further. Equation (3.6), which is equivalent to Eq. (3.2), is of the form $[J\epsilon^2 + K\epsilon + L]x_2 = 0$, where J, K, and L are $N \times N$ matrices. A shift of eigenvalue to $\epsilon' \equiv \epsilon - c$, where c is constant, produces an equation of the same form, $\left[J'\epsilon'^2 + K'\epsilon' + L'\right]x_2 = 0$, with new matrices $J' = J$, and $K' = 2c + K$, and $L' = Jc^2 + Kc + L$. Now we know that $x_2 \neq 0$, so ϵ' can equal zero if and only if the determinant of L' is equal to zero. Therefore,

$[J'\epsilon'^2 + K'\epsilon' + L']x_2 = 0$ has the same eigenvalues ϵ' and vectors x_2 as the ordinary eigenvalue problem

$$\begin{pmatrix} 0 & L' \\ L' & K' \end{pmatrix} \begin{pmatrix} y \\ x_2 \end{pmatrix} = \epsilon' \begin{pmatrix} L' & 0 \\ 0 & -J' \end{pmatrix} \begin{pmatrix} y \\ x_2 \end{pmatrix}, \tag{4.4}$$

where y is a dummy vector. If $\epsilon' = 0$, then the vector y so defined is not unique, and it may be tricky to solve Eq. (4.4) numerically.

The matrix L' becomes diagonal, $L' \propto D$, where $D_{nm} \equiv (z\zeta_n - Zc/)\delta_{nm}$, if the value of c is set to $c(z) = \sigma\left[1 - \left(z\alpha/(\gamma+1)\right)^2\right]^{1/2}$, where $\sigma = \pm 1$ is an arbitrary sign. We need c to be a real number and therefore restrict z so that $z\alpha \leq \gamma + 1$. After rearranging Eq. (4.4), we find the matrix equation

$$\alpha^2 \begin{pmatrix} 2c(z)D & D \\ D & -Z/z \end{pmatrix} \begin{pmatrix} y \\ x_2 \end{pmatrix} = \left[\epsilon + c(z)\right] \begin{pmatrix} D & 0 \\ 0 & T \end{pmatrix} \begin{pmatrix} y \\ x_2 \end{pmatrix}, \tag{4.5}$$

where the matrix in the place of the matrix M in Eq. (3.2) is now diagonal. We remark that if we set the value of z to $(1+\gamma)Z/|\kappa|$, and set the sign σ to $-\kappa/|\kappa|$, then we recover Eq. (3.2), with the dummy vector y becoming equal to x_1. The matrix M in Eq. (3.2) is accidentally diagonal for this value of z, which equates the exponent of the ξ functions to the exponent of the bound state Φ_0.

If y is to be unique, D_{nn} must never be zero, and so we must avoid having at the same time $c < 0$, and $z = Z(\gamma+1)/\left[(\gamma+n)^2+(Z\alpha)^2\right]^{1/2}$ for some $n = 1, \ldots, N$; the parameter z will equal one of these values only if one of the first N (exact) bound-state wavefunctions (corresponding to one of the eigenvalues $\epsilon_1, \ldots, \epsilon_N$) is a linear combination of the $2N$ basis vectors Q. Most numerical algorithms for the extraction of the eigenvalues of Eq. (4.5) require the matrix appearing on the

right-hand side to be positive definite, and so all the elements of D to be positive; we will therefore impose on z the bounds

$$\begin{cases} 0 < z\alpha < 1+\gamma\,, & c < 0\,, \\ \dfrac{(1+\gamma)Z\alpha}{\sqrt{(1+\gamma)^2+(Z\alpha)^2}} < z\alpha < 1+\gamma\,, & c > 0\,, \end{cases} \tag{4.6}$$

which are also sufficient to keep y unique.

The vectors x_2 for one sign of κ determine the normalized eigenfunctions for both signs of κ, according to Eq. (3.5) and the proportionality in Eq. (3.9). The upper and lower components are given by

$$\begin{aligned} \phi_{\pm\kappa}(r) &= \frac{\epsilon}{|\epsilon|}\, V(\kappa)^{-1}\, |\epsilon - \eta(\kappa)|^{-1/2}\, |\epsilon \mp \eta(\kappa)|^{-1/2} \sum_n [x_2(\kappa)]_n\, B(\pm\kappa)\xi_n(r)\,, \\ \theta_{\pm\kappa}(r) &= V(\kappa)^{-1}\, |\epsilon - \eta(\kappa)|^{-1/2}\, |\epsilon \mp \eta(\kappa)|^{+1/2} \sum_n [x_2(\kappa)]_n\, \xi_n(r)\,, \end{aligned} \tag{4.7}$$

where the normalization constant $V(\kappa)$ is given in terms of $x_2(\kappa)$ by

$$\begin{aligned} \frac{V^2(\kappa)}{\alpha^2} &= x_2\, D x_2 + Z\,\left[c - \eta(\kappa)\right]\, x_2 \cdot x_2 \\ &\quad + \left\{ \frac{\left[\eta(\kappa)-\epsilon\right]^2}{(Z\alpha)^2} + \frac{1}{\kappa^2} - \frac{z^2}{Z^2(\gamma+1)^2} \right\}\, Z^2\, x_2\, T x_2\,. \end{aligned} \tag{4.8}$$

To solve Eqs. (4.5), (4.7) and (4.8) numerically for eigenvalues and eigenvectors requires only $O(N^2)$ computer operations and, if each eigenvector can be overwritten by the next, only $O(N)$ locations in memory. To solve the original matrix problem, Eq. (3.2), in all other known Slater bases—even Goldman's orthogonal Laguerre basis [3]—otherwise requires $O(N^3)$ computer operations and $O(N^2)$ locations in memory [24]. The eigenvectors may be found rapidly by inverse iteration; after scaling the vectors in (4.5) so that the matrix in place of D is just the unit matrix, we need solve per pass but one $N \times N$ matrix equation involving one symmetric tridiagonal matrix. Inverse iteration is particularly easy to

apply because the $2N$ eigenvalues of Eq. (3.2) are all distinct, as we will prove in Sec. V. Numerical tests show the positive eigenvalues converge from above, as expected, to the exact bound state eigenvalues. In double precision FORTRAN, we find that $\epsilon(\kappa)$ and $|\epsilon(\kappa)+\eta(\kappa)|^{1/2}x_2(\kappa)$, evaluated for both signs of κ, agree with each other, and with the results of a quadruple-precision calculation, to parts in 10^{13}, even for $2N$ as large as 4800. This basis is a hundred times larger than the basis used in Ref. [3]. A sample of the numerical results for $2N = 400$ is shown in Table 1.

V. ANALYTIC SOLUTION IN THE ξ BASIS

The eigenvalues and lower component functions θ of the matrix problem for the Dirac Coulomb Hamiltonian [Eq. (3.10a)] are related, by the correspondence in Eq. (3.11), to the eigenvalues and eigenfunctions of the matrix problem for the Schrödinger Coulomb Hamiltonian [Eq. (3.10b)]. Yamani and Reinhardt [26] showed that in the ξ basis, and for integer values of γ, that the solutions to Eq. (3.10b) may be expressed analytically in terms of the Pollaczek polynomials and their zeros. Their solution was extended over noninteger (positive) γ in part of the work of Bank and Ismail [27]. To derive the corresponding analytic solutions for the Dirac problem, it is convenient to follow the notation of Yamani and Reinhardt, and work not with the functions ξ but with the set of functions

$$\phi_n(r,\gamma,\lambda) = (\lambda r)^{\gamma+1}\, e^{-\lambda r/2}\, L_n^{2\gamma+1}(\lambda r), \qquad n = 0,1,\ldots,N-1\,, \tag{5.1}$$

where $\gamma > 0$ and $\lambda > 0$ are parameters. These functions are related to the functions ξ by

$$\xi_{n+1}(r,\gamma,z) = \left[\frac{n!}{2\Gamma(2\gamma+n+2)}\right]^{1/2} \phi_n(r,\gamma,\lambda)\Big|_{\lambda=2z/(\gamma+1)}\,. \tag{5.2}$$

Consider the Schrödinger problem $H_S\psi = E\psi$, with

$$H_S = -\frac{1}{2}\frac{d^2}{dr^2} + \frac{\gamma(\gamma+1)}{2r^2} - \frac{Z'}{r} \ . \tag{5.3}$$

Following Yamani and Reinhardt [26], with some change of notation [28], we expand the functions ψ according to

$$\psi \ = \ \sum_{n=0}^{N-1} b_n \ w_n(r) \ = \ \sum_{n=0}^{N-1} b_n \ \frac{n!}{\Gamma(n+2\gamma+2)} \ \phi_n \ . \tag{5.4}$$

The matrix eigenvalue problem $\langle w_m|H_S|w_n\rangle b_n = E\langle w_m|w_n\rangle b_n$ requires that the coefficients b_n satisfy the recurrence

$$(n+1)b_{n+1} - 2\left[(n+\gamma+1-2Z'/\lambda)\,x + 2Z'/\lambda\right] b_n + (n+2\gamma+1)b_{n-1} \ , \tag{5.5}$$

for $n = 0,\ 1,\ \ldots,\ N-1$, with the boundary conditions $b_{-1} = 0$ and $b_N = 0$. Here the quantity x and the eigenvalue E are related by

$$E = \frac{\lambda^2}{8}\frac{1+x}{1-x} \ , \qquad \text{or} \qquad x = \frac{E-\lambda^2/8}{E+\lambda^2/8} \ . \tag{5.6}$$

The Pollaczek polynomials $P_n^{\mu}(x;a,b)$ are polynomials of degree n in x which depend on three parameters μ, a, and b. They may be defined by the recurrence

$$\begin{aligned}(n+1)P_{n+1}^{\mu}(x;a,b) \ - \ 2[(n+\mu+a)x+b]\ P_n^{\mu}(x;a,b) \\ + \ (n+2\mu-1)\ P_{n-1}^{\mu}(x;a,b) \ = \ 0 \ ,\end{aligned} \tag{5.7}$$

for $n = 0, 1, \ldots,$ with the initial conditions $P_{-1} \equiv 0$ and $P_0 \equiv 1$. Comparing the two recurrences, we have

$$b_n \propto P_n^{\gamma+1}\left(x; -\frac{2Z'}{\lambda}, +\frac{2Z'}{\lambda}\right) \ . \tag{5.8}$$

That b_N must vanish requires that

$$P_N^{\gamma+1}\left(x; -\frac{2Z'}{\lambda}, +\frac{2Z'}{\lambda}\right) = 0 \ . \tag{5.9}$$

The N eigenvalues E are selected by the requirement that x be one of the N zeros of this polynomial. The eigenvalues ϵ and lower component functions θ for the Dirac problem, Eq. (3.10a), follow by solving Eq. (5.9) for the $2N$ pairs of values of x and Z'—or equivalently, using Eq. (5.6), the $2N$ pairs of values E and Z'—such that the correspondences (3.11a) and (3.11b) are satisfied. That there are precisely $2N$ such pairs follows from the graphical argument used in Sec. III.

For an introduction to the Pollaczek polynomials, see Szegö [23]. For the Coulomb problems, we need deal only with the special case $P_n(x;a) \equiv P_n^{\mu}(x;a,-a)$ [28] and only with the range of parameters $\mu > 1$ and $a \neq 0$. While these polynomials are orthogonal with respect to a positive weight function when $a < 0$, or when $a > 0$ and $a > \mu$, no such weight function exists if $a > 0$ and $a \leq \mu$ [29]. For the Coulomb problems, the weight function does not exist when the potential is attractive ($Z' > 0$) and when λ is small (so that the basis functions ϕ fall slowly as $r \to \infty$). The classic theory of orthogonal polynomials [23,29] is not applicable to polynomials that lack a weight function, and we have to derive the properties of the polynomials, and of their zeros, from scratch.

That the polynomials have N real zeros follows from their association with the eigenvalues of an Hermitian matrix eigenvalue problem of dimension $N \times N$. We prove that the N zeros are all distinct. We remark that $x = 1$ is never a zero of $P_n^{\mu}(x;a)$ because the explicit formula [31] for the Pollaczek polynomial reduces for $x = 1$ to

$$P_n^{\mu}(1;a) = \frac{\Gamma(2\mu+n)}{n!\,\Gamma(2\mu)}\,, \tag{5.10}$$

which is never zero for $\mu > 1$. Consider the function F_M defined by

$$F_M(x,a,b,\gamma,\lambda) \equiv \sum_{n=0}^{M-1} \frac{n!}{\Gamma(n+2\gamma+2)}\, P_n^{\gamma+1}(x;a,b)\, \phi_n(r,\gamma,\lambda)\,. \tag{5.11}$$

The eigenfunction ψ is a special case of F_M, evaluated with $a = -b = -2Z'/\lambda$, with $M = N$, and with x equal to a special value. We can evaluate the following set of integrals:

$$\begin{aligned} \langle F_M | F_M \rangle &= \frac{2}{\lambda} [(1-x)S_1 - (a+b)S_2] \ ; \\ \langle F_M | r^{-1} | F_M \rangle &= S_2 \ ; \\ \left\langle F_M \left| -\frac{d^2}{dr^2} + \frac{\gamma(\gamma+1)}{r^2} \right| F_M \right\rangle &= \frac{\lambda}{2} [(1+x)S_1 - (a-b)S_2] \ . \end{aligned} \tag{5.12}$$

Here the sums S_1 and S_2 are defined by

$$\begin{aligned} S_1 &\equiv \sum_{n=0}^{M-1} P_n^{\gamma+1}(x;a,b)\ P_n^{\gamma+1}(x;a,b)\ \frac{n!\,(n+\gamma+1+a)}{\Gamma(n+2\gamma+2)} \ , \\ S_2 &\equiv \sum_{n=0}^{M-1} P_n^{\gamma+1}(x;a,b)\ P_n^{\gamma+1}(x;a,b)\ \frac{n!}{\Gamma(n+2\gamma+2)} \ . \end{aligned} \tag{5.13}$$

Consider what happens when $a = -b$. Then we have $0 \le \langle F_M^2 \rangle = S_1 \cdot 2(1-x)/\lambda$. If x is a zero of $P_N(x;a)$, then $x \neq 1$, and so $S_1(x) \neq 0$. From the recursion relation (5.7), we can derive [29] the Christoffel-Darboux sum formula,

$$\begin{aligned} \sum_{n=0}^{N-1} \frac{n!\,(n+\gamma+1+a)}{\Gamma(n+2\gamma+1)}\ P_k^{\gamma+1}(x;a,b)\ P_k^{\gamma+1}(x;a,b) \ &= \ \frac{N!}{2\Gamma(N+2\gamma+1)} \\ \times \ \left[P_{N-1}^{\gamma+1}(x;a,b)\ \frac{dP_N^{\gamma+1}}{dx}\ (x;a,b) - P_N^{\gamma+1}(x;a,b)\ \frac{dP_{N-1}^{\gamma+1}}{dx}(x;a,b) \right] . \end{aligned} \tag{5.14}$$

From this, for $b = -a$, we have

$$\begin{aligned} S_1 &= \sum_{n=0}^{M-1} \frac{n!\,(n+\gamma+1+a)}{\Gamma(n+2\gamma+1)} P_n(x;a)\ P_n(x;a) \\ &= \frac{M!}{2\Gamma(M+2\gamma+1)} \left[P_{M-1}(x;a)\ \frac{dP_M}{dx}\ (x;a) - P_M(x;a)\ \frac{dP_{M-1}}{dx}\ (x;a) \right] . \end{aligned} \tag{5.15}$$

Suppose a polynomial $P_M(x;a)$ has a multiple root. Then we must have both $P_M(x;a) = 0$ and $dP_M/dx\,(x;a) = 0$ for some x. That would make the right-hand side of Eq. (5.15) vanish, so we would have $S_1 = 0$, which is impossible. Therefore all the M real zeros of $P_M(x,a)$ are distinct [30]. We can conclude that the Schrödinger matrix eigenvalue problem in the basis ϕ—and by the graphical argument presented in Sec. III, the corresponding Dirac matrix eigenvalue problem in Eq. (3.10a)—does not have degenerate eigenvalues. Equation (5.15) also shows that $P_{M-1}(x)$ and $P_M(x)$ cannot have a common zero. The interleaving of the eigenvalues for the Dirac problem, proved for an arbitrary basis in Sec. III, now ensures that as N is increased, the p^{th} positive eigenvalue cannot stay the same but must decrease, and the p^{th} negative eigenvalue cannot stay the same but must increase.

As was shown by Yamani and Reinhardt [26], the normalized eigenvectors for the Schrödinger problem are $\theta_S = A_S^{-1}\psi$, with

$$A_S^2 = \frac{2(1-x)}{\lambda}\,\frac{N!}{2\Gamma(N+2\gamma+1)}\left[P_{N-1}(x;a)\,\frac{dP_N}{dx}\,(x;a)\right], \tag{5.16}$$

where x is a zero of $P_N(x;-2Z'/\lambda)$. For the Dirac problem, we also have $\tilde{\theta} = A^{-1}\psi$, where we must choose both Z' and x so that Eq. (5.9) and Eq. (3.11) hold. To get the correctly normalized lower component, θ, we see from Eq. (3.22) that we need not only the integral $\langle\psi^2\rangle$, but also $\langle\psi^2/r\rangle$. The second integral involves the sum S_2, which unfortunately has no known closed form, even for the restricted range of parameters required.

We can try to extract S_2 from the matrix eigenvalue equation, $\langle\psi H_S\psi\rangle = E\langle\psi|\psi\rangle$. That program fails, because the functions ψ have an odd property. Consider F_M as a trial function and calculate the trial energy E_F defined by

$$E_F \equiv \frac{\langle F_M H_S F_M\rangle}{\langle F_M^2\rangle}\,. \tag{5.17}$$

This can be rewritten in terms of S_1 and S_2 as

$$\left[(1+x) - \frac{8E_F}{\lambda^2}(1-x)\right] S_1 - \left[2\left(a + \frac{2Z'}{\lambda}\right) - (a+b)\left(1 + \frac{8E}{\lambda^2}\right)\right] S_2 = 0 \,. \quad (5.18)$$

For $a = -2Z'/\lambda$, and $b = -a$, which hold for the eigenstates ψ of the Schrödinger Coulomb problem, the dependence on S_2 cancels, so we cannot extract the value of S_2. For $F_M \equiv F_M(x; -2Z'/\lambda, +2Z'/\lambda, \gamma, \lambda)$ we have the relation

$$\frac{\langle F_M H_S F_M \rangle}{\langle F_M^2 \rangle} = \frac{\lambda^2}{8} \frac{1+x}{1-x} \,. \quad (5.19)$$

For $M = N$ and for the appropriate value of x, Eq. (5.19) expresses the expected relation between an eigenstate ψ and its eigenvalue E. What is surprising is that the right-hand side of this equation is independent of M, and so the left-hand side must be also. Therefore, if we find an eigenstate ψ for the Schrödinger problem, with eigenvalue E and with $\psi \propto \sum_{n=0}^{N-1} b_n \phi_n$, and if we define a new function f equal to the sum of the first $k \leq N$ terms of the sum, then $\langle f H_S f \rangle / \langle f | f \rangle = E$ for all k. The eigenstates of the Dirac problem have a similar property. If we find an eigenstate Φ, with eigenvalue ϵ and $\Phi \propto \sum_{n=0}^{N-1} \left[a_n B(\kappa)\, \phi_n,\, a'_n \phi_n\right]$, where a_n and a'_n are coefficients, and if we define a new function f equal to the sum of the first $k \leq N$ terms of the sum, then $\langle f h f \rangle = \epsilon \langle f | f \rangle$ for all k. In a basis of type P for $\kappa < 0$, this property is also possessed (trivially) by the eigenvector corresponding to Φ_0. In both the Schrödinger and the Dirac problems, the expectation value of the energy is unexpectedly independent of the number of terms kept in the sum.

VI. A SECOND BASIS

We now consider the second simple basis in which variational solutions for the Dirac Coulomb problem can be constructed. Much of the work closely parallels that of Secs. I through V, and we omit the obvious formal proofs. In this section, symbols without a caret [e.g., κ, γ, $q(\kappa)$, $\eta(\kappa)$, and $B^\dagger(\kappa)$] have the same meaning as in earlier sections, while symbols marked with a caret (e.g., $\widehat{\phi}$) are merely analogs of similar quantities (e.g., ϕ) used in the earlier sections, but are not identical. Choosing $\sin 2\varphi = \alpha Z/\kappa$ with $\cos 2\varphi = +\gamma/\kappa$, the Dirac Coulomb Hamiltonian in Eq. (1.3) transforms to $\widehat{h}\widehat{\Phi} = \epsilon\widehat{\Phi}$, with $\widehat{\Phi} = (\widehat{\phi}, \widehat{\theta})$, and

$$\widehat{h}(\kappa) = \begin{pmatrix} \eta(-\kappa) & -B^\dagger(-\kappa) \\ -B(-\kappa) & -\eta(-\kappa) + A \end{pmatrix} . \tag{6.1}$$

In terms of its components, the equation $\widehat{h}(\kappa)\widehat{\Phi} = \epsilon\widehat{\Phi}$ reads

$$\begin{aligned} \left[\eta(-\kappa) - \epsilon\right]\, \widehat{\phi} - B^\dagger(-\kappa)\, \widehat{\theta} = 0 \, , \\ -B(-\kappa)\, \widehat{\phi} + \left[-\eta(-\kappa) - \epsilon + A\right]\, \widehat{\theta} = 0 \, . \end{aligned} \tag{6.2a,b}$$

The system of equations (6.2) has for $\epsilon = \eta(-\kappa)$ no solutions that are normalizable and that have a finite expectation value of $1/r$. Solving Eq. (6.2a) for $\widehat{\phi}$ and substituting into Eq. (6.2b), we find the new equations

$$\begin{aligned} \widehat{\phi} \;&=\; \left(\frac{-1}{\epsilon - \eta(-\kappa)}\right) B^\dagger(-\kappa)\widehat{\theta} \, , \\ \left[-\frac{d^2}{dr^2} + \frac{(\gamma-1)\gamma}{r^2} - \frac{2Z\epsilon}{r} - \left(\frac{\epsilon^2 - 1}{\alpha^2}\right)\right] \widehat{\theta} \;&=\; 0 \, . \end{aligned} \tag{6.3a,b}$$

Equation (6.3b) has a solution $\widehat{\theta}_f = r^\gamma \, \exp(-Zr/\kappa)$ when ϵ has the illegitimate value $\eta(-\kappa)$ and when the function $\widehat{\phi}$ given by Eq. (6.3a) is undefined. For $\kappa > 0$ the function $\widehat{\theta}_f$ happens to be normalizable, but it and its eigenvalue must be deleted from the spectrum of solutions of Eq. (6.3b) to get the spectrum of the legitimate solutions of the actual eigenvalue problem, Eq. (6.2).

We solve Eq. (6.3b) by comparing it to the Schrödinger equation for a charge in the Coulomb potential of a charge Z':

$$\left[-\frac{d^2}{dr^2}+\frac{l(l+1)}{r^2}-\frac{2Z'}{r}\right]\theta_S(r)=2E\,\theta_S(r)\ , \tag{6.4}$$

There is a solution to Eq. (6.4), with $l=\gamma-1$ and $Z'=Z\epsilon$, for every solution to Eq. (6.3b). The bound states of Eq. (6.4) have $Z'<0$ and eigenvalues

$$E_p(Z')=-Z'^2/2(\gamma+p)^2, \qquad p=0,1,\ldots\ . \tag{6.5}$$

The eigenvalues of Eq. (6.3b) are consequently

$$\epsilon_p=\left[1+\left((Z\alpha)^2/(\gamma+p)\right)\right]^{-1/2}, \tag{6.6}$$

for $p=0,\ 1,\ \ldots$. The solution to Eq. (6.3b) that has $\epsilon=\eta(-\kappa)$ occurs when $p=0$ and $\kappa>0$. Deleting this solution, we find that for $\kappa>0$, the index p of the discrete eigenvalues ϵ_p of Eq. (6.2) runs, as expected, $p=1,\ 2,\ \ldots$.

Now consider what happens if we return to the original eigenvalue problem, Eq. (6.2), and expand $\widehat{\phi}$ and $\widehat{\theta}$ each in the basis of functions

$$\widehat{\phi}=-\sum_{j=1}^{N}(\widehat{x}_1)_j\,B^\dagger(-\kappa)w_j\ , \qquad \text{and} \qquad \widehat{\theta}=\sum_{j=1}^{N}(\widehat{x}_2)_j\,w_j\ . \tag{6.8}$$

Assume that the function that solves $B^\dagger(-\kappa)f=0$ does not belong to the set $\{w\}$, so all the basis vectors are linearly independent. Assume the functions w are well-enough behaved that for all n, m,

$$\left\langle B^\dagger(-\kappa)w_n|B^\dagger(-\kappa)w_m\right\rangle\ =\ \left\langle w_n|B(-\kappa)B^\dagger(-\kappa)|w_m\right\rangle\ . \tag{6.9}$$

Then we find the matrix eigenvalue equation

$$\begin{pmatrix}\eta(-\kappa)\widehat{M} & \widehat{M}\\ \widehat{M} & -\eta(-\kappa)U+A\end{pmatrix}\begin{pmatrix}\widehat{x}_1\\ \widehat{x}_2\end{pmatrix}=\epsilon\begin{pmatrix}\widehat{M} & 0\\ 0 & U\end{pmatrix}\begin{pmatrix}\widehat{x}_1\\ \widehat{x}_2\end{pmatrix}, \tag{6.10}$$

and the equivalent pair of separate equations

$$\eta(-\kappa)\,\widehat{M}\widehat{x}_1 + \widehat{M}\widehat{x}_2 = \epsilon\widehat{M}\widehat{x}_1 \ ,$$
$$\widehat{M}\widehat{x}_1 + \left[-\eta(-\kappa)\,U + A\right]\,\widehat{x}_1 = \epsilon U\widehat{x}_2 \ , \qquad (6.11a,b)$$

where $\widehat{M}_{nm} = \langle B^\dagger(-\kappa)w_n | B^\dagger(-\kappa)w_m\rangle$. Because the N functions $B^\dagger(-\kappa)w$ are linearly independent, the matrix $\widehat{M}$ is positive definite. At least one of the vectors $\widehat{x}_1$ and $\widehat{x}_2$ must be nonzero. Then Eq. (6.11b) shows that $\widehat{x}_2 \neq 0$, and Eq. (6.11a) shows that $\widehat{x}_1 \neq 0$ and $\epsilon \neq \eta(-\kappa)$. Therefore $\widehat{x}_1$ and $\widehat{x}_2$ are proportional,

$$\widehat{x}_1 \ = \ \frac{\widehat{x}_2}{\epsilon - \eta(-\kappa)} \ , \qquad (6.12)$$

and the variational wavefunctions satisfy the differential equation

$$\widehat{\phi}(r) \ = \ \left[\frac{-1}{\epsilon - \eta(-\kappa)}\right]\ B^\dagger(-\kappa)\,\widehat{\theta}(r) \ . \qquad (6.13)$$

Eliminating $\widehat{x}_1$ in Eq. (6.11b) yields the matrix equation

$$\sum_{m=1}^{N}\left\langle w_n\left|-\frac{d^2}{dr^2} + \frac{(\gamma-1)\gamma}{r^2} + \frac{1-\epsilon^2}{\alpha^2} - \frac{2Z\epsilon}{r}\right| w_m\right\rangle [\widehat{x}_2]_m = 0 \ . \qquad (6.14)$$

Comparing, as in Sec. III, Eq. (6.14) to the corresponding Schrödinger problem now yields that there are N positive and N negative eigenvalues ϵ. The negative eigenvalues are bounded from above by -1, and the p^{th} positive eigenvalue, $p = 1, 2, \ldots, N$, is bounded from below by ϵ_{p-1} (not, in this basis, by ϵ_p). Let the set $\{w\}$ be complete. Then for $\kappa < 0$, as $N \to \infty$ the p^{th} positive eigenvalue converges from above to ϵ_{p-1}, and its eigenfunction converges in mean-square to the corresponding exact bound-state wavefunction. For $\kappa > 0$, the $(p+1)^{\text{th}}$ eigenvalue and eigenfunction converge similarly. The lowest eigenvalue converges, however, to ϵ_0, and the corresponding eigenfunction is an approximation to the extra solution of Eq. (6.3b), in that $\widehat{\theta}_N/\langle\widehat{\theta}_N^2\rangle^{1/2}$ converges in mean-square to $\widehat{\theta}_f/\langle\widehat{\theta}_f^2\rangle^{1/2}$. Just

as the corresponding exact solution of Eq. (6.3b) must be discarded to get a valid set of exact eigenstates, this numerical solution of Eq. (6.14) must be discarded to get a valid set of approximate eigenstates.

We may harmlessly expand the basis for $\widehat{\phi}$ by adding m extra basis functions of the form $(f_j, 0)$, where the functions f_j are themselves linearly independent and are also linearly independent of the N functions $B^\dagger(-\kappa)w$. The original $2N$ eigenvalues and eigenfunctions are unchanged, and there are m new eigenvectors with a common eigenvalue $\epsilon = \eta(-\kappa)$, with lower components that are zero, and with upper components that are linear combinations of the functions $f_j(r) - \sum_{n=1}^{N} \langle f_j | w_n \rangle w_n(r)$. These new eigenvectors do not converge as $N \to \infty$ and are wholly meaningless, so there is no point in so expanding the basis.

Suppose the functions $\{w\}$ are well-enough behaved so that, for both signs of κ, Eq. (6.9) holds and the solution of $B^\dagger(\kappa)f = 0$ does not belong to $\{w\}$. Then the eigenvalues calculated for opposite signs of κ are equal, and the lower component functions corresponding to equal eigenvalues are proportional, with

$$\widehat{\theta}_{-\kappa}(r) = \pm \left(\frac{\epsilon + \eta(-\kappa)}{\epsilon - \eta(-\kappa)} \right)^{1/2} \widehat{\theta}_{\kappa}(r) \; . \tag{6.16}$$

If we expand the functions $\widehat{\theta}$ in the basis $\xi_n(r, \gamma - 1, z)$ [see Eq. (4.1)], we can construct a sparse matrix eigenvalue problem along the lines shown in Sec. IV. If we instead use the functions $\phi_n(r, \gamma - 1, \lambda)$ [see Eq. (5.1)], we can express the matrix eigenvalues and eigenfunctions analytically in terms of the Pollaczek polynomials and their zeros. To get the resulting formulæ, we need only substitute $\gamma \to \gamma - 1$ everywhere in Secs. IV and V. The only formula not obtained by this simple translation is the one that gives the expectation value of the energy in the Sturmian basis; this takes the following form. If we find an eigenstate $\widehat{\Phi}$ with eigenvalue ϵ and with $\widehat{\Phi} \propto \sum_{n=0}^{N-1} [\, a_n \, B^\dagger(-\kappa) \, \phi_n(r, \gamma - 1, \lambda), \; a'_n \, \phi_n(r, \gamma - 1, \lambda) \,]$,

where a_n and a'_n are coefficients, and if we define a new function f equal to the sum of the first $k \leq N$ terms of the sum, then $\langle f|\widehat{h}|f\rangle = \epsilon\langle f|f\rangle$ for all k.

The Slater bases used most often by Goldman and Drake [2–4,6] are examples of this second basis. It is possible to find a set of N independent functions for which $\{w\}$, $\{B^\dagger(-\kappa)w\}$, and $\{B^\dagger(+\kappa)w\}$ describe the same set. Then the same eigenfunctions and eigenvalues are obtained by expanding both g and f in Eq. (1.3) directly in the basis $\{w\}$, and by diagonalizing $H(\kappa)$, as are obtained by using the second basis in its usual form. (This trick is not available in the first basis, because it is impossible to find N functions for which $\{w\}$ and $\{B(\kappa)w\}$ describe the same set, and which are all square-integrable and have a finite expectation value for the potential $1/r$.) The set of Slater functions they used, $w_n \propto r^{\gamma+n}e^{-\lambda r}$, for $n = 0, \ldots, N-1$, is one example of such a set, and is moreover complete. The multi-exponential set $\{r^\gamma e^{-\lambda_j r}\}$, or the Gaussian set $\{r^\gamma e^{-\lambda_j r^2} \oplus r^{\gamma+1}e^{-\lambda_j r^2}\}$, both of which are complete for an appropriate set of values $\{\lambda_j > 0\}$, are other possibilities. Using the Slater set Drake and Goldman have observed that (1) the numerical eigenvalues calculated for opposite signs of κ are degenerate; (2) for $\kappa > 0$ the numerical eigenstate whose eigenvalue converges to ϵ_0 is spurious; and (3) sum rules depending on the completeness of the numerical eigenstates become sensible once the spurious state is discarded. We have proved that the numerical eigenstates must have these properties.

VII. RADIAL INTEGRALS USEFUL FOR MATRIX ELEMENTS

For the evaluation in a Sturmian basis of matrix elements involved in the emission or absorption of radiation [32], we draw attention to the following expression [33] of the key characteristic integral over a spherical Bessel function, j_L:

$$\int_0^\infty e^{-r\cos\beta}\, j_L(r\sin\beta) r^\lambda\, dr = \left(\frac{\pi}{2\sin\beta}\right)^{1/2} \Gamma(\lambda+L+1)\, P_{\lambda-1/2}^{-L-1/2}(\cos\beta)\,. \quad (7.1)$$

Here $P_\nu^\mu(x)$ is a Legendre function [22]. In a sum over $2N$ intermediate states, typically we need $\gtrsim N$ integrals where the (noninteger) parameter λ increases successively by one; these can easily be evaluated using the upwardly stable recursion [34]

$$(\nu-\mu+1)\, P_{\nu+1}^\mu(x) \;=\; (2\nu+1)\, xP_\nu^\mu(x) - (\nu+\mu)\, P_{\nu-1}^\mu(x)\,, \quad 0 \le x < 1\,, \quad (7.2)$$

starting from only a pair of initial values calculated, for example, by [34]

$$\Gamma(1-\mu)\, P_\nu^\mu(\cos\beta) \;=\; \left[\tan\frac{\beta}{2}\right]^{-\mu} F\left[-\nu,\, \nu+1;\, 1-\mu;\, \sin^2\left(\frac{\beta}{2}\right)\right]\,. \quad (7.3)$$

The n^{th} term of this hypergeometric series diminishes asymptotically no slower than $(1/2)^n$. The Legendre function $P_\nu^{-L-1/2}(x)$ for integer $L \ge 0$ is equal to various finite sums of elementary functions. There results, for example, the evaluation [34]

$$\int_0^\infty e^{-r\cos\beta}\, j_L(r\sin\beta)\, r^\lambda\, dr \;=\; (\sin\beta)^L\, \frac{\Gamma(\lambda+L+1)}{(2L+1)!!}\, \frac{\sin(\lambda\beta)}{\lambda\beta}\, K_L\,, \quad (7.4)$$

where K_L is defined by the recursion

$$\begin{aligned} K_0 &= 1\,, \\ K_1 &= \left(\frac{3}{1-\lambda^2}\right) \frac{\lambda\cot(\lambda\beta) - \cot\beta}{\sin\beta}\,, \\ \left(\frac{n^2-\lambda^2}{4n^2-1}\right) K_n &= -\cos\beta K_{n-1} + K_{n-2}\,, \qquad n \ge 2\,. \end{aligned} \quad (7.5)$$

This recursion is numerically unstable for small β because the desired solution, which is $O(1)$, is overrun by the other solution which grows as $O(2^L\beta^{-2L})$. Fortunately the series in Eq. (7.3) is rapidly convergent for small β.

VIII. VARIATIONAL EIGENSTATES FOR ANY POTENTIAL

There exists a minimum principle for the solutions to the Dirac equation for any potential, not for just the Coulomb potential. This principle uses an r-dependent unitary transformation to decouple the equations for the traditional large and small radial wavefunctions; the transformed equations correspond to a Sturm-Liouville equation whose minimum principle provides the bounds on the eigenvalues and the convergence of the wavefunctions. The radial Dirac equation for the potential corresponding to a charge distribution of total charge Z is $H\psi = \epsilon\psi$, where

$$H = \begin{pmatrix} 1 - Z\alpha v(r) & \alpha\left(\frac{\kappa}{r} - \frac{d}{dr}\right) \\ \alpha\left(\frac{\kappa}{r} + \frac{d}{dr}\right) & -1 - Z\alpha v(r) \end{pmatrix} . \tag{8.1}$$

For a point nucleus the function $v(r)$ is equal to α/r. The radial Dirac equation $H\psi = \epsilon\psi$ is an example of a singular equation, both because it is defined on an unbounded interval, $0 < r < \infty$, and because the function κ/r is singular at one end of this interval even if the potential $v(r)$ is not. We content ourselves with proving that our minimum principle works for any regular Dirac equation; our experience with the Coulomb problem will allow us to judge that it will work for any singular Dirac equation. Consider the equation $H(x)Y = \lambda Y$, where $H(x)$ is defined by

$$\begin{pmatrix} p_{11}(x) & p_{12}(x) \\ p_{21}(x) & p_{22}(x) \end{pmatrix} \begin{pmatrix} y_1 \\ y_2 \end{pmatrix} + \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \frac{d}{dx} \begin{pmatrix} y_1 \\ y_2 \end{pmatrix} = \lambda \begin{pmatrix} y_1 \\ y_2 \end{pmatrix} . \tag{8.2}$$

A solution is sought on the closed interval $[0, \pi]$; we assume the functions p are bounded and continuous, and that $p_{12} = p_{21}$. The boundary conditions for this regular problem are given by

$$\begin{aligned} y_1(0)\sin\alpha + y_2(0)\cos\alpha &= 0 \ , \\ y_1(\pi)\sin\beta + y_2(\pi)\cos\beta &= 0 \ , \end{aligned} \tag{8.3}$$

for some values of α and β. The eigenvalues λ are known [36] to be real and simple, and form a numerable set over $-\infty < \lambda < \infty$.

Use the unitary transformation $Z = UY$ defined by

$$\begin{pmatrix} z_1 \\ z_2 \end{pmatrix} = \begin{pmatrix} \cos\varphi & \sin\varphi \\ -\sin\varphi & \cos\varphi \end{pmatrix} \begin{pmatrix} y_1 \\ y_2 \end{pmatrix} \tag{8.4}$$

to get the new equation $hZ = \lambda Z$. Here, $h = Q + \left(\begin{smallmatrix} 0 & -1 \\ 1 & 0 \end{smallmatrix}\right) d/dx$, and the matrix Q has elements

$$\begin{aligned} Q_{11} &= -\frac{d\varphi}{dx} + p_{11}\cos^2\varphi + p_{12}\sin 2\varphi + p_{22}\sin^2\varphi \ , \\ Q_{12} &= Q_{21} = p_{12}\cos 2\varphi + \frac{1}{2}(p_{22} - p_{11})\sin 2\varphi \ , \\ Q_{22} &= -\frac{d\varphi}{dx} + p_{11}\sin^2\varphi - p_{12}\sin 2\varphi + p_{22}\cos^2\varphi \ . \end{aligned} \tag{8.5}$$

Suppose we choose $\varphi(x)$ so that $Q_{11} = C$, a constant [37]. Then there is a solution to the differential equation $hZ = \lambda Z$ that has $\lambda = C$ and $Z = (0, z_2)$, where

$$z_2(x) = \exp \int_0^x p_{12}(x)\cos\left[2\varphi(x)\right] + \frac{1}{2}\left[p_{22}(x) - p_{11}(x)\right]\sin\left[2\varphi(x)\right]\, dx \ , \tag{8.6}$$

and there is a corresponding solution to the equation $H\psi = C\psi$ for which

$$\begin{aligned} \psi_1(0) &= -\sin\varphi(0) \ , \\ \psi_2(0) &= \cos\varphi(0) \ . \end{aligned} \tag{8.7}$$

The system of equations $H\psi = C\psi$ has a unique solution [36] for this boundary condition for any value of $\varphi(0)$. All the solutions $\varphi(x)$ to the (apparently intractable) nonlinear differential equation $Q_{11} = C$ may be found by finding the solutions ψ to the linear differential equation $H\psi = C\psi$, with this boundary condition on ψ. Of all the solutions $\varphi(x)$, pick one for which C is equal to an eigenvalue and ψ is equal to an eigenfunction of Eq. (8.2), with the new boundary conditions

$$\begin{aligned} -\psi_1(0)\sin\alpha + \psi_2(0)\cos\alpha &= 0 \ , \\ -\psi_1(\pi)\sin\beta + \psi_2(\pi)\cos\beta &= 0 \ . \end{aligned} \tag{8.8}$$

Unless α and β are zero, ψ will not be an eigenfunction of Eq. (8.2) with the boundary conditions in Eq. (8.3). (It is assumed that C cannot accidentally be equal to an eigenvalue of that problem, unless α and β are zero.) The equations for z_1 and z_2 are now

$$z_1 = \frac{1}{\lambda - C}\left(Q_{12} - \frac{d}{dx}\right) z_2 \ ,$$

$$\left[-\frac{d^2}{dx^2} + Q_{12}^2 + \frac{dQ_{12}}{dx} + (\lambda - C)(C + Q_{22}) - (\lambda^2 - C^2)\right] z_2 = 0 \ , \tag{8.8a,b}$$

and the boundary conditions are

$$\begin{aligned} z_2(0) &= 0 \ , \\ z_2(\pi) &= 0 \ . \end{aligned} \tag{8.10}$$

We chose the boundary conditions on ψ in Eq. (8.8) so that the boundary conditions on z_2 would be independent of λ [38].

The equation $[-d^2/dx^2 + q(x)]z_2 = \Lambda z_2$, together with the boundary conditions of Eq. (8.10), defines a regular Sturm-Liouville problem; the function $q(x)$ need

only be summable. This problem has an infinite set of real, distinct eigenvalues Λ, bounded from below [36]. Therefore, one can solve Eq. (8.8b) by solving instead the regular Sturm-Liouville problem

$$\left[-\frac{d^2}{dx^2} + Q_{12}^2 + \frac{dQ_{12}}{dx} + Z''(C + Q_{22})\right] z_2 = \Lambda z_2 \ , \tag{8.11}$$

subject to the boundary conditions of Eq. (8.10), and to the constraints $\Lambda = \lambda^2 - C^2$ and $Z'' = \lambda - C$. Meeting these constraints is equivalent to plotting the curves $\Lambda^{(j)}(Z'')$ and seeking the points where they cross the parabola $\Lambda(Z'') \equiv Z''^2 + 2Z''C$. This parabola is zero when $Z'' = 0$, and is concave up. Because the interval $[0, \pi]$ is finite, the eigenvalues of Eq. (8.11) are discrete, and the curves $\Lambda^{(j)}(Z'')$ are continuous for all Z''; when $Z'' = 0$, the eigenvalues are greater than zero, and they are asymptotically linear with Z'' as $Z'' \to \pm\infty$. Therefore, to each curve $\Lambda^{(j)}(Z'')$ there correspond at least two solutions of Eq. (8.8), one with $Z'' > 0$ and $\lambda > C$, and one with $Z'' < 0$ and $\lambda < C$.

Consider diagonalizing $hZ = \lambda Z$ in the basis of N functions:

$$z_1 \ = \ \sum_{j=1}^{N} (x_1)_j \left[Q_{12}(x) - \frac{d}{dx}\right] w_j(x) \ , \quad \text{and} \quad z_2 \ = \ \sum_{j=1}^{N} (x_2)_j \, w_j(x) \ . \tag{8.12}$$

We let the N functions w_j vanish at $x = 0$ and $x = \pi$. As in Sec. III, we find the following equations for the vectors x_1 and x_2:

$$x_1 \ = \ \frac{x_2}{\lambda - C} \ ,$$

$$\sum_{m=1}^{N} \left\langle w_n \left| -\frac{d^2}{dx^2} + Q_{12}^2 + \frac{dQ_{12}}{dx} + Z''(C + Q_{22}) - (\lambda^2 - C^2) \right| w_m \right\rangle [x_2]_m \ = \ 0 \ . \tag{8.13a, b}$$

A graphical argument similar to that in Sec. III establishes that there are N numerical eigenvalues λ less than C, and N greater than C. Now suppose we found

p numerical eigenvalues λ with $C < \lambda^{(1)} \leq \lambda^{(2)} \leq \ldots \leq \lambda^{(p)} < \lambda_p$, where λ_p is the p^{th} exact eigenvalue greater than C. Then, corresponding to the value of $Z''(\lambda^{(p)})$ assigned to $\lambda^{(p)}$, there must be p numerical eigenvalues Λ of Eq. (8.13b), all less than the value Λ_p assigned to the exact eigenvalue λ_p. But the numerical eigenvalues of Eq. (8.13b) must lie above the exact eigenvalues of Eq. (8.11), because the latter is a Sturm-Liouville equation whose eigenvalues obey a minimum principle. Therefore for $Z'' = Z''(\lambda^{(p)})$, there must be p exact eigenvalues Λ of Eq. (8.11) less then Λ_p. The curves $\Lambda^{(j)}(Z'')$ corresponding to these eigenvalues must cross the parabola $\Lambda(Z'')$ such that there are p exact eigenvalues λ of Eq. (8.8b) less than λ_p. This is a contradiction, because there cannot be more than $p-1$ eigenvalues less than λ_p, so all the numerical eigenvalues greater than C must lie above their corresponding exact eigenvalues. Similarly, all those less than C must lie below their corresponding exact eigenvalues. The proof that the numerical eigenvalues converge to the corresponding exact eigenvalues, and that the eigenfunctions converge in mean-square, follows the same lines as the proof in Sec. III for the Coulomb potential.

We have thus established a minimum principle for the regular case. Proofs for the singular case require more training in mathematics than we possess, but we have no doubt that, at least for physically meaningful potentials that are finite at the origin, they can be obtained as limits as the finite interval over which the regular case is defined tends toward infinity. We can, however, make some general remarks. The principle is in fact easier to apply in the singular case, because the boundary conditions on the function ψ are relaxed. For example, for any value of C, the Coulomb equation has two linearly independent solutions, one for which g and f are bounded at the origin, and one for which they are singular. A linear combination of these solutions may diverge strongly at the origin and

at infinity; nonetheless any linear combination will define an acceptable function $\varphi(r)$, with $\sin\varphi(r)$ and $\cos\varphi(r)$ continuous on $0 \leq r < \infty$.

All our work with the Coulomb potential amounts to choosing, as functions ψ for a given κ, particular solutions of $H\psi = C\psi$, with $C = \pm\gamma/\kappa$. The plus sign leads to our first basis and the minus sign to the second. We chose solutions such that the functions $z_2(r)$ for the two bases were respectively $z_2 \sim r^{\mp\gamma}e^{\pm Zr/\kappa}$. Notice that when $\kappa > 0$ and $C = +\gamma/\kappa$, the function $z_2(r)$ (and therefore the function ψ) diverges both at the origin and at infinity, but still defines a useful unitary transformation. For an arbitrary potential in an unbounded interval there will be similar freedom.

One eigenvector can always be meaningless or missing, because the upper function ϕ is expanded in the set resulting from operating on $\{w\}$ with the operator $J \equiv (Q_{12} - d/dr)$. When $J^\dagger f = 0$ has a normalizable solution $f(r)$, as in the first basis for $\kappa < 0$, we exclude an exact eigenvector with eigenvalue C. This eigenvector must be added back in to complete the basis. When $Jf = 0$ has a normalizable solution, as in the second basis for $\kappa > 0$, we insert a spurious eigenvector. This eigenvector is associated with numerical eigenvalues converging to C, and it must be deleted from the numerical spectrum. When neither $J^\dagger f = 0$ nor $Jf = 0$ has a normalizable solution, as in the first basis for $\kappa > 0$ or in the second basis for $\kappa < 0$, we neither lose nor gain an eigenvector, and the set of numerical eigenvalues and eigenvectors may be used without any patching.

The variational method we have outlined might seem difficult to work, in that we need one exact solution of Eq. (8.1), or equivalently, of $h_{11} = C$, in order to obtain the function $\varphi(r)$. We can, however, pick a simple analytic function $\varphi(r)$, and solve $Q_{11} = C$ for the corresponding function $v(r)$ and separation constant C. By tuning $\varphi(r)$, we can construct a minimum principle for a function $v(r)$ that

is close to some potential of interest. Inasmuch as most physical potentials—for example, the potential of a distributed nuclear charge or the effective potential of a many-electron atom—are only approximately known, this seems an adequate method.

Finally, the unitary transformation that makes the Q_{11} constant may have some purely mathematical use, as it reduces the spectral theory [36] of at least some Dirac operators to the established spectral theory of Sturm-Liouville operators.

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A: THE RELATIVISTIC STURMIAN FUNCTIONS

As originally defined by Rotenberg [39] and as used by most practitioners [40], the Coulomb Sturmian functions, usually called merely the Sturmian functions, are the functions

$$S_{nl} = \frac{1}{2}\left[\frac{(n-l-1)!}{[(n+l)!]^3}\right]^{1/2} e^{-kr}(2kr)^{l+1}\tilde{L}^{2l+1}_{n+l}(2kr)\ . \qquad (A.1)$$

There are defined for real $k > 0$, integer $l \geq 0$, and $n = l+1, l+2, \ldots$. They satisfy the orthogonality relation $\langle S_{nl}|2/r|S_{ml}\rangle = \delta_{nm}$. The quantity $\tilde{L}$ is a Laguerre polynomial according to an definition obsolete among mathematicians and almost obsolete among physicists. We have chosen to use the modern standardization [22] of the Laguerre polynomials, for which $L^{\alpha}_{n}(x)$ for any $\alpha > 0$, integer or noninteger, is a polynomial of degree n in x and for which the coefficient of x^n has the value $(-1)^n/n!$. The relation between the two definitions for integer l is

$$\tilde{L}^{2l+1}_{n+l}(x) = -1(n+l)!\, L^{2l+1}_{n-l-1}(x)\ . \qquad (A.2)$$

Once this difference is understood the relation between our function ξ, as defined in eq. (4.1), and Rotenberg's Sturmian function S_{nl} is seen to be

$$\xi_{n-l}\big(r, \gamma = l, z = k(l+1)\big) = -1 \times S_{nl}(r,k)\ . \qquad (A.3)$$

The sign can be tracked back to the sign in Eq. (A.2). The functions ξ are all positive in the neighborhood of the origin.

Because of the identity in Eq. (A.3) we have chosen to refer to our functions ξ as relativistic Sturmian functions, or where no confusion is possible, simply as Sturmian functions. We refer to a set of functions ξ_n, for $n = 1,\ldots, N$, as a Sturmian basis set or a Sturmian basis. Such a set is obviously equivalent to a

particular set of Slater functions with a non-integer leading power, $r^{\gamma+n}e^{-\lambda r}$, for $n = 0, \ldots, N-1$. For the Dirac equation we need functions with two components; a basis set one of whose two components is expanded in a Sturmian or Slater basis we will also call a Sturmian or Slater basis, though this description does not define such a basis uniquely.

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8. For example, see Ref. [18], Sec.VII 3.2, p. 273, or the original papers by W. Rayleigh, *Philosophical Transactions of the Royal Society, London*, A, 161, 77 (1870); and by W. Ritz, *Journal fuer die reine und angewandte Mathematic* (Crelle), Vol. CXXXV, 1908.
9. In terms of Goldman's operators $A^{\pm}$, defined in Ref. [6], we have $B(\kappa) = -A^{+}(\kappa)$ and $B^{\dagger}(\kappa) = +A^{-}(\kappa)$. Also our operator A is equal to Goldman's operator $A(\kappa)$ plus $\eta(\kappa)$; our definitions of κ and $\eta(\kappa)$ match his.

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12. Goldman's proof [6] of this point (for the special case of a Slater basis) is incomplete. Referring to the equations and notations of Ref. [6], we can define a lower component function θ_i' for $\kappa > 0$ by 3.27a, and conclude that 3.22 holds. We can define a corresponding upper component function ϕ_i' by 3.18, with $\kappa > 0$, so that 3.19 holds. If 3.20 held for $\kappa > 0$ as well, then the defined function (ϕ_i', θ_i') would indeed be a variational eigenstate with $\kappa < 0$. However, we cannot reach 3.20 from 3.22 without assuming the function defined by 3.27a and 3.18 is normalized, $\langle \phi_i' | \phi_i' \rangle + \langle \theta_i' | \theta_i' \rangle = 1$, and no justification for this assumption is given. Therefore one cannot conclude that the eigenvalues for opposite signs of κ must be equal; this equality is essential to Goldman's proof that the eigenvalues for $\kappa > 0$ do not fall in the "forbidden gap," $-1 \leq \epsilon < |\eta|$. The equality he requires follows at once from our Eq. (3.6).

    This repaired, Goldman's work suffices to prove that the p^{th} positive eigenvalue is bounded from below by ϵ_1, and that it decreases as the size of the basis increases. Therefore it converges to some limit, but it is not proved that this limit is ϵ_p; similarly the negative eigenvalues converge to some limit, but it is not proved that this limit is -1.

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16. The inclusion theorem is a consequence of the Courant minimax theorem. For example, see Joel N. Franklin, *Matrix Theory* (Prentice Hall, Inc., 1968), Sec. 6.3.

17. This definition of $E(p, Z')$ allows for the possibility, which we have not been able to exclude, that the N curves $E^{(j)}(Z')$ may cross. Thus, if the curves $E^{(1)}(Z')$ and $E^{(2)}(Z')$ were to cross once, at some value $Z' \equiv Z'_{12}$, then $E(1, Z')$ would be equal to $E^{(1)}(Z')$ for $Z' \leq Z'_{12}$, and would be equal to $E^{(2)}(Z')$ for $Z' \geq Z'_{12}$.

18. As an indication of the potential subtleties, we note that a functional $F(y) = \int_a^b f(x, y, y')\, dx$ may have a minimum value for some function $y(x)$, and yet there may exist a sequence of functions y_1, y_2, ... such that $F(y_n)$ limits to $F(y)$, yet $y_n(x)$ does not limit to $y(x)$ everywhere in $[a, b]$. For examples, see H. Sagan, *Boundary and Eigenvalue Problems in Mathematical Physics* (Dover Publications, Inc., New York, 1989), Sec. VII 1.4, pp. 248-253.

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29. For example, see T. S. Chihara, *An Introduction to Orthogonal Polynomials* (Gordon and Breach Science Publishers, New York, 1978), Theorems 4.5 and 4.6.

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34. A. Erdélyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi, *Higher Transcendental Functions, Volume I* (McGraw-Hill Book Company, Inc., 1953), Eqs. (3.8.12) and (3.5.9). To derive Eqs. (7.4) and (7.5), see Eqs. (3.8.11), (3.6.12), and (3.6.13).

36. For example, see B. M. Levitan and I. S. Sargsjan, *Sturm-Liouville and Dirac Operators* (Kluwer Academic Publishers, 1990).

37. If instead, we seek $\varphi(x)$ so that $h_{22} = C$, with $y_1(0)/y_2(0) = \cot\varphi(0)$, we get the same equations as if we used the function $\varphi(x) - \pi/2$ to set $h_{11} =$ C, with $y_1(0)/y_2(0) = \tan\varphi(0)$. To find all the possible bases it is therefore sufficient to try to set only h_{11} equal to a constant.

38. The only other constructions that yield boundary conditions on z_2 that are independent of λ arrange for z_1 to equal zero at one or both endpoints; then $Bz_2 = 0$ at one or both endpoints. These constructions also give valid minimum principles.

39. M. Rotenberg, Annals of Physics **19**, 262 (1962); Adv. At. Mol. Phys. B **23**, 233 (1970).

40. For example, see A. R. Edmonds, J. Phys. G **6**, 1603 (1973); A. Macquet, Phys. Rev. A **15**, 1088 (1977); C. W. Clark and K. T. Taylor, J. Phys. B **15**, 1175 (1982), and J. Phys. B **15**, 1175 (1982); D. Delande and J. C. Gay, J. Phys. B **19**, L173 (1986); R. M. Potvliege and R. Shakeshaft, Phys. Rev.

A **39**, 1545 (1989), and Phys. Rev. A **38**, 1098 (1988); L. J. Dube and J. T. Broad, J. Phys. B **23**, 1711 (1990); E. Karule and R. H. Pratt, J. Phys. B **24**, 1585 (1991); T. J. Winter, Phys. Rev. A **43**, 4727 (1991). There is some variety in the overall normalization for the Sturmian functions adopted by these various authors; also, some use L and some $\tilde{L}$ to define the Laguerre polynomials.

Table 1

Column 2 shows a sample of the 200 positive energy eigenvalues, indexed in Column 1 in order of increasing energy, from a solution in double precision of Eqs. (4.5), (4.7), and (4.8) for $Z = z = 92$, $\alpha = 1/137.036\bar{0}$, $\kappa = 1$, and $2N = 400$. The underlined digits in Column 2 are the first contaminated by round-off error. Column 3 shows the eigenvalues from another inverse iteration routine, written in quadruple precision. Column 4 shows the fractional error between the double and quadruple precision results. Column 5 shows the fractional error between the quadruple precision eigenvalues for bound states and the corresponding Sommerfeld values; a positive error means the variational eigenvalue lies (correctly) above the Sommerfeld. Some values are negative because of round-off error.

Table 1

1	9.3304196879495E-01	9.3304196879495E-01	4.3E-17	1.7E-33
2	9.7129255046708E-01	9.7129255046708E-01	2.7E-15	2.9E-33
3	9.8427712040503E-01	9.8427712040502E-01	7.6E-15	-6.2E-33
4	9.9012266260062E-01	9.9012266260062E-01	2.8E-15	-1.0E-32
5	9.9323209176943E-01	9.9323209176942E-01	6.5E-15	-1.1E-32
6	9.9507740297513E-01	9.9507740297511E-01	1.3E-14	-1.3E-32
7	9.9626039606096E-01	9.9626039606094E-01	1.6E-14	-1.4E-32
8	9.9706353738649E-01	9.9706353738647E-01	1.4E-14	-1.8E-32
9	9.9763346229836E-01	9.9763346229834E-01	1.2E-14	-2.0E-32
10	9.9805237301537E-01	9.9805237301536E-01	1.1E-14	3.3E-30
11	9.9836922962717E-01	9.9836922962716E-01	1.1E-14	1.9E-24
12	9.9861465831169E-01	9.9861465831168E-01	9.0E-15	1.1E-19
13	9.9880860859954E-01	9.9880860859953E-01	7.4E-15	9.1E-16
14	9.9896452521643E-01	9.9896452521642E-01	6.7E-15	1.6E-12
15	9.9909173633374E-01	9.9909173633374E-01	6.3E-15	6.5E-10
...	.....	.....	.....	.....
196	8.2009746568666E+00	8.2009746568667E+00	1.0E-14	
197	9.8826417422065E+00	9.8826417422065E+00	3.6E-15	
198	1.2485488417102E+01	1.2485488417102E+01	1.5E-14	
199	1.7096321858787E+01	1.7096321858788E+01	7.6E-14	
200	2.7892987982837E+01	2.7892987982842E+01	1.6E-13	