Minimax variational approach to the relativistic two-electron problem

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A minimax formulation for the time-independent Dirac equation is extended to the two-particle problem. The question of solutions of the minimax formulation is discussed and related to the continuum dissolution problem. The approach is applied to the ground state and the $n=2$ complex of states of He-like ions. Variational calculations are made for bases with a small number of basis functions, varying the nonlinear parameters, as well as for large-dimensional configuration-interaction-type bases.

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I. INTRODUCTION

The energy levels and other properties of two-electron ions continue to be of great experimental and theoretical interest after 70 years. One of the problems on the theoretical side is the inclusion of the so-called correlation effects, that is, the energy and wave function corrections that arise from our inability to solve the three-body problem exactly. In the nonrelativistic approximation this problem can be said to be nonexistent. From the original work of Hylleraas [1,2] to the contemporary highly accurate calculations of Drake [3] and Baker *et al.* [4], the state has advanced so that theoretical uncertainties are negligible compared to experimental uncertainties.

The theoretical situation is less satisfactory for the relativistic theory. Apart from fundamental questions as to the actual problem that is to be solved, the problem of solving approximately the two-electron Dirac equation analogous to the two-electron Schrödinger equation presents serious difficulties that arise, as will be discussed extensively below, because the powerful variational approach used in the nonrelativistic problem is not directly applicable to the Dirac equation. Four methods in current application can be identified. The first, which has been extensively pursued by Drake [5–7], is to compute relativistic corrections in terms of a power series in $Z\alpha$ using the highly accurate approximate wave functions computed nonrelativistically. Another group of approaches is to solve the relativistic pair equation of many-body perturbation theory [8,9]. This program suffers from the problem that the angular momentum expansion of the wave function is slowly convergent. A third approach [10] is to make large-scale configuration-interaction (CI) calculations, using a basis of products of solutions of the single-particle Dirac equation. The fourth approach, which is applicable more generally to many-electron systems, is the multiconfiguration Dirac-Fock (MCDF) method [11–13]. These also present the difficulty of the slow convergence of the angular momentum expansion.

The problem of the slow convergence of the angular momentum expansion, which arises generally in any calculation of the CI type [14,15], is avoided in the nonrelativistic case by the use of ''explicitly correlated wave functions,'' i.e., wave functions that depend explicitly on the interelectronic distance r_{12}. (An interesting alternative to the explicit introduction of the variable r_{12} into the wave function has been proposed recently by Goldman [16].) However, use of such trial wave functions requires application of the variational principle or its generalization to the Hylleraas-Undheim theorem [17] or Poincaré principle [18]. (The latter asserts that if the Hamiltonian is diagonalized in a finite basis, the kth eigenvalue is an upper bound to the exact kth energy.) The variational principle fails immediately in application to the Dirac equation, in that the expectation value of the Dirac Hamiltonian is unbounded from below because of the negative energy continuum in its spectrum.

A number of methods to circumvent this problem in the case of the one-particle Dirac equation have been proposed [19–26]. However, these are not, in general, clearly applicable to the two-particle problem. In this article we discuss the possibility of generalizing the minimax approach to the single-particle problem that has been proposed by one of us [27] to the two-electron problem. This approach to the Dirac equation will be reviewed in Sec. II and the generalization to the two-electron problem will be described and discussed in Sec. III. The situation in the latter problem is complicated by questions of the proper formulation of the problem and questions concerning the existence of solutions. Aspects of the relationship of these questions to the minimax approach will be discussed in some detail.

The remaining sections describe some applications of the approach to demonstrate its feasibility. In particular, the results indicate that calculated energies are in fact practical upper bounds to the energies, although the theoretical formulation does not guarantee this.

The calculations described are of two types. In the first, nonlinear parameters in the wave function are varied; it is in this sense that the term ''variational calculation'' is often used. The second type of calculation are CI calculations in which the wave function is expanded in Slater states; these are of course also variational in that the expansion coefficients serve as variational parameters. These calculations are intended to demonstrate the validity of the approach; further

studies using explicitly correlated basis functions are in progress.

A problem in relativistic calculations that has been extensively discussed is the appropriate form of basis functions to use. One important aspect concerns the analytic behavior of the functions at the nucleus. Another is related to the spurious solutions that can arise [28,29] in the solution of the Dirac-Coulomb problem. The choice of basis sets for the present calculations will be discussed in detail in Sec. IV. Some calculational details are described in Sec. V. In Sec. VI low-dimensional results, varying the nonlinear parameters, and large-dimensional results, with the parameters fixed, are given for the ground-state energy. Corresponding results for the $n=2$ complex of states are given in Sec. VII.

In the following, units such that $e=m=\hbar=1$ will be used throughout. In the calculations described, $c=1/\alpha=137.036$.

II. MINIMAX APPROACH TO THE SINGLE-PARTICLE PROBLEM

In this section, the minimax variational approach to the single-particle problem will be reviewed in order to clarify the issues involved in extending it to the two-particle problem. The time-independent, one-particle Dirac equation for a potential $V(\mathbf{r})$ is usually written in the form

$$[V(\mathbf{r})+c^2]g+c\,\boldsymbol{\sigma}\cdot\mathbf{p}f=eg,$$

$$c\,\boldsymbol{\sigma}\cdot\mathbf{p}g+[V(\mathbf{r})-c^2]f=ef, \tag{1}$$

where g and f are two-component spinors customarily called the ''large'' and ''small'' components. The expectation value of the Dirac Hamiltonian for a normalized wave function is given by

$$\langle H_D\rangle=\langle g|V(\mathbf{r})+c^2|g\rangle+2c\langle f|\boldsymbol{\sigma}\cdot\mathbf{p}|g\rangle+\langle f|V(\mathbf{r})-c^2|f\rangle. \tag{2}$$

The variational formulation of the Dirac equation (1) is based on the equation [27]

$$e=\min_g\left[\max_f\langle H_D\rangle\right]. \tag{3}$$

It is straightforward to show that, if the constraint $\langle g|g\rangle+\langle f|f\rangle=1$ is included by using the Lagrange multiplier method, the variational problem (3) leads to the Dirac equations (1).

It is of interest, however, to go into the derivation of Eq. (3) in more detail. It should be emphasized that the order of finding the minimax is important; $\langle H_D\rangle$ is to be maximized on f for any fixed g. The result is a functional of g that is to be minimized on g. If the potential $V(\mathbf{r})$ is bounded from above, as is usually the case in practice, it can be shown as follows that the maximization problem must have a solution. It can be seen that, for fixed g, $\langle H_D\rangle$ has an upper bound for $\langle H_D\rangle$ as a functional of f. This upper bound, which depends on g, will be denoted by $M[g]$. Then, for a fixed g and arbitrary f

$$\langle g|V(\mathbf{r})+c^2|g\rangle+2c\langle f|\boldsymbol{\sigma}\cdot\mathbf{p}|g\rangle+\langle f|V(\mathbf{r})-c^2|f\rangle-M[g]\times[\langle g|g\rangle+\langle f|f\rangle]\leqslant 0. \tag{4}$$

It can be noted that this equation is valid independent of the normalization of the wave function. Equation (4) can be rewritten, eliminating the cross term by completing the square in f, as

$$\left\langle g\left|V(\mathbf{r})+c^2+\boldsymbol{\sigma}\cdot\mathbf{p}\frac{c^2}{M[g]+c^2-V(\mathbf{r})}\boldsymbol{\sigma}\cdot\mathbf{p}-M[g]\right|g\right\rangle+\langle f_d|V(\mathbf{r})-c^2-M[g]|f_d\rangle\leqslant 0, \tag{5}$$

where

$$f_d=f-\frac{c}{M[g]+c^2-V(\mathbf{r})}\boldsymbol{\sigma}\cdot\mathbf{p}g. \tag{6}$$

From this it is evident that the maximum $M[g]$ is actually attained, for $f_d=0$, or for

$$f=\frac{c}{M[g]+c^2-V(\mathbf{r})}\boldsymbol{\sigma}\cdot\mathbf{p}g, \tag{7}$$

which is the second of the Dirac equations if $e=M[g]$.

Substituting for f from Eq. (7) in Eq. (2) gives, after some manipulation,

$$\langle H_D\rangle=M[g]+\left\langle g\left|V(\mathbf{r})+c^2+\boldsymbol{\sigma}\cdot\mathbf{p}\frac{c^2}{M[g]+c^2-V(\mathbf{r})}\boldsymbol{\sigma}\cdot\mathbf{p}-M[g]\right|g\right\rangle, \tag{8}$$

which is to be minimized subject to the constraint

$$\langle g|g\rangle+\left\langle g\left|\boldsymbol{\sigma}\cdot\mathbf{p}\frac{c^2}{[M[g]+c^2-V(\mathbf{r})]^2}\boldsymbol{\sigma}\cdot\mathbf{p}\right|g\right\rangle=1. \tag{9}$$

The variational derivative with respect to g is given by

$$\frac{\delta\langle H_D\rangle}{\delta g}=\left[V(\mathbf{r})+c^2+\boldsymbol{\sigma}\cdot\mathbf{p}\frac{c^2}{M[g]+c^2-V(\mathbf{r})}\boldsymbol{\sigma}\cdot\mathbf{p}-M[g]\right]g+\left[1-\langle g|g\rangle-\left\langle g\left|\boldsymbol{\sigma}\cdot\mathbf{p}\frac{c^2}{[M[g]+c^2-V(\mathbf{r})]^2}\boldsymbol{\sigma}\cdot\mathbf{p}\right|g\right\rangle\right]\times\frac{\delta M[g]}{\delta g}. \tag{10}$$

In view of Eq. (9), the variational derivative is zero if g satisfies the equation

$$\boldsymbol{\sigma}\cdot\mathbf{p}\frac{c^2}{M[g]+c^2-V(\mathbf{r})}\boldsymbol{\sigma}\cdot\mathbf{p}g+[V(\mathbf{r})+c^2]g=M[g]g. \tag{11}$$

This, together with Eq. (7), is the first of the Dirac equations. Thus a solution of the variational problem is a solution of the Dirac equations.

The properties of Eq. (11) can be considered further by writing it in the form

$$H(\mu)g_n(\mu)=\epsilon_n(\mu)g_n(\mu), \tag{12}$$

where

$$H(\mu)=\boldsymbol{\sigma}\cdot\mathbf{p}\frac{c^2}{\mu+c^2-V(\mathbf{r})}\boldsymbol{\sigma}\cdot\mathbf{p}+V(\mathbf{r})+c^2. \tag{13}$$

The second-order differential operator $H(\mu)$ is similar in structure to the Schrödinger operator and evidently has the same spectral properties. If $V(\mathbf{r})<0$, as is usually the case, it can be seen that it is bounded above by the corresponding Schrödinger operator with the denominator replaced by $2c^2$ and the bound-state spectrum will be below the Schrödinger spectrum. The positive energy eigenvalues of the Dirac are then the eigenvalues of $H(\mu)$ that satisfy the identity

$$\epsilon_n(e)=e. \tag{14}$$

If $V(\mathbf{r})>-2c^2, \epsilon_n(-c^2)>-c^2$. It can be seen from the definition of $H(\mu)$ that $\epsilon_n(\mu)$ is a monotonically decreasing function of μ and therefore that Eq. (14) has a unique solution for each n. It can also be observed that if $\tilde{\epsilon}_n$ is an upper bound to ϵ_n, the corresponding solution of (14) is an upper bound to the Dirac equation eigenvalue. In the case of the Coulomb potential, the inequality $V(\mathbf{r})<-2c^2$ is violated at small r and it is well known that the solution of the Dirac equation in this case breaks down for $Z>c$.

It is of course true that an approximate energy eigenvalue computed from Eq. (3) is not a variational upper bound to the exact energy, so that the minimax principle is not a complete panacea for the variational collapse problem. On the other hand, Eq. (5) shows that the amount by which it fails to be an upper bound is quadratic in the error f_d. Therefore the minimax energy is effectively an upper bound if the small component is approximated to a greater degree of accuracy than the large component.

In practical calculations, the problem is usually treated by expanding g and f in finite bases $\{\phi_m, m\leqslant M\}$ and $\{\chi_n, n\leqslant N\}$, respectively, where the two sets may be assumed to be orthonormal. The variational problem for the expansion coefficients leads to a matrix eigenvalue problem

$$\begin{bmatrix} V+c^2 & cW \\ cW^T & U-c^2 \end{bmatrix}\begin{bmatrix}\mathbf{x}\\ \mathbf{y}\end{bmatrix}=e\begin{bmatrix}\mathbf{x}\\ \mathbf{y}\end{bmatrix}, \tag{15}$$

where $\mathbf{x}$ and $\mathbf{y}$ are the expansion coefficients for g and f, respectively, and

$$\begin{aligned} v_{ij}&=\langle\phi_i|V(\mathbf{r})|\phi_j\rangle,\\ w_{ij}&=\langle\phi_i|\boldsymbol{\sigma}\cdot\mathbf{p}|\chi_j\rangle,\\ u_{ij}&=\langle\chi_i|V(\mathbf{r})|\chi_j\rangle. \end{aligned} \tag{16}$$

The second variation in $\langle H_D\rangle$ with respect to variations in $\mathbf{x}$ and $\mathbf{y}$ is given by

$$\begin{aligned}\delta^2(\langle H_D\rangle)=&\,\delta\mathbf{x}^T(V+c^2-e)\,\delta\mathbf{x}+2c\,\delta\mathbf{x}^T W\,\delta\mathbf{y}\\ &+\delta\mathbf{y}^T(U-c^2-e)\,\delta\mathbf{y}.\end{aligned} \tag{17}$$

This is negative for variations in $\mathbf{y}$ provided the matrix $U-c^2-e$ is negative definite. For $V(\mathbf{r})<0$, this is true provided $e>-c^2$, i.e., e is above the negative energy continuum. It was shown in [27] that the lowest N eigenvalues of Eq. (15) are below $-c^2$ and the M largest eigenvalues are above $-c^2$. Therefore the solution of the minimax problem in this matrix approximation is the $(N+1)$st eigenvalue.

The question of whether the minimax estimate is effectively an upper bound depends on whether the basis $\{\chi_n\}$ can give a more accurate representation for f than the basis $\{\phi_m\}$ can give for g. These considerations are related to the *kinetic balance principle*, which has often been taken as a partial solution to the variational collapse problem. This principle asserts that if a function ϕ is included in the large component basis then $\boldsymbol{\sigma}\cdot\mathbf{p}\phi$ should be included in the small component basis, or its span. It is evident from the above discussion that the minimax estimate for e is a true upper bound if, for any g, the exact f, as given by Eq. (7), is contained in the span of the small component basis. This is true, for example, in the limit $c\to\infty$ if the kinetic balance principle is satisfied. This shows that the theory goes over into the correct nonrelativistic limit if the kinetic balance principle is followed.

In actual calculations, the basis functions for g and f are typically taken in the form $P_n(r)e^{-\alpha r}$ or $r^{\gamma-1}P_n(r)e^{-\alpha r}$ multiplying a spin-angular factor, where P_n is a polynomial of degree n. Equation (7) is then not satisfied exactly, but it is plausible that if the polynomial approximation for f is of higher degree than for g, the minimax estimate will be an upper bound for the exact energy. (The question of the dependence of the accuracy of an approximation on the degree of the approximation has been recently discussed in detail by Hill [30].)

It is generally accepted that in going from the single-particle problem to the many-particle problem, the many-particle wave function should be formed in the Fock space of products of single-particle wave functions that are positive energy eigenfunctions of the single-particle problem. It is not entirely clear which potential should define the single-particle problem although it seems most plausible to choose the bare nucleus Coulomb potential.

The problem of projecting onto positive energy states (the PEP problem) is, however, not a simple one. We consider now the relation of this problem to the minimax principle. The exact solutions of the Dirac equation for the defining potential will be denoted by (u_n, v_n) with eigenvalues e_n. It will be assumed that any g can be expanded in the form

$$g=\sum_n{}' \ \alpha_n u_n \tag{18}$$

where the prime on the summation denotes a sum on the positive energy states. Then f corresponding to the PEP of g is given by

$$f_{\mathrm{PEP}}=\sum_n{}' \ \alpha_n v_n. \tag{19}$$

It is clear that if, for a particular g, the small-component basis contains the corresponding $f_{\rm PEP}$, the result of maximizing $\langle H_D\rangle$ on f is at least as large as $\langle H_D\rangle_{\rm PEP}$. Therefore the minimax energy is an upper bound to the PEP energy and they are clearly equal if g is the exact ground-state large-component wave function.

More generally, if g is given by Eq. (18), f, as given by Eq. (7), is given by

$$f=\sum_n{}' \ \frac{e_n+c^2-V(\mathbf{r})}{M[g]+c^2-V(\mathbf{r})}\alpha_n v_n \tag{20}$$

and

$$f-f_{\rm PEP}=\sum_n{}' \ \frac{e_n-M[g]}{M[g]+c^2-V(\mathbf{r})}\alpha_n v_n . \tag{21}$$

The magnitude $f-f_{\rm PEP}$ can be estimated as $(\langle\delta e\rangle/c^2)Z\alpha$, where $\langle\delta e\rangle$ is an estimate of the spread of energies in the components of g and the factor $Z\alpha$ reflects the fact that the expansion is in the small components v_n.

III. MINIMAX APPROACH TO THE TWO-PARTICLE PROBLEM

The two-electron Dirac wave function Ψ has four components, which will be denoted $\phi_{ll},\phi_{sl},\phi_{ls},\phi_{ss}$, each of which is a four-component spinor. The pairs of equations in the single-particle Dirac equation generalize to a system of four equations that can be written in terms of the components as

$$\begin{aligned}
&[V_T+2c^2]\phi_{ll}+c\boldsymbol{\sigma}_1\cdot\mathbf{p}_1\phi_{sl}+c\boldsymbol{\sigma}_2\cdot\mathbf{p}_2\phi_{ls}=e\phi_{ll},\\
&V_T\phi_{ls}+c\boldsymbol{\sigma}_1\cdot\mathbf{p}_1\phi_{ss}+c\boldsymbol{\sigma}_2\cdot\mathbf{p}_2\phi_{ll}=e\phi_{ls},\\
&V_T\phi_{sl}+c\boldsymbol{\sigma}_1\cdot\mathbf{p}_1\phi_{ll}+c\boldsymbol{\sigma}_2\cdot\mathbf{p}_2\phi_{ss}=e\phi_{sl},\\
&[V_T-2c^2]\phi_{ss}+c\boldsymbol{\sigma}_1\cdot\mathbf{p}_1\phi_{ls}+c\boldsymbol{\sigma}_2\cdot\mathbf{p}_2\phi_{sl}=e\phi_{ss},
\end{aligned} \tag{22}$$

where V_T is the total potential-energy operator. If the Breit interaction is included there are additional terms that mix ϕ_{ls} and ϕ_{sl} in the middle two equations and ϕ_{ll} and ϕ_{ss} in the first and fourth equations.

The energy functional for a normalized wave function is

$$\begin{aligned}
\langle H_D\rangle=&\langle\phi_{ll}|V_T+2c^2|\phi_{ll}\rangle+2c\langle\phi_{sl}|\boldsymbol{\sigma}_1\cdot\mathbf{p_1}|\phi_{ll}\rangle\\
&+2c\langle\phi_{ls}|\boldsymbol{\sigma}_2\cdot\mathbf{p_2}|\phi_{ll}\rangle+\langle\phi_{ls}|V_T|\phi_{ls}\rangle\\
&+\langle\phi_{sl}|V_T|\phi_{sl}\rangle+2c\langle\phi_{ss}|\boldsymbol{\sigma}_1\cdot\mathbf{p_1}|\phi_{ls}\rangle\\
&+2c\langle\phi_{ss}|\boldsymbol{\sigma}_2\cdot\mathbf{p_2}|\phi_{sl}\rangle+\langle\phi_{ss}|V_T-2c^2|\phi_{ss}\rangle.
\end{aligned} \tag{23}$$

If ϕ_{ll} is expanded in N_{ll} basis functions, etc., the result is a matrix diagonalization problem of dimension $N_{ll}+N_{ls}+N_{sl}+N_{ss}$. In the nonrelativistic limit, there are N_{ll} eigenvalues close to $2c^2$, $N_{ls}+N_{sl}$ eigenvalues near 0, and N_{ss} eigenvalues near $-2c^2$. The eigenvalue of interest in the two-electron ground-state problem is the smallest of the eigenvalues near $2c^2$, i.e., the smallest of the N_{ll} largest eigenvalues. The variational problem that picks out this eigenvalue is

$$e=\min_{\phi_{ll}}\left[\max_{\phi_{ls},\phi_{sl},\phi_{ss}}\langle H_D\rangle\right]. \tag{24}$$

This leads us to Eq. (24) as the appropriate generalization of Eq. (3) to the two-particle problem. Physically, the components of the wave function with a ''small'' label produce the Dirac term for the kinetic energy, which should be maximized for the physical wave function. It is evident that a solution of this equation is also a solution of Eq. (22). This minimax formulation of the two-electron problem does not appear to be directly related to that of Rosenberg [31], which is based on the maximization of the energy with respect to an effective potential describing the electron-electron scattering amplitude.

If ϕ_{ls} and ϕ_{sl} are eliminated from these equations, it is found that

$$\begin{aligned}
\langle H_D\rangle=&\left\langle\phi_{ll}\left|V_T+2c^2+\boldsymbol{\sigma}_1\cdot\mathbf{p}_1\frac{c^2}{e-V_T}\boldsymbol{\sigma}_1\cdot\mathbf{p}_1+\boldsymbol{\sigma}_2\cdot\mathbf{p}_2\frac{c^2}{e-V_T}\boldsymbol{\sigma}_2\cdot\mathbf{p}_2\right|\phi_{ll}\right\rangle+2\left\langle\phi_{ll}\left|\boldsymbol{\sigma}_1\cdot\mathbf{p}_1\frac{c^2}{e-V_T}\boldsymbol{\sigma}_2\cdot\mathbf{p}_2\right.\right.\\
&\left.\left.+\boldsymbol{\sigma}_2\cdot\mathbf{p}_2\frac{c^2}{e-V_T}\boldsymbol{\sigma}_1\cdot\mathbf{p}_1\right|\phi_{ss}\right\rangle+\left\langle\phi_{ss}\left|V_T-2c^2+\boldsymbol{\sigma}_1\cdot\mathbf{p}_1\frac{c^2}{e-V_T}\boldsymbol{\sigma}_1\cdot\mathbf{p}_1+\boldsymbol{\sigma}_2\cdot\mathbf{p}_2\frac{c^2}{e-V_T}\boldsymbol{\sigma}_2\cdot\mathbf{p}_2\right|\phi_{ss}\right\rangle .
\end{aligned} \tag{25}$$

This expression for $\langle H_D\rangle$ reveals a problem in principle that arises with the proposed formulation: $\langle H_D\rangle$ is unbounded from above under arbitrary variations in ϕ_{ss}. Although the last term in Eq. (25) contains the very large and negative term $-2c^2$, if ϕ_{ss} contains momentum components larger than c, they can overcome this negative term so that $\langle H_D\rangle$ can be arbitrarily large. This problem does not arise in the calculations described here since the choice of basis functions constrains the momentum components of ϕ_{ss}. Conceivably, however, if the nonlinear parameters in the basis functions (see below) were to exceed c, problems could arise.

The lack of a global maximum in $\langle H_D\rangle$ for a fixed ϕ_{ll} does not preclude the possibility of local maxima, and indeed the calculations reported below demonstrate their existence at least in calculations in finite-dimensional subspaces. It can also be argued that the many successful Dirac-Hartree-Fock, and multiconfigurational Dirac-Fock, calculations are finding such local maxima.

The question of whether local maxima of $\langle H_D\rangle$ exist is related to the question of whether bound-state solutions of Eq. (22) exist. This has been called into question because of the continuum dissolution problem or Brown-Ravenhall disease [32], which has been extensively discussed in the litera-

ture. This problem suggests that there are no solutions of Eq. (22) since such a solution could decay into a continuum of degenerate states in which one particle is in a negative energy state and the other is in a state of large positive energy. Since both problems are associated with components in the wave function of large momenta, it is likely that they are related.

This relationship can be established by the following observation. Equations (24) and (25) indicate that the two-electron Dirac problem can be modified in a variety of ways to guarantee the existence of an upper bound. For example, ϕ_{ss} could be replaced in Eq. (22) by an integral transformed function, e.g.,

$$\phi_{ss}(\mathbf{r}_1,\mathbf{r}_2)\rightarrow \frac{1}{(2\pi)^6}\int_{|\mathbf{p_1}|<\mathbf{c}} d\mathbf{p}_1 \int_{|\mathbf{p}_2|<c} d\mathbf{p}_2 \int d\mathbf{r}_1' \times \int d\mathbf{r}_2' e^{i\mathbf{p}_1\cdot(\mathbf{r}_1-\mathbf{r}_1')} e^{i\mathbf{p}_2\cdot(\mathbf{r}_2-\mathbf{r}_2')} \phi_{ss}(\mathbf{r}_1',\mathbf{r}_2'). \tag{26}$$

This slight modification of the problem removes the large momentum components from ϕ_{ss} so that $\langle H_D\rangle$ is bounded from above. It also projects out products of free particle states in which one particle has large positive energy. This integral transform in essence ''smears'' ϕ_{ss} over distances comparable to the Compton wave length. A solution of the modified variational problem is then also a solution of the modified Dirac equation. Thus, even though the existence of a solution of the Dirac equation is open to question, it is plausible that solutions exist for a very similar problem and indeed for any problem in which the momentum components in ϕ_{ss} are constrained to be less than c.

However, the general viewpoint [33] in coping with the continuum dissolution problem is that Eq. (22) is not the correct formulation for the two-particle problem. Rather, the proper Hilbert space for the problem is the product space formed from products of *positive energy solutions* of the one-particle problem in an external potential, i.e., the PEP of the Hilbert space. This is equivalent to projecting the potential energy operators into this subspace. The problem of actually carrying out this projection has not been solved, although Cheng *et al.* [34] have carried out CI calculations within this framework.

The PEP principle indicates that the proper constraint on the admissable variational trial functions is that they should be contained in the PEP Hilbert space. It is plausible to assume that for for an arbitrary ϕ_{ll}, there exist functions $\phi_{ls},\phi_{sl},\phi_{ss}$ such that the two-electron Dirac wave function that they define is in the PEP projection. This can be shown to be true if the PEP is onto free-particle positive energy states by using Fourier transforms. In the single-electron case, if the PEP is to be made onto the free-particle positive energy solutions, then for a given $g(\mathbf{r})$,

$$f(\mathbf{r})=\int \frac{c\boldsymbol{\sigma}\cdot k}{c\sqrt{c^2+k^2}+c^2}\tilde{g}(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{k}, \tag{27}$$

where $\tilde{g}(\mathbf{k})$ is the Fourier transform of $g(\mathbf{r})$. This expression can be readily generalized to the two-electron case. However, we are not aware of any proof of this result for nonzero single-particle potentials.

It can now be asserted that if, for a particular ϕ_{ll}, the variational basis for the functions $\phi_{ls},\phi_{sl},\phi_{ss}$ is large enough to include the corresponding PEP wave function, then the result of the minimax calculation must be at least as large as energy given by the PEP wave function.

The question of whether the PEP components are contained within the trial function space is related to the kinetic balance principle. In the single-particle case, the PEP is given by Eq. (27). If $\tilde{g}(\mathbf{k})$ contains only momentum components small compared to c, this becomes $f(\mathbf{r})=\boldsymbol{\sigma}\cdot pg(\mathbf{r})/(2c)$, with the correction being of order $(k/c)^2$ or, equivalently, $(Z/c)^2$. Thus, if the kinetic balance principle is imposed on the trial wave function and PEP is to be made onto free-particle states, the minimax energy provides an upper bound to the true energy up to terms of order $(Z/c)^2$.

IV. BASIS SETS

The basis functions used in the calculations described below are taken to be antisymmetrized products of single-particle functions coupled to a total angular momentum J. The single-particle wave functions are of the form

$$\psi_{n\kappa}(r)=r^{\gamma-1}r^{n-|\kappa|}e^{-\lambda r}\Omega_{\kappa m}(\theta,\phi), \quad l<n\leqslant N. \tag{28}$$

Here $\gamma=[\kappa^2-Z^2/c^2]^{1/2}$ and $\Omega_{\kappa m}$ is the two-component spinor formed when spin angular momentum 1/2 is coupled to orbital angular momentum l to give angular momentum j:

$$\Omega_{\kappa m}=\sum \langle \tfrac{1}{2}\mu l m_l|jm\rangle Y_{lm_l}(\theta,\phi)\chi_\mu . \tag{29}$$

κ is the quantum number usually introduced to describe the Dirac equation solutions in spherical symmetry, defined by $\kappa=-l-1$ for $j=l+\frac{1}{2}$ and $\kappa=l$ for $j=l-\frac{1}{2}$. In the tables, these functions will be denoted by nl_j. The integer n is assigned according to the usual spectroscopic convention; $n>l$ with an exception to be discussed below.

The spinors $\Omega_{\kappa m}$ satisfy the identity

$$i\boldsymbol{\sigma}\cdot\mathbf{p}r\Omega_{\kappa m}=(\kappa+2)\Omega_{-\kappa m}. \tag{30}$$

It is well known that in spherical symmetry the single-particle Dirac equation can be separated by choosing the wave function in the form

$$\psi_{\kappa m}=\begin{bmatrix} ig(r)\Omega_{\kappa m} \\ f(r)\Omega_{-\kappa m}\end{bmatrix}. \tag{31}$$

The form chosen for the basis functions is dictated by the behavior of the single-particle Dirac wave function close to the nucleus; for the Coulomb problem Eq. (10) takes the form

$$-\frac{Z}{r}g+c\left[-\frac{d}{dr}+\frac{\kappa-1}{r}\right]f=0,$$

$$c\left[\frac{d}{dr}+\frac{\kappa+1}{r}\right]g-\frac{Z}{r}f=0. \tag{32}$$

These equations show that g and f have the same power-law behavior at the nucleus as given in Eq. (28) with $n=\kappa$.

An important comment should be made concerning the functions with $\kappa>0$. In the nonrelativistic limit, in which $\gamma=|\kappa|=l$, these behave like r^{l-1} for small r rather than as the usual r^l behavior. The solutions of the Coulomb-Dirac problem are of the form

$$\psi_{nlm}=Ar^{\gamma-1}e^{-\lambda r}\begin{bmatrix}P_{n-1}(r)\Omega_{\kappa m}\\ Q_{n-1}(r)\Omega_{-\kappa m}\end{bmatrix}, \tag{33}$$

where n can be viewed as the usual principal quantum number and $P_{n-|\kappa|}(r)$ and $Q_{n-|\kappa|}(r)$ are polynomials of degree $n-|\kappa|$, i.e., of degree one higher than for the corresponding solution of the Schrödinger equation in the $\kappa>0$ case. The constant term in the polynomial P_l vanishes in the nonrelativistic limit, but it is important to include it at larger Z values. These contributions to the bases in the $\kappa>0$ case will be labeled $1p_{1/2}$, $2d_{3/2}$, etc.

A second point concerning the states with $\kappa>0$ concerns the ''spurious solutions'' that can arise for particular choices of the basis. For example, if the Dirac matrix with $\kappa=1$ for the Coulomb problem is diagonalized in the basis of Eq. (28) with an equal number of identical large and small component functions to find $p_{1/2}$ states, a physically spurious eigenvalue at the $1s_{1/2}$ ground-state energy is obtained [28,29]. The true solution is also found, but it is associated with the next larger eigenvalue. Extensive calculations show that this spurious eigenvalue is readily eliminated by modifying the basis. For example, if the three large component functions and four small component functions are used with the exact value of the nonlinear parameter α, the exact $2p_{1/2}$ energy is obtained as third largest eigenvalue. Similarly, if two large component and two small component functions are used and the nonlinear parameters are varied, minimax solutions are found for which the third largest is a close approximation to the true value. Therefore, to eliminate possible problems from spurious states, if r ''large'' single-particle states for some $\kappa>0$ are included in the large-large basis, $r+1$ corresponding ''small'' states will be included in the large-small and small-small bases. It has been found that if this is not done and the small states exactly pair off with the large states, as prescribed by the kinetic balance principle, a spurious root contaminates the spectrum and displaces the physical ground state so as to correspond to the next largest eigenvalue. On the other hand, if the nonlinear parameters are varied, this problem is removed.

V. CALCULATIONAL DETAILS

The basis functions used in the calculations are antisymmetrized products of single-particle functions of the form given in Eq. (28) coupled to give total angular momentum quantum numbers J,M. The basis states for ϕ_{ll} can then be written $|n_1\kappa_1\alpha_1;n_2\kappa_2\alpha_2;JM\rangle$. Similarly the basis states for ϕ_{ls} are written $|n_1\kappa_1\beta_1;n_2\kappa_2\gamma_1;JM\rangle$ and the basis states for ϕ_{ss} are written $|n_1\kappa_1\delta_1;n_2\kappa_2\delta_2;JM\rangle$. Because of antisymmetry, the Hamiltonian matrix is reduced from the 4×4 block form to a 3×3 block form since the functions ϕ_{sl} and ϕ_{ls} are not linearly independent. In the CI-like calculations, all possible products (n_1,n_2) for a particular choice of (κ_1,κ_2) are included. The nonlinear parameters β,γ,δ are to be chosen to maximize $\langle H_D\rangle$ and the parameters α are chosen to minimize $\langle H_D\rangle$. According to the kinetic balance principle, if a particular pair (κ_1,κ_2) occurs in ϕ_{ll}, the pairs $(\kappa_1,-\kappa_2)$ and $(\kappa_2,-\kappa_1)$ must occur in ϕ_{ls} and the pair $(-\kappa_1,-\kappa_2)$ must occur in ϕ_{ss}, with the corresponding n values. It must be observed, however, that the principle is not strictly satisfied since the nonlinear parameters can differ in the three different bases.

The triangular transformations to orthonormal bases for the three functions $\phi_{ll},\phi_{ls},\phi_{ss}$ are constructed from these basis states using the standard Gram-Schmidt procedure.

Overlap integrals and the matrix elements of the nuclear attraction energy and the kinetic-energy operators are computed for these basis functions in a straightforward way using standard angular momentum techniques and are expressed in terms of the γ function. The matrix elements of the operator r_{12}^{-1} require the calculation of integrals of the form

$$I=\int\int r_1^{S_1}e^{-\alpha_1 r_1}Y_{LM}(\theta_1,\phi_1)^*\frac{1}{r_{12}}r_2^{S_2}e^{-\alpha_2 r_2}\times Y_{LM}(\theta_2,\phi_2)d\mathbf{r}_1d\mathbf{r}_2. \tag{34}$$

These are calculated in momentum representation as

$$I=8\int_0^\infty F_{S_1L}(k,\alpha_1)F_{S_2L}(k,\alpha_2)dk, \tag{35}$$

using numerical Gauss-Laguerre integration. The functions $F_{SL}(k,\alpha)$ are the spherical Bessel transforms of the radial factors, defined by

$$F_{SL}(k,\alpha)=\int_0^\infty j_L(kr)r^Se^{-\alpha r}r^2dr. \tag{36}$$

In the case $L=0$,

$$F_{S0}(k,\alpha)=\frac{\Gamma(S+2)}{kR^{S+2}}\sin(S+2)\Phi, \tag{37}$$

where $\alpha+ik=Re^{i\Phi}$. For $L>0$, $F_{SL}(k,\alpha)$ can be obtained from the recurrence relation

$$F_{SL}(k,\alpha)=\frac{L+S+1}{k}F_{S-1,L-1}(k,\alpha)-\frac{\alpha}{k}F_{S,L-1}(k,\alpha). \tag{38}$$

The minimax calculation of the nonlinear parameters $\alpha,\beta,\gamma,\delta$ can be greatly facilitated if the derivatives of $\langle H_D\rangle$ are known. A method for calculating the first and second derivatives analytically will be described separately.

TABLE I. Ground-state energy in the case $Z=8$ computed for states of the form $\phi_{ll}=ns_{1/2}n's_{1/2}$, $\phi_{ls}=ns_{1/2}n'p_{1/2}$, $\phi_{ss}=np_{1/2}n'p_{1/2}$. N_{ll}, N_{ls}, and N_{ss} give the total number of large-large, large-small, and small-small states, respectively. α is the nonlinear parameter for the large-large states, β is the nonlinear parameter for the large factor in the large-small states, and γ is the nonlinear parameter for the small factors. E_Z is the energy computed with the nonlinear parameters fixed at $Z=8$ and $E_{\rm var}$ is the result of the variational calculation.

N_{ll}	N_{ls}	N_{ss}	E_Z	$E_{\rm var}$	α	β	γ
1	1	1	−59.048 334	−59.146 390	7.6866	7.6866	7.6873
3	4	3	−59.156 13	−59.158 386	7.7168	7.7217	7.7050
3	6	6	−59.156 13	−59.158 386	7.7168	7.7217	7.9747
6	9	6	−59.172 727	59.173 710	8.7595	8.7569	8.7594
6	12	10	−59.172 727	59.173 710	8.7593	8.7569	8.7594
10	16	10	−59.174 013	−59.174 249	9.2317	9.2478	9.2315

The minimax procedure in the nonlinear parameters leads to a directional search problem that can be written in the matrix form

$$\begin{bmatrix} X & Y \\ Y^T & Z \end{bmatrix} \begin{bmatrix} \Delta\alpha \\ \Delta\beta \end{bmatrix} = -\begin{bmatrix} \mathbf{a} \\ \mathbf{b} \end{bmatrix}. \tag{39}$$

The matrix is the Hessian matrix of second derivatives, the right-hand side is the vector of first derivatives, and the first entries in the vectors belong to large-large parameters and the second entries belong to the large-small and small-small parameters. At a minimax, the vector of first derivatives must vanish, the matrix Z must be negative definite, and the matrix

$$X - YZ^{-1}Y^T \tag{40}$$

must be positive definite.

VI. RESULTS FOR GROUND STATES

In this section we present the results of various calculations for the $1s_{1/2}^2\,{}^1S_0$ ground states for ions of different Z values to indicate the validity of the minimax approach and to discuss a number of considerations concerning its successful application. In all the calculations, the electron-electron potential is taken to be the pure Coulomb potential. The nonlinear parameters occurring in the large-large component will be denoted by α, parameters in the large-small component by β and γ, respectively, and the parameters in the small-small component by δ.

The lowest-order calculation has $N_{ll}=N_{ls}=N_{ss}=1$ with $\phi_{ll}=1s_{1/2}^2$, $\phi_{ls}=1s_{1/2}1p_{1/2}$, and $\phi_{ss}=1p_{1/2}^2$. In the case $Z=2$, the energy without varying the parameters ($\alpha=\beta=\gamma=\delta=2$) is $-2.750\,015$. The minimax calculation, constrained with $\beta=\gamma=\delta$, gives an energy of $-2.847\,794$, with all the parameter values equal to 1.6875 to four decimal places. Permitting the small component nonlinear parameters to vary separately did not change this result.

The same calculations with $Z=8$ give an energy of $-59.048\,334$ when the nonlinear parameters are fixed at 8.0. When the parameters are varied, with $\beta=\gamma=\delta$, the result is $-59.146\,390$ with $\alpha=7.6866$ and $\beta=\gamma=\delta=7.6870$. Allowing the parameters to vary independently gives the same energy to the accuracy shown, with $\beta=7.6866$ and $\gamma=\delta=7.6873$. The corresponding result of the calculation of Cheng *et al.* [34] is $-59.174\,716$.

At $Z=90$ the energy with the parameters fixed at 90.0 is -9166.7040. When the parameters are varied, with $\beta=\gamma=\delta$ the energy is -9166.8906 obtained for $\alpha=89.496, \beta=\gamma=\delta=89.567$. If β is allowed to vary independently, with $\gamma=\delta$ the energy is raised slightly, to -9166.8832 with $\alpha=89.516$, $\beta=89.516$, and $\gamma=\delta=89.646$. Allowing γ and δ to vary separately does not change the results to this accuracy.

These results suggest that, although it is important to include small component factors, as dictated by the kinetic balance principle, to prevent the variational collapse, the detailed results are insensitive to small changes in the parameters. This has been looked at further by including terms of the form $1s_{1/2}2p_{1/2}$ in the large-small basis and of the form $1p_{1/2}2p_{1/2}$ and $2p_{1/2}2p_{1/2}$ in the small-small basis. Including these additional terms does not affect the results, perhaps because maximizing on the nonlinear parameters incorporates these terms implicitly. Including the $n=3$ terms as well, for the above optimized parameter values, does not affect the results for $Z=2$ and $Z=8$, but raises the energy for $Z=90$ slightly to -9166.8808, an increase of 2 parts in 10^7. Table I presents results for low-dimensional CI-type calculations in which the nonlinear parameters are varied. The variational calculation on the nonlinear parameters converges very rapidly, in four or five iterations, when only one large or small single-particle state is included in the calculation. However, if more than one single-particle state is included, so that the energy surface is a function of a large number of parameters, it becomes difficult to find the local minimaxes in the surface. For this reason, the variational calculation is constrained to three nonlinear parameters: α, the nonlinear parameter in the large-large states; β, the nonlinear parameter in the large factor in the large-small states, and γ, the nonlinear parameter in the small component factors. With this constraint on the variation, the calculation again converges rapidly. It may be noted that the parameters tend to increase as the dimension increases; evidently this is to compensate for the fact that as n increases, the orbital radii increase. The result of a large dimension calculation in the $z=8$ case with 45 $ns_{1/2}n's_{1/2}$ large-large states and the corresponding large-small and small-small states varying the

TABLE II. Results for the ground-state energy for $Z=2$, 8, and 90 from large-scale matrix diagonalization calculations. The first two columns show the large and small single-particle factors added at each step in the calculation and the third column shows the overall dimension of the matrix for the $Z=2$ and 8 calculations.

L	S	N	$Z=2$	$Z=8$	$Z=90$
$1s_{1/2}$	$1p_{1/2}$	3	−2.750 115	−59.048 344	−9166.7040
	$2p_{1/2}$	6	−2.750 115	−59.048 344	−9166.7013
$2s_{1/2}$	-	10	−2.850 364	−59.156 318	−9166.9024
$3s_{1/2}$	$3p_{1/2}$	21	−2.878 252	−59.172 727	−9166.9053
$4s_{1/2}$	$4p_{1/2}$	36	−2.878 733	−59.174 013	−9166.9057
$5s_{1/2}$	$5p_{1/2}$	55	−2.879 003	−59.174 395	
$6s_{1/2}$	$6p_{1/2}$	78	−2.879 074	−59.174 542	
$7s_{1/2}$	$7p_{1/2}$	105	−2.879 101	−59.174 597	
$1p_{1/2}$	$1s_{1/2}$				
$2p_{1/2}$	$2s_{1/2}$				
	$3s_{1/2}$	120	−2.886 443	−59.183 046	−9166.9080
$3p_{1/2}$	$4s_{1/2}$	132	−2.886 516	−59.183 011	
$4p_{1/2}$	$5s_{1/2}$	150	−2.886 553	−59.183 089	
$5p_{1/2}$	$6s_{1/2}$	171	−2.886 559	−59.183 108	
$6p_{1/2}$	$7s_{1/2}$	196	−2.886 558	−59.183 109	
$2p_{3/2}$	$2d_{3/2}$	199	−2.897 946	−59.194 171	−9166.9169
$3p_{3/2}$	$3d_{3/2}$	206	−2.899 721	−59.198 154	−9166.9234
$4p_{3/2}$	$4d_{3/2}$	217	−2.900 192	−59.199 164	−9166.9260
$5p_{3/2}$	$5d_{3/2}$	232	−2.900 378	−59.199 543	
$6p_{3/2}$	$6d_{3/2}$	251	−2.900 466	−59.199 724	
$7p_{3/2}$	$7d_{3/2}$	274	−2.900 503	−59.199 801	
$2d_{3/2}$	$2p_{3/2}$				
$3d_{3/2}$	$3p_{3/2}$				
	$4p_{3/2}$	289	−2.901 400	−59.201 146	
$4d_{3/2}$	$5p_{3/2}$	302	−2.901 406	−59.201 177	
$3d_{5/2}$	$3f_{5/2}$	305	−2.901 847	−59.201 632	−9166.9261
$4d_{5/2}$	$4f_{5/2}$	312	−2.902 250	−59.202 256	−9166.9267
$5d_{5/2}$	$5f_{5/2}$	323	−2.902 456	−59.202 659	−9166.9272
$6d_{5/2}$	$6f_{5/2}$	338	−2.902 577	−59.202 887	
$7d_{5/2}$	$7f_{5/2}$	357	−2.902 636	−59.203 011	

nonlinear parameters is −59.174 07, which is very close to the result of Cheng *et al.* [34] of −59.174 16.

Results of two calculations in which the large-small and small-small bases are incremented by adding an additional small component single-particle factor are included in Table I, showing that to the indicated accuracy, there is no change in the energy. This supports the above remark that the energy result is essentially insensitive to the small components in the wave function provided the kinetic balance principle is followed. Moreover, as the quality of the wave function is improved by varying the nonlinear parameters or by adding functions systematically to the large and small bases, the energy result decreases and appears to be bounded from below. It therefore appears that the minimax approach is in effect equivalent to the standard variational approach.

It can also be noted that the effect on the energy of varying the nonlinear parameters is smaller than that of adding an additional single-particle state in the bases. Thus, although the variation of the nonlinear parameters illustrates the validity of the minimax approach and is an elegant approach, it is computationally very inefficient compared with the simpler approach of increasing the dimension of the matrix diagonalization problem with a fixed value of the nonlinear parameters.

TABLE III. Results for the $n=2$ energies for $Z=2$, 8, and 90 obtained by varying the nonlinear parameters in the lowest-dimensional basis. In most cases the nonlinear parameters α,β, and γ are almost the same. For the $2p_{1/2}$ orbital the parameter γ differs somewhat from α and β. ΔE gives the excitation energy of the state in cm^{-1} (converted using R_∞) above the ground-state energies of −2.847 794, −59.146 390, and −9166.8832 given by the calculations described at the beginning of Sec. VII.

Term	Z	E	α_1	α_2	ΔE
$2s\ ^1S_0$	2	−2.142 974	1.997	0.558	154 690
$2s\ ^3S_1$	2	−2.174 355	2.003	0.633	147 802
$2p\ ^1P_1$	2	−2.122 498	2.003	0.482	159 184
$2p\ ^3P_0$	2	−2.130 800	1.991	0.545	157 361
$2p\ ^3P_1$	2	−2.130 799	1.991	0.545	157 362
$2p\ ^3P_2$	2	−2.130 798	1.991	0.545	157 362
$2s\ ^1S_0$	8	−38.280 233	7.96	3.58	4579 580
$2s\ ^3S_1$	8	−38.576 670	8.01	3.65	4514 520
$2p\ ^1P_1$	8	−38.097 207	8.01	3.46	4619 750
$2p\ ^3P_0$	8	−38.295 484	7.96	3.62	4576 230
$2p\ ^3P_1$	8	−38.294 024	7.96	3.62	4576 550
$2p\ ^3P_2$	8	−38.291 040	7.96	3.62	4577 210
$2s\ ^1S_0$	90	−5782.722	89.9	47.5	7.427 35(8)
$2s\ ^3S_1$	90	−5789.181	90.0	47.6	7.413 18(8)
$2p\ ^1P_1$	90	−5635.585	a	a	7.750 28(8)
$2p\ ^3P_0$	90	−5790.842	89.9	51.6[b]	7.409 53(8)
				44.8[c]	
$2p\ ^3P_1$	90	−5789.815	a	a	7.451 79(8)
$2p\ ^3P_2$	90	−5637.331	90.0	44.6	7.746 45(8)

[a] See the text.
[b] $\alpha=\beta$.
[c] γ.

In Table II we present results of larger-scale diagonalizations with the nonlinear parameters fixed at Z for $Z=2$, 8, and 90. The large-large basis states are all products that couple to $J=0$ of the single-particle states listed cumulatively in the first column and the large-small and small-small bases are constructed similarly. At each step, in which a single-particle state of a particular κ is added to the set of large factors, the corresponding state with the sign of κ changed is added to the set of small factors. The exception is in the case of $\kappa>0$, as discussed above. It can be observed that when the large and small factors are added pairwise in this way, as indicated by the principle of kinetic balance, the energies decrease monotonically with two minor exceptions. Thus the resulting energies are effectively upper bounds to the exact energy. It is also evident that the rate of convergence is discouragingly slow, both for increasing n values and increasing l values.

It should be commented that in the calculations for $Z=90$, eigenvalues below the physical eigenvalue, but considerably above $-2c^2$, appeared in the spectrum below the N_{ll} eigenvalue. These arise because the single-particle energies in the bases used become large and they therefore reflect the Brown-Ravenhall problem. These did not present a problem in the calculations reported here, but if somewhat larger

TABLE IV. Results for the $n=2$ energies for $Z=8$ obtained in CI calculations for various basis sets as described in the text. The dimension of the matrix is also given for each calculation.

Basis	$2s\ ^1S_0$	$2s\ ^3S_1$	$2p\ ^1P_1$	$2p\ ^3P_1$
$1s_{1/2}2s_{1/2}$				
$1p_{1/2}2p_{1/2}$	−38.180 226	−38.567 166	−38.091 454	−38.292 151
$2p_{3/2}3p_{3/2}$	57	97	72	
$+3s_{1/2}$	−38.288 573	−38.578 185	−38.093 792	−38.295 422
	77	117	108	
$+4s_{1/2}$	−38.289 185	−38.578 266	−38.094 419	−38.295 526
	105	145	144	
$+4p_{1/2}$	−38.289 319	−38.578 306	−38.097 093	−38.298 374
	129	185	176	
$+4p_{3/2}$	−38.289 823	−38.578 337	−38.097 487	−38.298 452
	149	233	208	
$+2d_{3/2}3d_{3/2}$	−38.290 021	−38.578 345	−38.099 733	−38.299 791
	174	338	338	
$+3d_{5/2}$	−38.290 146	−38.578 390	−38.102 905	−38.300 249
	178	362	362	
$+4d_{5/2}$	−38.290 190	−38.578 417	−38.102 978	−38.300 282
	190	394	386	

bases had been used, they could possibly have become larger than the physical ground-state energy, thereby confusing the proper identification of the ground state.

Cheng *et al.* [34] give a detailed breakdown of the various contributions to the ground-state energy in the case $Z=8$. The energy contributions from terms of the form $nsn's$ is $-59.174\,716$ compared with $-59.174\,597$ in this calculation. Terms of the form $npn'p$ contribute $-0.025\,393$ compared with $-0.025\,109$ here and terms of the form $ndn'd$ contribute $-0.003\,454$ compared with $-0.003\,051$. The calculations of Cheng *et al.* are of much higher dimension, including 25 single-particle states for each l value. In that calculation, small components are not varied independently of the large components; therefore each single-particle state in their calculation corresponds to two functions in the present calculation.

VII. RESULTS FOR THE $N=2$ STATES

To demonstrate the applicability of the minimax approach to excited states, the results of calculations for the $n=2$ states are given in Table III. In these calculations, the large-large component is of the form $1s_{1/2}(\alpha_1)2l_j(\alpha_2)$, where $l=s$ or $l=p$ and $j=1/2$ or 3/2. The large-small component is of the form $1s_{1/2}(\beta_1)2l'_j(\gamma_2)$ and the small-small component is of the form $1p_{1/2}(\gamma_1)2l'_j(\gamma_2)$ $(l+l'=2j)$. However, for the $2p_{1/2}$ large component state, both the $1s_{1/2}$ and the $2s_{1/2}$ small component states are included. Again the minimization procedure described above converges very rapidly and with no apparent ambiguities.

The two P_1 states are mixtures of the $1s_{1/2}2p_{1/2}$ and $1s_{1/2}2p_{3/2}$ configurations and these have both been included in the calculations. For $Z=90$ the states are essentially pure j-j coupled, the effect of mixing is very small, and the nonlinear parameters of the dominant component are the same as for the corresponding state of different J, i.e., $J=0$ for the $p_{1/2}$ state and $J=2$ for the $p_{3/2}$ state.

Table IV shows the results of CI-type calculations for the $n=2$ states and the trend of the results as the size of the basis increases for the $Z=8$ case. The large-large basis is constructed in the form $nl_j(\alpha_1)n'l'_{j'}(\alpha_2)$, $\alpha_1=8.0$, $\alpha_2=4.0$, where the nl_j range over the same set, as shown in column 1 for both the core and valence electron. The large-small and small-small bases are constructed similarly, with l replaced by the complementary value $2j-l$, except that in the $\kappa>0$ case extra orbitals such as $1p_{1/2}$ are added, as discussed above. Again the results indicate that as the "quality" of the calculation increases, the energy eigenvalues decrease, suggesting an effective upper bound principle. It may be of some interest to compare the energy differences from the ground state with observed values [35]. The computed and observed differences in cm^{-1} are respectively, for $^1S_0$, 4 589 760 and 4 588 558; $^3S_1$, 4 526 510 and 4 525 340; $^1P_1$, 4 630 850 and 4 629 362; $^3P_1$, 4 587 550 and 4 586 400. The systematic difference of about 1200 cm^{-1} can be largely attributed to the Breit interaction energy in the ground state, which is about 1130 cm^{-1} [34]. The remaining energy differences are well within the uncertainties from the truncation of the angular momentum and polynomial expansions.

VIII. DISCUSSION

The results of the variational calculations in which the nonlinear parameters are varied show that the minimax principle can be applied generally to the two-electron problem. The results of the CI calculations show that this method can be successfully applied to the relativistic problem; this is of course well known from the extensive successful MCDF calculations that have been made in addition to CI calculations [36]. Despite the lack of a global upper bound in variations of ϕ_{ls}, ϕ_{sl}, and ϕ_{ss} the evidence is clear that local minimax points can be found that provide a good approximation to the physical energies and wave functions.

The evidence of these calculations is that if the large-small and small-small components of the wave function are chosen according to the principles described here, the energy calculated is effectively an upper bound to the true energy. Since the projection onto positive energy states introduces an additional constraint on the small-small component, maximizing on the small-small component should yield an energy result above the energy computed in the basis of positive energy states.

These successful calculations indicate that it will be possible to extend the the methods that have been developed to explicitly correlated wave functions to overcome the problem of the slow convergence in the angular momentum and polynomial expansions. This approach is currently under active investigation.

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