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# Minimax Principle for the Dirac Equation

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The problem of calculating the eigenvalues of the Dirac equation by the finite-basis expansion method is studied. Bounds for the eigenvalues are obtained explaining the numerical results on the spectrum that have been observed previously. It is argued that the problem of variational collapse can be avoided by finding the minimum over the wave-function large component of the maximum over the wave-function small component of the energy functional. A numerical example is discussed.

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There has been a great deal of recent interest in the problem of solving the Dirac equation for particle bound states by finite-basis expansion methods. This problem is becoming increasingly important since the study of relativistic effects in molecular physics is of increasing interest and finite-basis expansions are an important practical method of constructing molecular wave functions. The problem of solving the Dirac equation in a finite basis has proved to be more difficult than the corresponding problem for the Schrödinger equation because of the so-called "variational collapse."[1] The problem is that one is seeking a highly excited state above all the negative-energy states. It turns out that it is not always possible to identify which physical state, if any, corresponds to a particular state arising from a matrix diagonalization, and that if nonlinear parameters are varied, almost any values for the matrix eigenvalues may be obtained.

In this article the matrix problem associated with the Dirac equation will be analyzed and bounds for the eigenvalues will be obtained. The Dirac equation and its matrix approximation can be formulated in terms of a minimax principle and a version of the Hylleraas-Undheim-MacDonald theorem[2,3] (HUM theorem) applies to the matrix formulation. The advantage of this minimax principle is that, as well as providing a formulation for the matrix problem, it provides a guide for the determination of nonlinear parameters.

There is no difficulty for the Schrödinger equation since it has been shown by Poincaré[4] that $e_i^{(N)} \geq e_i$ where $e_i^{(N)}$ is the $i$th eigenvalue of the matrix approximation and $e_i$ is the $i$th exact eigenvalue. (In this article the eigenvalues of an $N \times N$ matrix are always taken to be ordered $e_1 \leq e_2 \leq \ldots \leq e_N$.) Thus one can, for example, minimize $e_i^{(N)}$ on nonlinear parameters and be assured of improving the energy and wave-function approximations. This is not possible for the Dirac equation since a particular eigenvalue can decrease arbitrarily into the hole-state continuum. In connection with this, we note that the HUM theorem asserts that as the size of a finite basis increases, a particular eigenvalue decreases, i.e., $e_i^{(N+1)} \leq e_i^{(N)}$. For $N \to \infty$, $e_i^{(N)} \to e_i$ if the basis is complete in the first Sobolev space (i.e., for first derivatives).

In this article the two-component radial Dirac equation in the form given by Drake and Goldman[5] (to be referred to as DG) will be considered:

$$\begin{aligned} V(r)g + c(-d/dr + \kappa/r)f &= eg, \\ c(d/dr + \kappa/r)g + [V(r) - 2c^2]f &= ef. \end{aligned} \tag{1}$$

The functions $g$ and $f$ are traditionally called the large and small components of the wave function, and $e$ is the energy relative to $c^2$ ($m = \hbar = 1$). All the considerations here apply equally, however, to the three-dimensional, four-component problem.

We consider introducing an orthonormal basis $\{\phi_i\}$ for the large components truncated by $1 \leq i \leq M$ and

an orthonormal basis $\{\chi_j\}$ for the small components truncated by $1 \leq j \leq N$. In practice, finite nonorthogonal sets are used but one can imagine augmenting these to form dense sets and carrying out the Gram-Schmidt orthogonalization.

The Dirac equation, projected into the truncated basis, is the $(M+N)\times(M+N)$ matrix equation

$$\begin{pmatrix} V & cW^\dagger \\ cW & U-2c^2 \end{pmatrix}\begin{pmatrix} \mathbf{x} \\ \mathbf{y} \end{pmatrix} = e\begin{pmatrix} \mathbf{x} \\ \mathbf{y} \end{pmatrix}, \tag{2}$$

where

$$v_{ij} = (\phi_i, V\phi_j), \quad w_{mi} = (\chi_m, [d/dr + \kappa/r]\phi_i),$$
$$u_{mn} = (\chi_m, V\chi_n), \tag{3}$$
$$1 \leq i,j \leq M;\ 1 \leq m,n \leq N.$$

It has been found by DG that, for a reasonable choice of basis sets, with $M = N$, the eigenvalue spectrum of Eq. (2) splits, with the first $N$ eigenvalues below $-2c^2$, apparently representing hole states, and the first few eigenvalues beyond the $N$th representing the lowest particle bound states. On the other hand, it has been found by Gazdy and Ladányi[6] that if the basis is not chosen appropriately, the eigenvalues representing particle bound states may decrease uncontrollably.

It is possible to obtain useful information about the eigenvalues of Eq. (2) by eliminating $\mathbf{y}$ to give the $M\times M$ matrix equation

$$Q(e)\mathbf{x} = [V + c^2 W^\dagger (2c^2 + e - U)^{-1} W]\mathbf{x} = e\mathbf{x}. \tag{4}$$

In this form, the equation resembles the Schrödinger equation, and if a complete set of small-component states were included, it would be the matrix form of the Schrödinger equation in the limit $c \to \infty$. It has been emphasized by Kutzelnigg[7] and Grant[8] that the problem of variational collapse is caused by the incompleteness of the small-component basis, so that the kinetic energy is underestimated.

The eigenvalues of $Q(e)$ defined in Eq. (4) will be denoted by $\lambda_i(e)$, $i = 1, 2, \ldots, M$. The eigenvalues of Eq. (2) are the solutions of the implicit equation

$$\lambda_i(e) = e. \tag{5}$$

The behavior of the eigenvalues of $Q(e)$ is shown in Fig. 1. The derivative of $Q(e)$ with respect to $e$ is negative definite so that $\lambda_i(e)$ is monotonically decreasing in $e$. If $Q(e)$ is calculated in the basis in which the matrices $V$ and $U$ are diagonal, we have

$$Q(e)_{ij} = v_i\delta_{ij} + c^2 \sum_{k=1}^{N} w_{ki}^*(2c^2 + e - u_k)^{-1} w_{kj}. \tag{6}$$

It is seen that for $e \to \pm\infty$, $\lambda_i(e) \to v_i$ where $v_i$ is an eigenvalue of $V$. Furthermore, $Q(e)$ is singular at $e = u_j - 2c^2$ where $u_j$ is an eigenvalue of $U$. For $e$ close to $u_j$, $Q(e)$ can be expressed as

$$Q(e) = A(e) + (2c^2 + e - u_j)^{-1}\mathbf{w}\mathbf{w}^\dagger,$$

where $A(e)$ is continuous at $u_j$. Using a basis of $\mathbf{w}$ and $M-1$ vectors orthogonal to $\mathbf{w}$ shows that there are $M-1$ eigenvalues continuous at $u_j$ and one eigenvalue that behaves like $(2c^2 + e - u_j)^{-1}$.

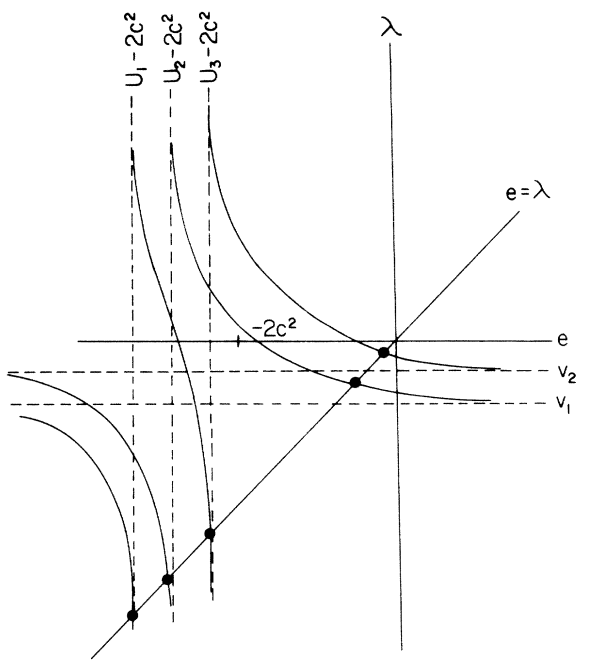


FIG. 1. Behavior of the eigenvalues of the matrix $Q(e)$ defined by Eq. (6) in the case $M=2$, $N=3$. The intersections of the curves with the line $e=\lambda$, shown by circles, give the eigenvalues of Eq. (2).

Inspection of Fig. 1 shows that the solutions of Eq. (5) are divided into two sets. The smallest $N$ roots satisfy $e_j < u_j - 2c^2$. The largest $M$ roots satisfy $e_{N+i} > v_i$. For a purely negative potential, $u_j < 0$ and $e_j < -2c^2$ for $1 \leq j \leq N$. A discussion similar to the above has been given previously by Löwdin.[9]

This result explains in part the observation by DG on the splitting up of the spectrum into $N$ apparent hole states and (with $M = N$ in their case) $M$ apparent particle states. It was also found by DG that for the Coulomb problem, the eigenvalues $e_{N+i}$ apparently converge downwards to the exact particle bound-state energies. There is an exception for $\kappa > 0$; in this case $e_{N+1}$ approaches a so-called spurious root. These results obtain, however, because DG use an appropriate basis; it will be argued below that they are not valid for a general choice of basis.

The bounds on the matrix eigenvalues show that the particle bound-state energies should be sought among the largest $M$ eigenvalues of Eq. (2). We will concentrate on the eigenvalue $e_{N+1}$ which presumably should

approximate the particle ground-state energy; $e_{N+1}$ will be denoted by $e(M,N)$. The HUM theorem shows that $e(M,N+1) \geq e(M,N)$. (The largest eigenvalues of a matrix increase, just as the smallest eigenvalues decrease, when one more basis vector is added.) Therefore, as $N$ increases, for fixed $M$, $e(M,N)$ increases.

If the potential is negative, the eigenvalues of $Q(e)$ are bounded above by the eigenvalues of the problem with $U=0$. The eigenvalues of this problem are in turn bounded by the eigenvalues of the nonlinear problem,

$$[V + c^2(2c^2+e)^{-1}T]\mathbf{x} = e\mathbf{x},$$

where $T$ is the Schrödinger kinetic-energy matrix in the large-component basis. It is easy to see from an argument similar to the one above that this nonlinear problem does have $M$ eigenvalues. Therefore $e(M,N)$ is bounded above independently of $N$ and, as $N$ increases, $e(M,N)$ increases to a finite limit $e(M,\infty)$.

This limit is the result that would be obtained if the small-component basis were complete. It is also seen that $e(M,N)$ provides a *lower* bound to $e(M,\infty)$; that is, $e(M,N)$ is a lower bound to the result obtained if the truncated large-component basis and the complete small-component basis are used. Furthermore, the HUM theorem implies that $e(M+1,N) \leq e(M,N)$. In the limit $N \rightarrow \infty$, this becomes $e(M+1,\infty) \leq e(M,\infty)$, so that $e(M,\infty)$, if it were known, would provide an upper bound to the exact energy. This is certainly true if the potential is bounded below by, say, $V_0$. Then $e(M,\infty) > v_1 > V_0$. A Coulomb potential is not bounded below; however, one can then consider a comparison potential that is bounded below such as the finite-nucleus case or a potential cutoff at small $r$. Then $e(M,\infty)$ is bounded below by the approximate eigenvalue which in turn is bounded below by the exact Coulomb eigenvalue, independently of the comparison potential. Thus, $e(M,N)$ provides a lower bound to some exact upper bound. This does not seem very useful, but it is probably the best result obtainable. It shows, however, that if there are nonlinear parameters, the correct way to treat them is to choose the small-component parameters to maximize $e(M,N)$ and then to choose the large-component parameters to minimize $e(M,N)$. A discussion similar to this has been given recently by Wood, Grant, and Wilson.[10]

These considerations show that the appropriate variational formulation for the Dirac equation particle ground state is that

$$e = \min_{g}\left[\max_{f}\frac{(\psi,H\psi)}{(\psi,\psi)}\right] \tag{7}$$

should be sought where $H$ is the Dirac Hamiltonian and $g$ and $f$ are the large and small components of the spinor $\psi$. Consider the case $M=N=1$ with basis functions $g$ and $f$. If $g$ is the exact large-component wave function, the maximum over $f$ is obtained for the exact $f$. On the other hand, if $g$ is arbitrary, the maximum over $f$ yields an upper bound to the exact $e$. Conversely, it is readily apparent that the variational problem, Eq. (7), leads to Eq. (1). Furthermore, if $g$ and $f$ are expanded in their finite bases, Eq. (7) leads to Eq. (2).

The $i$th excited state can be characterized also by Eq. (7) if $g$ is a linear combination of $i$ arbitrary functions, $f$ is arbitrary, and $e$ is the largest eigenvalue of the $(i+1)$-dimensional matrix problem. This provides a generalization of Poincaré's principle to the Dirac equation.

These results show that, in practice, to obtain an estimate for the energy of the $i$th particle bound state, one should search for the minimax of $e_{N+i}$ on any nonlinear parameters in the large and small components. The validity of this approach has been confirmed in a number of calculations; a simple example is discussed below.

It has been observed by various authors[7,11] that, if the finite bases are chosen so that for any $g$ in the span of the large-component basis, $(d/dr+\kappa/r)g$ is in the span of the small-component basis, then $e(M,N)$ is an upper bound to the exact energy. This can be readily seen from the above discussion. In this case

$$(\chi_{N+M}, [d/dr+\kappa/r]\phi_i) = 0, \quad m = 1,2,\ldots. \tag{8}$$

The matrix of Eq. (2) is reducible into independent blocks. Enlarging the small-component basis has no effect and $e(M,N) = e(M,N+m) = e(M,\infty)$.

Similarly, if for any $f$ in the span of the small-component basis, $(-d/dr+\kappa/r)f$ is in the span of the large-component basis, $e(M,N) = e(\infty,N)$. As $N$ increases, $e(M,N)$ increases to the exact energy, and $e(M,N)$ is therefore a lower bound.

To illustrate the minimax principle, we consider the problem studied by DG, the Coulomb problem with $Z=92$ and $c=137$. Their results are presented largely for the case $\kappa=-1$; the case $\kappa=1$, which has the added complication of the spurious root, will be considered here. A simple calculation with $M=N=1$, the basis functions being $\phi_i(r) = re^{-\alpha r}$ and $\chi_1(r) = re^{-\beta r}$, has been carried out. It is found that there is a minimax in the energy functional, as a function of the nonlinear parameters $\alpha$ and $\beta$, for $\alpha \approx 31.7$ and $\beta \approx 123.0$. The energy at this point is $-1264.9$ which can be compared with the exact $2p_{1/2}$ energy of $-1257.54$. Values of the energy functional in the neighborhood of the minimax are given in Table I. The minimum in $\alpha$ for the maximum in $\beta$ close to $\alpha=32$, and $\beta=125$, is evident; on the other hand, if $\alpha$ were varied for fixed $\beta$ almost any result could be obtained.

TABLE I. Values of the $2p_{1/2}$ Coulomb energy for $Z=92$ calculated with $M=N=1$ for various values of the nonlinear parameters $\alpha$ and $\beta$.

| $\beta/\alpha$ | 30.0 | 31.0 | 32.0 | 33.0 | 34.0 |
|---|---|---|---|---|---|
| 115.0 | −1262.04 | −1265.83 | −1269.22 | −1272.35 | −1275.37 |
| 120.0 | −1262.59 | −1264.32 | −1265.43 | −1266.09 | −1266.46 |
| 125.0 | −1265.93 | −1265.89 | −1265.04 | −1263.55 | −1261.57 |
| 130.0 | −1271.68 | −1270.13 | −1267.60 | −1264.25 | −1260.23 |
| 135.0 | −1279.49 | −1276.70 | −1272.74 | −1267.79 | −1261.99 |

The problem of determining nonlinear parameters variationally is not an easy one. The most practical strategy is to choose the nonlinear parameters variationally for a simple problem, such as the one above, and then to enlarge the basis. As an example, the energy has been calculated with the parameters above and $M=N=8$, the bases being $\phi_i(r)=r^i e^{-\alpha r}$, $\chi_i(r)=r^i e^{-\beta r}$, $1\leq i\leq 8$. The energy result in this case is $-1257.58$.

In this approximate calculation for the $2p_{1/2}$ energy, the spurious solution has completely disappeared. If, however, we try to find the exact solution using the basis appropriate to the problem, $\phi_i(r)=r^{\gamma+i-1}e^{-\alpha r}$, $\chi_i(r)=r^{\gamma+i-1}e^{-\beta r}$, $\gamma=[\kappa^2-(Z/c)^2]^{1/2}$, $i=1,2$, and searching on $\alpha$ and $\beta$, the exact solution occurs as $e_4$ rather than $e_3$. The minimax search on $e_3$ leads as expected to an approximate result for the $2p_{1/2}$ energy. This problem is a special one associated with the exact solution and the special basis chosen and should not arise in an approximate calculation.

The problem of spurious roots has been addressed by Goldman,[12] who has shown that in the atomic case they can be rejected by imposition of an energy-independent boundary condition on the ratio $g/f$ for $r\rightarrow 0$. This approach is not directly applicable to the molecular-orbital problem, however. Application of the minimax principle should reduce or eliminate the problem with spurious roots if nonlinear parameters are used. I note in passing that another criterion that may be useful in the molecular-orbital case is to calculate the Schrödinger energy by use of the large-component wave function. It is found that for the spurious solutions found by DG this is large and positive rather than approximating the Dirac energy as it does for the physical roots.

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