Upper bounds to the eigenvalues of the no-pair Hamiltonian

Rocio Jáuregui, Carlos F. Bunge, and Eugenio Ley-Koo
Instituto de Física, Universidad Nacional Autónoma de México Apartado Postal 20-364, México 01000, Mexico
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A *Dirac-like* Hamiltonian H with two-body terms, and its no-pair Hamiltonian $H^+=\Lambda^{++}H\Lambda^{++}$ where Λ^{++} is related to a one-particle Hamiltonian h_0, are studied in finite-basis representations $\mathbf{H}$ and $\mathbf{H}^+$. Using finite-basis eigenfunctions of h_0, it holds $E_i^+ \leqslant E_{\mathcal{N}^-+i}$, $i>0$, where $E_{\mathcal{N}^-+i}$ and E_i^+ are the ordered eigenvalues of $\mathbf{H}$ and $\mathbf{H}^+$, and $\mathcal{N}^-$ is the difference between the dimensions of $\mathbf{H}$ and $\mathbf{H}^+$. The states of order $i \leqslant \mathcal{N}^-$ exhibit continuum dissolution. In contrast, those of order $\mathcal{N}^-+i$, $i>0$, are bounded from below and after application of a variational principle they represent bound states. [S1050-2947(97)08702-7]

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The starting point of atomic calculations for relativistic atomic structures is the no-pair Hamiltonian H^+ [1–3]

$$H^+=\Lambda^{++}H\Lambda^{++}, \tag{1}$$

$$H^+\Psi_i^+=E_i^+\Psi_i^+, \tag{2}$$

where Λ^{++} is a product of one-particle projection operators,

$$\Lambda^{++}=\prod_{i=1}^{N}\lambda^+(i), \tag{3}$$

$$\lambda^+(1)=\sum_{n(\epsilon_n>0)}|u_n^+(1)\rangle\langle u_n^+(1)|, \tag{4}$$

and u_n^+'s are the positive-energy eigenfunctions of a one-particle operator $h_0(1)$ yet to be specified:

$$h_0(1)u_n^+(1)=\epsilon_n u_n^+(1), \quad \epsilon_n>0. \tag{5}$$

The negative-energy eigenfunctions

$$h_0(1)u_n^-(1)=\epsilon_n u_n^-(1), \quad \epsilon_n<0 \tag{6}$$

are defined likewise. Thus in projection operator theory (POT) a (+) state means a positive-energy eigenfunction of a suitable one-particle operator h_0, and similarly for (–) states.

The choice of h_0 completely specifies the Hamiltonian H^+, and defines a set of state functions over which the quantized QED fields may act. This formulation allows the consistent incorporation of QED effects using perturbation theory and, at the same time, it delimits the validity of Eqs. (1)–(5), implicitly showing the relevance of the negative-energy states excluded by POT. At present there is great interest in going beyond a POT formulation [4], particularly in connection with the calculation of transition probabilities [5], which are gauge dependent unless negative-energy states are incorporated.

In Eq. (1), H is a relativistic N-particle Hamiltonian

$$H=H_D+V_{e\text{-}e}, \tag{7}$$

where H_D is a sum of one-particle *Dirac* Hamiltonians h_D,

$$H_D=\sum_{i=1}^{N}h_D(i), \tag{8}$$

$$h_D=c\vec{\alpha}\cdot\vec{p}+\beta mc^2-\frac{Z}{r}, \tag{9}$$

and $V_{e\text{-}e}$ is a two-body electron-electron interaction. According to [1–3,6,7], the use of H is meaningless, since ''by turning on slowly the electron-electron interaction the system can make real transitions to states where one electron has a large negative energy and the other electron is in the positive-energy continuum'' [1], an effect known as *continuum dissolution* or Brown-Ravenhall ''disease'' [2]. Furthermore, it is widely held [1,3] that the equation for stationary states,

$$H\Psi=E\Psi, \tag{10}$$

has no bound state solutions. The purpose of this paper is to study finite-basis representations $\mathbf{H}$ and $\mathbf{H}^+$ of the operators H and H^+, and to discuss its physical consequences.

Let us define an m-dimensional one-particle basis of normalizable *Dirac* bispinors

$$\Psi_{n_i l j m_j}^{(i)}=\frac{1}{r}\begin{pmatrix} P_{n_i l j}(r)\mathcal{Y}_{\kappa m_j} \\ iQ_{n_i l' j}(r)\mathcal{Y}_{-\kappa m_j}\end{pmatrix}. \tag{11}$$

This one-particle basis will be called a *single primitive* (SP) basis. To obtain a finite-basis representation $\mathbf{h}_0$ of h_0, this original m-dimensional SP basis is supplemented with another complementary set of m *Dirac* bispinors,

$$\Psi_{n_i l j m_j}^{(i+m)}=\frac{1}{r}\begin{pmatrix} P_{n_i l j}(r)\mathcal{Y}_{\kappa m_j} \\ -iQ_{n_i l' j}(r)\mathcal{Y}_{-\kappa m_j}\end{pmatrix}, \tag{12}$$

differing from the first m in the minus sign preceding the lower components Q. In analogy with the SP set, the full $2m$-dimensional one-particle basis will be called a *double primitive* (DP) set. *All* Dirac-Hartree-Fock (DHF) calculations to date [8,9] use DP sets. The P and Q radial functions are always chosen so as to avoid variational collapse [10] at the one-particle level. A finite-basis representation in terms

of m positive-energy and m negative-energy eigenfunctions of h_0 is obtained by diagonalizing $\mathbf{h}_0$ in a DP basis,

$$\mathbf{h}_0(1)\mathbf{u}_n^+(1)=\epsilon_i\mathbf{u}_n^+(1), \quad \epsilon_n>0, \quad n=1,\ldots,m, \quad (13)$$

$$\mathbf{h}_0(1)\mathbf{u}_n^-(1)=\epsilon_n\mathbf{u}_n^-(1), \quad \epsilon_n<0, \quad n=1,\ldots,m. \quad (14)$$

We will now focus on configuration-interaction (CI) expansions in which *all* configuration state functions that can be constructed from the given SP basis are included, known as *full* CI. Full CI is always an absolute invariant, *viz.* the spectrum of the full CI matrix $\mathbf{H}^{(\mathrm{SP})}$ is independent of any nonsingular linear transformations among the one-particle basis. In other words, the $\mathcal{N}(m)$ eigenvalues $E_i^{(\mathrm{SP})}$ and eigenfunctions $\mathbf{C}_i^{(\mathrm{SP})}$ of $\mathbf{H}^{(\mathrm{SP})}$,

$$\mathbf{H}^{(\mathrm{SP})}\mathbf{C}_i^{(\mathrm{SP})}=E_i^{(\mathrm{SP})}\mathbf{C}_i^{(\mathrm{SP})}, \quad i=1,2,\ldots,\mathcal{N}(m), \quad (15)$$

are entirely determined by the SP basis. We shall always assume that the eigenvalues $E_i^{(\mathrm{SP})}$ are arranged in nondecreasing order, $E_1^{(\mathrm{SP})}\leqslant E_2^{(\mathrm{SP})}\cdots\leqslant E_{\mathcal{N}(m)}^{(\mathrm{SP})}$. Everyone doing relativistic CI today uses Eq. (15), or truncations of it, with some kind of positive-energy orbitals $\{\mathbf{u}_n^+, n=1,\ldots,m\}$, namely, $\mathbf{H}^+=\mathbf{H}^{(\mathrm{SP})}$.

Let us now consider a full CI expansion using the entire $2m$-dimensional DP set. Its full CI matrix $\mathbf{H}$ gives rise to an eigenproblem of dimension $\mathcal{N}(2m)$,

$$\mathbf{H}\mathbf{C}_i=E_i\mathbf{C}_i \quad i=1,2,\ldots,\mathcal{N}(2m). \quad (16)$$

Equation (16), dealing with the complete spectrum of H, including negative-energy N-particle states, has not been considered before. Clearly, the left upper corner of $\mathbf{H}$ up to rows and columns of order $\mathcal{N}(m)$ can always be made to coincide with $\mathbf{H}^{(\mathrm{SP})}$. If $\mathcal{N}^-(2m)$ is defined as the difference between the dimensions of $\mathbf{H}$ and $\mathbf{H}^{(\mathrm{SP})}$,

$$\mathcal{N}^-(2m)=\mathcal{N}(2m)-\mathcal{N}(m), \quad (17)$$

a corollary of the interleaving theorem [11] for finite-size Hermitian matrices yields

$$E_i^{\mathrm{SP}}\leqslant E_{\mathcal{N}^-(2m)+i}, \quad i>0, \quad (18)$$

indicating that the eigenvalues E_i^{SP} of relativistic CI calculations with SP bases will always lie *below* the eigenvalues $E_{\mathcal{N}^-(2m)+i}$ of the CI matrix $\mathbf{H}$, whatever choice of SP bases is made, including *any* kind of $\{\mathbf{u}_n^+, n=1,\ldots,m\}$.

The first question about Eq. (18) is what happens if the eigenvalues of order $\mathcal{N}^-+i$, $i>0$, are minimized upon general variations of the nonlinear parameters defining the DP basis. The *general behavior* will be illustrated with full CI for U^{90+} $1s^2$ with a DP basis of 12 $1s_{1/2}$ orbitals. Thus $m=6$, the CI size is $\mathcal{N}(2m)=78$, and $\mathcal{N}^-(2m)=57$. We use Eqs. (11) and (12) with radial functions

$$P_{n_ilj}(r)=Q_{n_ilj}(r)=r^\gamma e^{-\lambda_i r}, \quad (19)$$

$$\gamma=\sqrt{\kappa^2-(\alpha Z)^2}, \quad \lambda_i=\eta a b^i, \quad i=1,\ldots,6. \quad (20)$$

We set $b=1.4$, while a was optimized at the nonrelativistic level. The scaling parameter η will be varied between 0 and 1. In Fig. 1 we show eigenvalues of $\mathbf{H}$ of orders 51–60 as a function of η. For definiteness, $V_{e-e}=\Sigma r_{ij}^{-1}$, thus H is taken as the *Dirac-Coulomb* Hamiltonian.

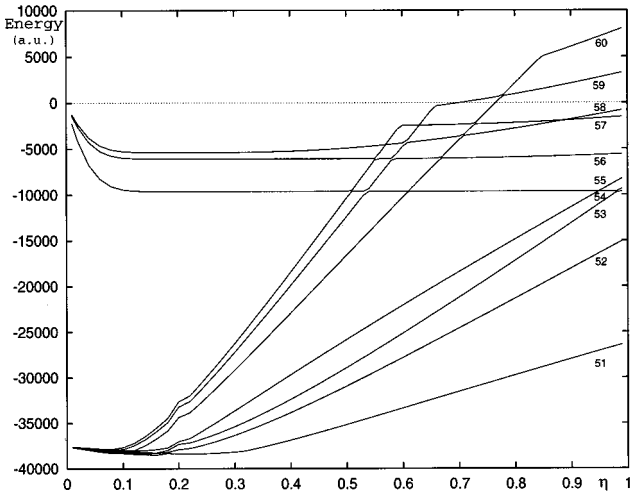

FIG. 1. Behavior of selected eigenvalues of $\mathbf{H}$ for U^{90+} $1s^2$ as a function of a scaling parameter η, exhibiting bound states above $E_{\mathcal{N}^-}$ and continuum dissolution at and below it.

According to Eq. (18), we must look for a target eigenvalue of order $\mathcal{N}^-(2m)+1=58$. However, for $\eta=1$, E_{58} is seen to be located just below the line signaling the zero of energy (fully ionized system), and high above its expected position around -9651 a.u. Furthermore, we find an eigenvalue E_b *and* an eigenfunction Ψ_b closely resembling the sought after N-particle electron state, within the first $\mathcal{N}^-(2m)$ eigenvalues, initially at position $N_b=53\leqslant\mathcal{N}^-(2m)$. The resemblance of Ψ_b with a bound state is linked to a bound character discussed below, associated to a dominant configuration expected to represent it.

Now we proceed to vary the scaling parameter η characterizing the radial functions P and Q, so as to lower as much as possible the target eigenvalue. This corresponds to moving leftwards in Fig. 1. We find that eventually a minimum energy for the target eigenvalue is reached at which point its eigenfunction faithfully represents the lowest state of the given symmetry. In the process in which the original DP basis is being *changed* into a relativistically energy-optimized DP basis, the energy E_b of the state Ψ_b varies slightly, while some of the eigenvalues above begin to approach E_b. A bit later, the lowest of them becomes almost *degenerate* with E_b. At this point, coinciding with an avoided crossing, there is a transfer of character from one state to another: the lower state exchanges its bound character with the state immediately above. Thereafter, the eigenvalue of order N_b, now deprived from its former bound-state character, starts to sink down toward $(N-2)mc^2$, around -37558 a.u. (after subtracting Nmc^2).

We shall now delve into the nature of the variational eigenfunctions. In Fig. 2 we amplify the region of Fig. 1 showing the *last* avoided crossing toward the buildup of the lowest bound state, corresponding to E_{58}, around -9651 a.u. and $\eta=0.5088$. In the vicinity of points A and A', the eigenvalue of order 58 is appreciably above the eigenvalue of order 57, which is at the approximately correct bound

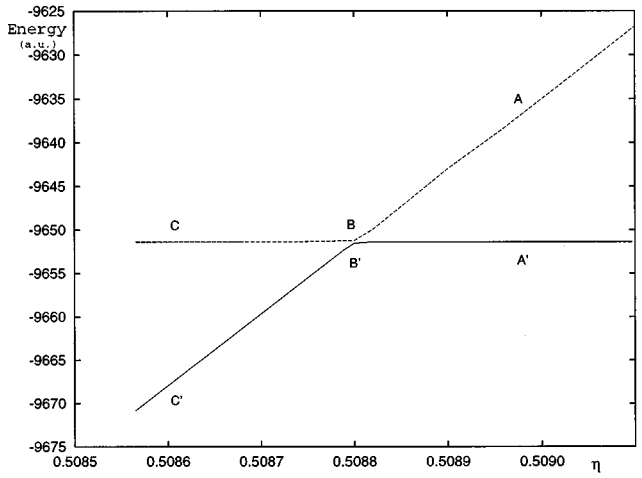

FIG. 2. Amplification of the neighborhood of the last avoided crossing of Fig. 1.

state energy. Points B and B' are very close to the avoided crossing. Toward the left, points C and C' show that while E_{58} stays close to the correct bound-state energy, E_{57} starts going down very quickly. An examination of the composition of the respective wave functions Ψ_{57} and Ψ_{58} shows how the bound-state character is transferred from level 57 to level 58 as the neighborhood of B and B' is crossed from right to left. In Table I, the dominant configurations of the respective eigenfunctions are shown through the CI coefficients a and b

$$\Psi \approx a[1s(+)^2]+b[2s(+)3s(-)], \tag{21}$$

$$2s(+)=\frac{1}{\sqrt{2}}[2s+3s], \quad 3s(-)=\frac{1}{\sqrt{2}}[2s-3s]. \tag{22}$$

In Eqs. (21) and (22), $1s(+)$, $2s$ and $3s$ denote the first three natural orbitals (NO's) [12,13], while $2s(+)$ and $3s(-)$ were constructed from corresponding NO's through Eq. (22) so that they are $(+)$ and $(-)$ orbitals, respectively. [A $(+)$ NO has positive expectation values of $c\vec{\alpha}\cdot\vec{p}$ and of the mass operator βc^2.] For $\eta=0.5090$ the positive bound-state orbital $1s(+)$ is almost doubly occupied in level 57, with a very small contribution from the $2s(+)3s(-)$ configuration directly related to continuum dissolution; meanwhile, level 58 exhibits a complementary orthogonal composition. For $\eta=0.5088$, both levels show practically equal contributions from the bound-state and continuum-dissolution configurations. Finally, for $\eta=0.5086$ the bound character has been definitely transferred to level 58, as expected, while level 57 dissolves into $2s(+)3s(-)$.

The values of η in the previous paragraph are still far from the optimized value $\eta=0.2635$ yielding the actual minimum for $E_{58}=-9651.385\ 651\ 88$. The corresponding eigenfunction for the optimal value of η is

$$\begin{aligned}\Psi_{58} \approx & 0.999\ 999[1s(+)^2]-0.001\ 388[2s(+)^2] \\ & -0.000\ 269[3s(+)^2]+0.000\ 065[4s(-)^2] \\ & -0.000\ 028[5s(+)^2]+0.000\ 010[6s(-)^2].\end{aligned} \tag{23}$$

Its dominant configurations are formed by $(+)$ NO's. Small contributions from $(-)$ NO's are present *only* in configurations with both electrons in the same orbital, whereas continuum-dissolution $(+)(-)$ configurations have completely disappeared. This result is consistent with the QED prediction that to fourth-order perturbation theory continuum-dissolution terms vanish identically [14]; it also incorporates the expected presence of configurations with both electrons in negative-energy states. In addition, the energy contribution of these $(-)$ NO's, when using DP bases, will always be of positive sign as a consequence of the interleaving theorem.

Many previous workers found these $(-)$ N-particle states and concluded that their existence would prevent the occurrence of authentic bound states; because H is not bound from below, the variational theorem cannot be applied to them. In contrast, the target $E_{\mathcal{N}^-+1}$ and all eigenvalues above it reach real minima corresponding to the ground and successive excited states: they do not dissolve into the continuum as those of order $\mathcal{N}^-(2m)$ and below. As m is increased, convergence to an *exact* bound state solution is *always* found; it may be from above, from below, or show oscillatory behavior [13], in contrast with the familiar nonrelativistic situation where convergence is from above. This suggests the existence of a *variational principle* for all states above $\mathcal{N}^-(2m)$, for any value of m.

A second question about Eq. (18) is how do the eigenvalues of $\mathbf{H}$ and $\mathbf{H}^+$ compare in actual calculations. In Table II we show that using POT with positive-energy NO and DHF eigenfunctions, the lowest eigenvalue of $\mathbf{H}^+$ for U^{90+} $1s^2$ sinks 843 and 3340 μhartree below $E_{\mathcal{N}^-+1}$, respectively, indicating the energy effect of negative-energy one-particle states, included in $\mathbf{H}$ but *not* in $\mathbf{H}^+$.

TABLE I. Variational parameter η, and energies and eigenfunctions of levels 57 and 58 in the neighborhood of the last avoided crossing, Fig. 2; energies in a.u., $c=137.0373$.

η	E_{57} E_{58}	Ψ_{57} Ψ_{58}
0.5090	−9651.3874	$0.999\ 92[1s(+)^2]+0.012\ 40[2s(+)3s(-)]$
	−9638.3541	$-0.012\ 40[1s(+)^2]+0.999\ 92[2s(+)3s(-)]$
0.5088	−9651.5430	$0.715\ 93[1s(+)^2]+0.698\ 17[2s(+)3s(-)]$
	−9651.2197	$0.698\ 17[1s(+)^2]-0.715\ 93[2s(+)3s(-)]$
0.5086	−9670.8397	$0.008\ 31[1s(+)^2]+0.999\ 97[2s(+)3s(-)]$
	−9651.3841	$0.999\ 96[1s(+)^2]-0.008\ 31[2s(+)3s(-)]$

TABLE II. Full CI calculations for Fe^{24+} and U^{90+} $1s^2$ ground states using a DP basis, and SP basis of positive-energy NO and DHF eigenfunctions. The three calculations use the same nine s Slater-type orbital bases. Energies in a.u., $c=137.035\,981$ for Fe^{24+} and $c=137.0373$ for U^{90+}.

Basis	Fe^{24+}	U^{90+}
DP	−665.8546 46	−9651.3855 03
(+) NO's	−665.8546 50	−9651.3863 46
(+) DHF orbitals	−665.8546 98	−9651.3888 43

Notice that the $\mathcal{N}(2m)$ eigenvalues of **H** are entirely determined by the DP set, independently of any *a priori* identification of (+) and (–) one-particle bases. Thus the third question about Eq. (18) is what happens if we *maximize* the energies $E_i^{(\mathrm{SP})}$, Eq. (16), with respect to a nonsingular linear transformation within the entire DP set? It immediately follows that Eq. (18) contains a minimax theorem, whose numerical consequences will be examined elsewhere [15], including the determination of *best* positive-energy orbitals in calculations beyond DHF.

Now one can ask a fourth question: is it possible, within a given DP basis, to find a SP basis such that

$$E_1^{\mathrm{SP}}=E_{\mathcal{N}^-(2m)+1}? \tag{24}$$

In [16] we show this to be the case at the independent-particle-model level of approximation, and this is the reason why our DHF results are in excellent agreement [16] with finite-difference DHF calculations. However, in general, beyond DHF, Eq. (24) cannot be satisfied.

It remains to answer the riddle posed by the Brown-Ravenhall argument at the beginning of this paper. We have solved the time-independent equation for stationary states, Eq. (10), with $V_{e\text{-}e}$ replaced by $\chi V_{e\text{-}e}$, where χ is varied between 0 and 100, $\chi=1$ corresponding to the actual physical situation. When considering a true atomic resonance, like nonrelativistic He $2s^2$, the various excited eigenvalues associated with resonant states as a function of χ show a behavior like the one exhibited on the right side of Fig. 1, with many saddle points and associated wave functions undergoing change of character in the vicinity of avoided crossings, similarly to continuum-dissolution states discussed before. Instead, if we return to the relativistic problem of Fig. 1 and use the optimal scaling parameter $\eta=0.2635$, for the relevant eigenvalues of order $\mathcal{N}^-(2m)+i$, $i>0$ we obtain a smooth behavior, *without* avoided crossings, even when $\chi=100$, one hundred times larger than its actual physical value. This behavior reinforces our argument about the bound character of the pertinent variational eigenfunctions.

In conclusion, we have rigorously shown, using the interleaving theorem, that after climbing over the first $\mathcal{N}^-$ eigenvalues of **H**, the remaining eigenvalues are upper bounds to the eigenvalues of the no-pair Hamiltonian. Its corresponding eigenfunctions incorporate both (+) and (–) one-particle states to all orders and are bonafide bound states, that is, without the Brown-Ravenhall disease, thus restoring physical meaning to the unprojected N-particle Hamiltonian. A wealth of numerical results have been obtained thereby [13,15–17], including excited states [13]; finite-basis DHF results of numerical quality for *any* open shells, and translation of nonrelativistic into relativistic results [16], and elastic electron scattering factors [17].

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