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On the Dirac equation in the algebraic approximation

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It is shown that the restrictive conditions of Wood et al. [1] are not necessary to reach the conclusion that the Dirac hamiltonian, projected onto the space of the large component, exhibits variational properties. The eigenvalue spectrum of matrix *approximations* to the partitioned hamiltonian (obtained by matrix partitioning) converges to the exact spectrum in the limit of infinite order (assuming completeness) but not necessarily from above as for true matrix representations (obtained from operator partitioning). Optimization of non-linear parameters is shown not to cause variational instabilities.

Key words: Variational stability - Basis set optimization - Bounds failures

In this short note we extend the recent work of Wood et al. [1] on the analysis of solutions of the 1-electron Dirac equation in the algebraic approximation. Wood et al. [1] showed that a partitioned (effective) two-component hamiltonian obtained by applying the partitioning technique [2] to the Dirac equation has several advantages, one of which is that under certain restrictive conditions [3] the partitioned hamiltonian has variational properties. Here we show that these restrictive conditions can be avoided.

The eigenvalue spectrum of the partitioned hamiltonian is identical to that of the 4-component Dirac equation and we use this fact to deduce properties of approximations to the bound state spectrum from its two component form. In particular, the convergence behaviour as the algebraic basis set is allowed to

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become complete, which we will show is not necessarily from above as for the bounded Schrödinger equation (but variational stability is guaranteed).

The time-independent Dirac equation, with restmass-energy subtracted, is

$$\begin{pmatrix} V & c\hat{\Pi} \\ c\hat{\Pi} & V-2c^2 \end{pmatrix}\begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix} = \varepsilon\begin{pmatrix} \Psi^L \\ \Psi^S \end{pmatrix} \tag{1}$$

where $\hat{\Pi} = \sigma \cdot \hat{p}$ and σ are the usual Pauli spin matrices and $\hat{p}$ the momentum. We take $V = -Z/r$ as the external potential of an infinitely heavy structureless point nucleus of charge Z.

Applying the partitioning technique of perturbation theory, or equivalently eliminating the small component Ψ^S, gives

$$\hat{H}^P(\varepsilon)\Psi^L = \varepsilon\Psi^L \tag{2}$$

where

$$\hat{H}^P(\varepsilon) = c\hat{\Pi}(\varepsilon - V + 2c^2)^{-1}c\hat{\Pi} + V \tag{3}$$

and can be identified as an effective (energy-dependent) hamiltonian. Introducing a normalized two-component square-integrable function Ψ, satisfying the usual boundary conditions for physical bound states and which, except for normalization, is otherwise arbitrary, allows us to define the expectation

$$F(\varepsilon) = \langle\Psi|\hat{H}^P(\varepsilon)|\Psi\rangle \tag{4}$$

and its restriction to $\mathbb{D}$

$$\mathbb{D} = \{\varepsilon | \varepsilon \geq -2c^2\} \tag{5}$$

$$f(\varepsilon) = F(\varepsilon)|_{\mathbb{D}}. \tag{6}$$

The restriction to $\mathbb{D}$ concentrates attention on "positive energy" solutions of Eq. (2). Reference to Eq. (3) shows that $f(\varepsilon)$ is finite on the whole of $\mathbb{D}$ since

$$(\varepsilon - V + 2c^2)^{-1} = r[(\varepsilon + 2c^2)r + Z]^{-1} \tag{7}$$

The behaviour of $f(\varepsilon)$ is well known [2] and has the following specific properties,

$$\text{(i) } f(\varepsilon) \text{ is finite and continuous on } \mathbb{D} \tag{8a}$$

$$\text{(ii) } f(\varepsilon+\Delta) < f(\varepsilon) \qquad (\Delta > 0) \tag{8b}$$

$$\text{(iii) } \lim_{\varepsilon\to\infty}[f(\varepsilon) - f(\varepsilon+\Delta)] = 0 \qquad (\Delta \text{ finite}) \tag{8c}$$

$$\text{(iv) } f(\varepsilon = -2c^2) > 0 \qquad (Z \leq c). \tag{8d}$$

Consequently the solution of

$$\varepsilon = f(\varepsilon) \tag{9}$$

exists and is unique. Equation (8d) distinguishes this work from that of Wood et al. [1] who require the restrictive assumption [3]

$$\lim_{\varepsilon\to\infty} f(\varepsilon) > -2c^2 \tag{10}$$

instead of Eq. (8d) to ensure the existence of a solution to Eq. (9). Note that $F(\varepsilon)=\varepsilon$ always has at least two solutions but Eqs. (8a–d) show that one and only one exists on $\mathbb{D}$. Equation (8d) can be demonstrated as follows

$$f(\varepsilon=-2c^2)=\langle\Psi|(c^2/Z)\hat{\Pi}r\hat{\Pi}-Zr^{-1}|\Psi\rangle \tag{11}$$

$$=(c^2/Z)\langle\Psi|\hat{R}+(\sigma\cdot\hat{l}+\hat{l}^2-Z^2/c^2)r^{-1}|\Psi\rangle \tag{12}$$

where $\hat{R}=-3d/dr-r\,d^2/dr^2$.

It can be shown by explicit partial integration that

$$\langle d/dr(r\Psi)|r^{-1}|d/dr(r\Psi)\rangle=\langle\Psi|\hat{R}-r^{-1}|\Psi\rangle \tag{13}$$

under the assumption that

$$\lim_{r\to\infty}(r^3\Psi^*(d/dr)\Psi)=0 \tag{14}$$

which must be considered an additional (reasonable) constraint on Ψ. The integral in Eq. (13) exists whenever the potential energy integral exists (a boundary condition on physical bound states).

Writing Eq. (12) as

$$(c^2/Z)[\langle\Psi|\hat{R}-r^{-1}|\Psi\rangle+\langle\Psi|(\sigma\cdot\hat{l}+\hat{l}^2+1-Z^2/c^2)r^{-1}|\Psi\rangle] \tag{15}$$

shows that Eq. (8d) is always satisfied.

To demonstrate the variational property of $\hat{H}^P(\varepsilon)$ on $\mathbb{D}$ we introduce the finite expansion

$$\Phi_i=\sum_{j=1}^{N}a_j^i\phi_j \tag{16}$$

where the $\{\phi_i\}$ satisfy the same boundary conditions as Ψ and are orthonormal. Optimization of the $\{a_j^i\}$ leads to the finite matrix equations

$${}^NH^P(\varepsilon)a^i={}^NE_i(\varepsilon)a^i \qquad (1\le i\le N,\ {}^NE_i(\varepsilon)\le{}^NE_{i+1}(\varepsilon)). \tag{17}$$

The ${}^NE_i(\varepsilon)$ have the same functional behaviour on $\mathbb{D}$ as $f(\varepsilon)$ and we therefore restrict

$${}^NE_i(\varepsilon):={}^NE_i(\varepsilon)|_{\mathbb{D}}. \tag{18}$$

As N is increased, Cauchy's interlace theorem states

$${}^{N+1}E_1(\varepsilon)\le{}^NE_1(\varepsilon) \qquad (\forall\varepsilon \text{ on } \mathbb{D}) \tag{19}$$

and consequently

$${}^{N+1}E_1({}^{N+1}E_1)\le{}^NE_1({}^NE_1) \tag{20}$$

i.e. convergence with respect to increasing N is from above. Making the usual assumption that the basis $\{\phi_i\}$ forms a complete set in the limit $N\to\infty$ leads to the conclusion that ${}^NE_i({}^NE_i)$ converges to an exact positive eigenvalue. It is worthwhile to point out that $\{\phi_i\}$ need not satisfy the proper cusp condition to

obtain convergence to exact eigenvalues from above (compare Schrödinger equation) and that for finite N, basis sets may be non-linearly optimized to minimize the lowest expectation on $\mathbb{D}$ (but in contrast to the Schrödinger equation the linear variational stationary point must be maintained).

Returning to the 4-component Dirac equation and introducing the expansions

$$\Psi^L = \sum_{i=1}^{N} a_i \phi_i, \qquad \Psi^S = \sum_{i=1}^{M} b_i \chi_i \tag{21}$$

where $\{\phi_i\}$, $\{\chi_i\}$ are orthonormal sets of scalar functions and $\{a_i\}$, $\{b_i\}$ are understood to be 2-component vectors, leads to a matrix equation that can also be partitioned to develop a matrix projection

$$H^P(\varepsilon) = c\Pi_{LS}(\varepsilon - V_{SS} + 2c^2)^{-1} c\Pi_{SL} + V_{LL}. \tag{22}$$

This is *not* a representation of Eq. (3) but instead a representation of

$$\hat{H}^{\text{approx}}(\varepsilon) = c\hat{\Pi}\hat{Q}[\hat{Q}(\varepsilon - V + 2c^2)\hat{Q}]^{-1}\hat{Q}c\hat{\Pi} + V \tag{23}$$

where

$$\hat{Q} = \sum_{i=1}^{M} |\chi_i\rangle\langle\chi_i|. \tag{24}$$

$\hat{H}^{\text{approx}}(\varepsilon)$ is now not only energy dependent but also $\{\chi_i\}$ dependent. In order that $\hat{H}^{\text{approx}}(\varepsilon)$ on $\mathbb{D}$ maintains separation of positive and negative energy states two conditions must be satisfied

(i) $c\hat{\Pi}\hat{Q}[\hat{Q}(\varepsilon - V + 2c^2)\hat{Q}]^{-1}\hat{Q}c\hat{\Pi}$ is positive definite on $\mathbb{D}$ (25a)

(ii) $\hat{H}^{\text{approx}}(\varepsilon = -2c^2)$ is positive definite. (25b)

The kinetic balance principle discussed by several authors and recently analysed by Stanton and Havriliak (1984) guarantees Eq. (25a) but is somewhat stronger than necessary. The small component function is expanded as

$$\Psi^S = \sum_{i=1}^{N} b_i'(\sigma \cdot \hat{p}\phi_i) \qquad (N = M) \tag{26}$$

giving $\Pi_{LS} = 1_{SS} = 2T_{LL}$.

In a kinetically balanced basis solutions of the matrix equations

$$H^P(\varepsilon)a = \varepsilon a \quad \text{on } \mathbb{D} \tag{27}$$

are known *not* to be bounded from below by the lowest exact eigenvalue [4, 5]. However, again assuming completeness in the limit $N \to \infty$ and that Eq. (25b) is satisfied, there will be exactly $2N$ solutions on $\mathbb{D}$ and convergence to exact eigenvalues will be obtained as $N \to \infty$. Consequently, non-linear optimization is again applicable without introducing variational instability [5] (the hessian is positive definite at the linear variational minimum).

Spurious solutions are only obtained when Eqs. (25a, b) are not satisfied and such basis sets should not be considered to give valid representations of the Dirac hamiltonian. For the matrix representation of $\hat{H}^{\text{approx}}$, Eq. (25b) takes the form

$$c^2 a^+ \Pi_{LS} (V_{SS})^{-1} \Pi_{SL} a < a^+ V_{LL} a \quad (\forall a). \tag{28}$$

Clearly finite basis sets can be constructed for which this condition is *not* satisfied at finite c. In practice it turns out rather easy to satisfy Eqs. (25a, b).

In Table 1 we provide numerical evidence for our conclusions. Three ($N = 8, 10, 11$) kinetically balanced gaussian basis sets have been chosen that are optimal for d states of the Schrödinger hamiltonian, and are used to describe the $d_{3/2}$ state of the Dirac hamiltonian ($Z = 92$, $c = 137.036$). This example shows that the calculated eigenvalue descends below the exact value ("variational collapse") and appears to oscillate about the exact value in the sequence $N = 8, 10, 11$. The mechanism of variational collapse is illustrated in Table 1, namely that Eq. (19) is not satisfied for $^{10}E_1$ and $^{11}E_1$ in the range $\varepsilon = -(1/5)c^2$ to $\varepsilon = +(1/5)c^2$. This is not entirely surprising since $\hat{H}^{\text{approx}}$ is basis set dependent and Cauchy's interlace theorem is not applicable. Variational collapse can be

Table 1. Results of calculations on the $d_{3/2}$ state of a 1-electron atom, $Z = 92$, $c = 137.036$, in three kinetically balanced gaussian basis sets

	$N = 8$	$N = 10$	$N = 11$
Exponents	9647.88168234	41858.18993339	42428.18831725
	2925.86162894	10638.92776925	11819.24997629
	1147.80947124	3796.87408079	4428.74445776
	514.39457393	1600.45488903	1918.23176668
	250.77150155	747.61208535	911.09792779
	129.37730581	374 86799708	462.73537583
	69.06409971	197.89938168	247.52326018
	36.80479377	108.41044671	137.92038053
		60.66591342	79.23602099
		33.60811991	46.29623207
			26.68139018
Schrödinger equation			
calculated	−470.222140	−470.222215	−470.222220
exact		−470.222222	
Lowest eigenvalue $H^P(\varepsilon)$			
$\varepsilon = -2c^2$	6268.27213	5920.54092	5205.80222
$\varepsilon = -(\frac{2}{5})c^2$	−396.37962	−396.38765	−396.39111
$\varepsilon = -(\frac{1}{5})c^2$	−445.93859	−445.94003	−445.93999
$\varepsilon = 0$	−495.48663	−495.48884	−495.48879
$\varepsilon = +(\frac{1}{5})c^2$	−545.03385	−545.03760	−545.03758
$\varepsilon = +(\frac{2}{5})c^2$	−594.58031	−594.58633	−594.58635
$\varepsilon = +2c^2$	−990.87015	−990.97242	−990.97357
Solutions $H^P(\varepsilon)a = \varepsilon a$			
calculated	−489.03509	−489.03713	−489.03707
exact		−489.03708	

clearly identified with the implicit use of a matrix approximation to the exact partitioned hamiltonian operator (incomplete small component) and not, for example, with failure to satisfy the proper cusp condition or other basis set deficiencies. This does not, of course, exclude the possibility that basis set sequences (including gaussian sets) can be found that converge from above.

We have chosen the $d_{3/2}$ state as example since this state behaves regularly at the origin and therefore variational collapse is not restricted to the $s_{1/2}$ and $p_{1/2}$ states that have singularities at the origin.

The analysis that we have presented for a 1-electron system is easily but less rigorously extendable to many electron systems where orbitals are determined by a (pseudo-1-electron) Fock-like hamiltonian. In these cases the matrix partitioning technique again leads to conditions (analogous to the conditions Eqs. (25a, b)) that should be satisfied to guarantee separation of positive and negative energy orbitals. We expect the kinetic balance criterium to be sufficient. Electronic configurations are then easily constructed as anti-symmetric products of positive energy orbitals and the total energy is prevented from collapsing into the negative energy sea.

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