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Variational solution of the single-particle Dirac equation in the field of two nuclei using relativistically adapted Slater basis functions

L. LaJohn[1], **J.D. Talman**[2]

[1] Department of Physics and Astronomy, University of Pittsburg, Pittsburg, PA 15260, USA,
[2] Department of Applied Mathematics and Centre for Chemical Physics, University of Western Ontario, London, Ontario, Canada N6A 5B7

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Abstract. A variational method for solving the time-independent single-particle Dirac equation in the Coulomb field of two nuclei is described. A minimax variational principle and basis functions that have the proper analytic behavior, i.e. behave like r^{γ}, γ non-integer, in the neighborhood of a nucleus, are used. A momentum space integration scheme for computing the necessary two-center integrals is described. Results are given for a standard test problem on two nuclei with $Z = 90$ with an internuclear separation of $2.0/Z$. The results confirm those of a previous calculation [F.A. Parpia and A.K. Mohanty, *Chem Phys Lett* 238: 209 (1995)].

Key words: Dirac equation – Minimax – Molecular geometry – Two-center Coulomb potential

1 Introduction

In this article a number of aspects of the problem of solving the time-independent single-particle Dirac equation in the Coulomb field of two nuclei are discussed. This problem is of current interest in part because of the importance of relativistic effects in the chemistry of heavy metals. Essentially all calculations of such effects have used atomic orbital expansions in terms of Gaussian orbitals. Although these may be one of the few reasonable alternatives for the calculation of the required multicenter integrals, their utility is limited because of the difficulty of adequately representing the singular behavior of the wave function at the nucleus. The argument is frequently made that the nucleus is not a point charge, the nuclear potential is finite at the nucleus and that Gaussian orbitals are appropriate because of this. This argument seems questionable in view of the great difference of length scales between the nucleus and even the inner electron orbitals. In any event, a large number of Gaussians are required to give an adequate description of the wave function near the nuclei.

It is well known [1] that the variational method cannot be applied directly to the Dirac equation, since no minimum of the expectation value of the Dirac Hamiltonian exists. Because of the presence of the negative energy states, the Dirac Hamiltonian is unbounded from below, and the energy expectation value can collapse into the negative energy continuum. Many approaches have been proposed to deal with this problem; most invoke some form of the principle of "kinetic balance", which imposes constraints of one form or another on the variational trial solution. This is discussed in detail below. However, two comments can be made. One is that to our knowledge none of these approaches has been demonstrated to give a rigorous upper bound to the energies. The second is that even if a method gives the correct energy, there is no guarantee of validity for the wave function. Indeed, Goldman [2] has given a simple example in which the correct $1s_{1/2}$ energy is given for the Coulomb problem for an essentially arbitrary wave function.

It has been shown [3] that the bound state problem for the Dirac equation can be formulated as a minimax problem, and this approach has been applied in a preliminary calculation [4]. An example considered in that article was of two nuclei of charge $Z = 90$ with a small separation of $2.0/Z$ bohr. The variational calculation was made using a basis of Slater-type orbitals. It was found that this basis seems to be inadequate to describe properly the known non-analytic behavior of the Dirac wave functions in the neighborhood of the nuclei, since the energy showed slow convergence with the addition of $s_{1/2}$ orbitals in the large component basis and the corresponding addition of $p_{1/2}$ orbitals in the small component basis. It was also noted that the calculation of the $1s_{1/2}$ energy of the corresponding hydrogen-like ion using the same basis was in error by about 25 a.u. A ground state energy for the same system of

Correspondence to: J.D. Talman

−9504.7567 a.u., obtained by using an extremely large basis of Gaussian orbitals, has been obtained by Parpia and Mohanty [5]. This paper will subsequently be referred to as PM. There has been some concern expressed (P. Pyykkö, personal communication) at the disagreement of this result with that given in Ref. [4] and that of Sundholm of −9461.9833 a.u. [6]. The results reported here are in essential agreement with those of PM.

In this article basis functions that have the proper analytic behavior, i.e. behave like r^γ, γ non-integer, in the neighborhood of a nucleus are used. It has been emphasized by Morgan [7] that the use of a basis that can emulate the singularity structure of the true wave function substantially improves the convergence properties of variational calculations. A momentum space integration scheme for computing the necessary two-center integrals is also described.

Although the primary focus of this work is in the chemistry of heavy atoms, it may also be applicable to the theory of heavy ion collisions. Although the latter problem leads to the time-dependent Dirac equation, it may be useful to be able to solve the time-independent equation efficiently at a range of values of the internuclear separation in solving the scattering problem in the adiabatic approximation.

2 Theory

The time-independent Dirac equation considered here is

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

Here $g(\mathbf{r})$ and $f(\mathbf{r})$ are the so-called large and small components of the wave function and are each two-component spinors. The units are chosen so that $e = m = \hbar = 1$ and the energy is taken relative to c^2, the electron rest energy. The potential considered here is that produced by nuclei of charge Z_1 and Z_2 centered at $\mathbf{a}_1$ and $\mathbf{a}_2$:

$$V(\mathbf{r}) = -\frac{Z_1}{|\mathbf{r}-\mathbf{a}_1|} - \frac{Z_2}{|\mathbf{r}-\mathbf{a}_2|} \ . \tag{2}$$

The minimax formulation of the Dirac equation is [1]

$$E = \min_{g\neq 0}\left[\max_f \langle H_D\rangle\right] \ , \tag{3}$$

where

$$\langle H_D\rangle = \frac{\langle g|V(\mathbf{r})|g\rangle + 2c\Re\langle f|\sigma\cdot\mathbf{p}|g\rangle + \langle f|V(\mathbf{r}) - 2c^2|f\rangle}{\langle g|g\rangle + \langle f|f\rangle} \ . \tag{4}$$

(It was not noted in [1] that g must belong to a space of dimension > 0.) If a constraint $\langle g|g\rangle + \langle f|f\rangle = 1$ is introduced with a Lagrange multiplier the minimax condition can be formulated in terms of a Lagrangian

$$\mathscr{L} = \langle g|V(\mathbf{r}) - \lambda|g\rangle + 2c\Re\langle f|\sigma\cdot\mathbf{p}|g\rangle + \langle f|V(\mathbf{r}) - 2c^2 - \lambda|f\rangle \ . \tag{5}$$

For a given g, the second of the Dirac equations is satisfied by the f that maximizes $\langle H_D\rangle$. The g that minimizes $\langle H_D\rangle$, with f a functional of g, then satisfies the first of the Dirac equations.

The minimax principle can be applied as well to compute excited states; the principle is applied, however, to the eigenvalue of λ_{N+k} of a matrix diagonalization problem in which the Dirac Hamiltonian is diagonalized in a basis of M large component functions and N small component functions. This result is an extension of the Hylleraas-Undheim theorem.

More rigorous mathematical arguments than that given in [1] have recently been constructed [8, 9]. These articles also give prescriptions for excited state eigenvalues that are generalizations of Rayleigh's principle for excited states.

A standard approximate method for solving variational problems of the form of Eq. (3) is to expand the functions $g(\mathbf{r})$ and $f(\mathbf{r})$ in terms of some bases of standard functions given analytically. This leads to a matrix eigenvalue problem of dimension $M + N$, where M and N are the number of functions in the large and small basis sets, respectively. Different approaches to the problem then center around different choices of these bases.

The basis functions will taken to be of the form

$$\phi_{\kappa m}(\mathbf{r}) = u(r)\Omega_{\kappa m}(\hat{r}) \ , \tag{6}$$

where

$$\Omega_{\kappa m}(\hat{r}) = \sum_{\mu+m_l=m}\left\langle \frac{1}{2}\mu l m_l \middle| jm\right\rangle Y_{lm_l}(\hat{r})\chi_\mu$$

is a spinor wave function in which spin $\frac{1}{2}$ is coupled to orbital angular momentum l to give a total angular momentum j. The label $\kappa = j + \frac{1}{2}$ for $j = l - \frac{1}{2}$ and $\kappa = -(j + \frac{1}{2})$ for $j = l + \frac{1}{2}$. These functions satisfy

$$\sigma\cdot\mathbf{r}\phi_{\kappa m}(\mathbf{r}) = ru(r)\Omega_{-\kappa m}(\hat{r}) \ , \tag{7}$$

$$\sigma\cdot\mathbf{p}\phi_{\kappa m}(\mathbf{r}) = -i\left[\frac{d}{dr} + \frac{\kappa+1}{r}\right]u(r)\Omega_{-\kappa m}(\hat{r}) \ . \tag{8}$$

Functions of this form will be taken centered on each nucleus.

In spherical symmetry, the Dirac equation can be reduced to two radial equations by writing $g(\mathbf{r}) = r^{-1}u(r)\Omega_{\kappa m}(\hat{r})$, $f(\mathbf{r}) = -ir^{-1}v(r)\Omega_{-\kappa m}(\hat{r})$. The result is

$$V(r)u(r) + c\left[-\frac{d}{dr} + \frac{\kappa}{r}\right]v(r) = Eu(r)$$
$$c\left[\frac{d}{dr} + \frac{\kappa}{r}\right]u(r) + [V(r) - 2c^2]v(r) = Ev(r) \ . \tag{9}$$

In the case of a Coulomb potential $V(r) = -Z/r$, the solutions of these equations behave, near the nucleus, like $[ar^{\gamma-1}, br^{\gamma-1}]$, where $\gamma = [\kappa^2 - (Z/c)^2]^{1/2}$ and $b/a = Z/c(\kappa - \gamma)$.

Normally, the ratio $|v(r)/u(r)| \ll 1$. However, in the Coulomb problem, if $\kappa > 0$, i.e. $j = l - \frac{1}{2}$, and $r < Z/c^2$, the ratio may be large. In this case, the functions u and v behave like r^{l-1} for small Z and r rather than like r^l as would be expected in the non-relativistic limit. The states nl have polynomial factors of degree $n - l + 1$ rather than $n - l$ as in the non-relativistic case.

The usual approach to the problem of variational collapse is to impose the principle of *kinetic balance* on the basis sets. Simply put, this requires that if a function $\phi(\mathbf{r})$ occurs in the basis for the large component, the function $\sigma \cdot \mathbf{p}\phi(\mathbf{r})$ should occur in the small component basis, or the span of the small component basis. However, there appear to be different ways of formulating this principle. In some, the coefficients of the small component basis functions are fixed by the relation $b/a = Z/c(\kappa - \gamma)$; in others the coefficients are to be independent parameters. In our view, the latter is more plausible for the following reason. The exact f is given by

$$f(\mathbf{r}) = c[E + Z/r + 2c^2]^{-1}\sigma \cdot \mathbf{p}g(\mathbf{r}) \ .$$

The variational problem involves finding the f that best represents the exact f for a given g. It is clear that allowing the coefficients to vary gives an upper bound in any case in which constraining them gives an upper bound.

If $|V(\mathbf{r})| \ll E + 2c^2$, the principle of kinetic balance should ensure that the equation for $f(\mathbf{r})$ is satisfied and an upper bound is obtained, at least approximately. However, this inequality is always violated by a Coulomb potential. A further problem that arises with a Coulomb potential is that the wave functions behave like $r^{\gamma-1}$ where $\gamma < 1$, for $r \to 0$. The principle of kinetic balance can then not be invoked for s states, since the small component orbitals would behave like $r^{\gamma-2}$ at small r and would not be normalizable.

A problem arises in the solution of the atomic Coulomb problem with the so-called spurious states that arise for $\kappa > 0$ [10, 11] in that if the basis is kinetically balanced, a spurious eigenvalue of the diagonalization problem occurs degenerate with the corresponding state at $-\kappa$, i.e. a $1p$, $2d$, etc state. This problem is readily eliminated in the minimax formulation, as has been extensively discussed by Kolakowska [12], by varying the non-linear parameters in the large and small component bases independently. The degeneracy can also be removed by using a small component basis of dimension higher than the large component basis.

In this article, the basis functions are taken to be of the form

$$\chi_{n\kappa m}(\mathbf{r}, \alpha) = r^{\gamma+n-2}\mathrm{e}^{-\alpha r}\Omega_{\kappa m}(\hat{\mathbf{r}}), \quad n = 1, 2, \ldots \ . \tag{10}$$

These functions satisfy

$$\sigma \cdot \mathbf{p} r^{\gamma+n-2}\mathrm{e}^{-\alpha r}\Omega_{\kappa m}(\hat{r}) = -i\left[-\alpha + \frac{\gamma + n + \kappa - 1}{r}\right] r^{\gamma+n-2}\mathrm{e}^{-\alpha r}\Omega_{-\kappa m}(\hat{r}) \ .$$

3 Overlap integrals

For this work, integrals of the form

$$I(\mathbf{a}) = \langle F_{\kappa' m'}(\mathbf{r} - \mathbf{a}) | G_{\kappa m}(\mathbf{r}) \rangle \ , \tag{11}$$

where F and G are of the form

$$F_{\kappa' m'}(\mathbf{r}) = r^{s'}\mathrm{e}^{-\alpha' r}\Omega_{\kappa' m'}(\hat{r}), \quad G_{\kappa m}(\mathbf{r}) = r^{s}\mathrm{e}^{-\alpha r}\Omega_{\kappa m}(\hat{\mathbf{r}}) \ , \tag{12}$$

are required.

The integral can be calculated using the identity, derived by Fourier transform methods,

$$\begin{aligned} &\int f_{l'm'}(\mathbf{r} - \mathbf{a})^* g_{lm}(\mathbf{r}) d\mathbf{r} \\ &= 8 \sum_{LM} i^{L+l'-l} \left[\frac{(2l+1)(2l'+1)(2L+1)}{4\pi}\right]^{1/2} \\ &\quad \times (-1)^m \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & L & l \\ -m' & M & m \end{pmatrix} Y_{LM}(\hat{\mathbf{a}}) \\ &\quad \times \int_0^\infty j_L(ka) \tilde{f}_{l's'}(k) \tilde{g}_{ls}(k) k^2 \, dk \end{aligned} \tag{13}$$

where

$$\begin{aligned} \tilde{f}_{l's'}(k) &= \int_0^\infty r^{s'+2}\mathrm{e}^{-\alpha' r} j_{l'}(kr) dr, \\ \tilde{g}_{ls}(k) &= \int_0^\infty r^{s+2} e^{-\alpha r} j_l(kr) dr \ . \end{aligned} \tag{14}$$

Using standard angular momentum techniques, $I(\mathbf{a})$ can be expressed, in the particular case that $\mathbf{a}$ is on the z-axis, by

$$\begin{aligned} I(\mathbf{a}) = \frac{2}{\pi}([l][l'][j][j'])^{1/2}(-1)^{m+1/2} &\sum_L i^{L+l'-l}[L] \\ &\times \begin{pmatrix} l' & L & l \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} j' & j & L \\ l & l' & \frac{1}{2} \end{Bmatrix} \delta_{m,\,m'} \begin{pmatrix} j' & L & j \\ -m & 0 & m \end{pmatrix} \\ &\times \int_0^\infty j_L(ka) \tilde{f}_{l's'}(k) \tilde{g}_{ls}(k) k^2 \, dk \ . \end{aligned} \tag{15}$$

For $l = 0$ it is readily found that

$$\tilde{g}_{0s}(k) = \Gamma(s+2) k^{-1} \mathrm{Im}[(\alpha - \mathrm{i}k)^{-(s+2)}] \tag{16}$$

and for higher value of l, $\tilde{g}_{ls}(k)$ can be computed from the recurrence relation

$$k\tilde{g}_{l+1,s}(k) = (l + s + 2)\tilde{g}_{l,s-1}(k) - \alpha \tilde{g}_{l,s}(k) \ . \tag{17}$$

The integrand in the k integration behaves like $k^{-S}\sin(kr - l\pi/2)$ for large k values where $S = s + s' + l + l' + 5$ and this slow decrease, together with the oscillatory behavior, makes accurate evaluation of the integral difficult. This difficulty can be avoided by transforming the integral into the complex plane, integrating on the intervals $[0, K]$ and $[K, K + (1 + i)\infty)$. The first integral can be computed using Gauss-Legendre integration, and the second by Gauss-Laguerre integration. Twenty mesh points were used in each of the two integrations; it was confirmed by increasing the number that this is adequate to give 8-digit accuracy.

4. Results

Minimax points have been found with a search method in which first and second derivatives of the energy are

obtained analytically [13]. The gradient vector with respect to the large and small non-linear parameters, respectively, will be denoted $(\mathbf{u}, \mathbf{v})$. The Hessian matrix of second derivatives can be written similarly as

$$\begin{bmatrix} A & B^{\mathrm{T}} \\ B & C \end{bmatrix} .$$

The energy can be expanded in terms of parameter increments $\mathbf{x}, \mathbf{y}$ in the large and small parameters respectively as

$$\begin{aligned} \delta E &= \mathbf{u}^{\mathrm{T}}\mathbf{x} + \mathbf{v}^{\mathrm{T}}\mathbf{y} + \tfrac{1}{2}\mathbf{x}^{\mathrm{T}}A\mathbf{x} + \mathbf{y}^{\mathrm{T}}B\mathbf{x} + \tfrac{1}{2}\mathbf{y}^{\mathrm{T}}C\mathbf{y} \\ &= \mathbf{u}^{\mathrm{T}}\mathbf{x} + \mathbf{v}^{\mathrm{T}}\mathbf{y} + \tfrac{1}{2}\mathbf{x}^{\mathrm{T}}A\mathbf{x} + \tfrac{1}{2}(\mathbf{y} + C^{-1}B\mathbf{x})^{\mathrm{T}}C(\mathbf{y} + C^{-1}B\mathbf{x}) . \end{aligned} \tag{18}$$

If C is negative definite, maximizing on $\mathbf{y}$ for fixed $\mathbf{x}$ gives the equation,

$$\mathbf{y} = -C^{-1}(\mathbf{v} + B\mathbf{x}) . \tag{19}$$

Substituting into Eq. (17) gives

$$\delta E = \mathbf{u}^{\mathrm{T}}\mathbf{x} + \tfrac{1}{2}\mathbf{x}^{\mathrm{T}}A\mathbf{x} - \tfrac{1}{2}(\mathbf{v} + B\mathbf{x})^{\mathrm{T}}C^{-1}(\mathbf{v} + B\mathbf{x}) . \tag{20}$$

A minimum on $\mathbf{x}$ is obtained if

$$\mathbf{x} = (A - B^{\mathrm{T}}C^{-1}B)^{-1}[-\mathbf{u} + B^{\mathrm{T}}C^{-1}\mathbf{v}] . \tag{21}$$

This provides a local minimum provided the matrix $A - B^{\mathrm{T}}C^{-1}B$ is positive definite.

The search for a minimax using this iteration scheme converges quadratically in the neighborhood of a solution. However, except in the lowest dimensional cases, the structure of the energy surface is very complex, and it is very difficult to find a suitable starting point. In particular, the matrices $-C$ and $A - B^{\mathrm{T}}C^{-1}B$ are not in general positive definite. In these cases, we defined a 'positive definite inverse' by

$$X_{\mathrm{pd}}^{-1} = \sum_{\lambda_i > 0} \lambda_i^{-1}\mathbf{w}_i\mathbf{w}_i^{\mathrm{T}}$$

in order to compute the parameter increments. Unfortunately, in many cases, the iterative process converges to a point at which $-C$ and $A - B^{\mathrm{T}}C^{-1}B$ are not positive definite. In all the variational results given here, the matrices $-C$ and $A - B^{\mathrm{T}}C^{-1}B$ are positive definite. There may be, in many situations, more than one minimax solution and in a few cases we have found more than one. In these cases, there is no way of asserting that one solution is better than another.

In Table 1 we present results for a number of minimax calculations for the system $Z_1 = Z_2 = 90$ with an internuclear separation of $2.0/Z$ using a basis of N s orbitals, i.e. $\kappa = -1(1)$ for the large (small) component orbitals centered at each nucleus. $n_{\max}$ is the highest degree of the polynomial factor of the basis functions. In all these calculations, the value of $c = \alpha^{-1}$ is 137.0359895. The unprimed results are obtained using orbitals with the proper behavior $(\gamma = [\kappa^2 - (Z/c)^2]^{1/2})$ at the origin and the primed results are obtained with $\gamma = |\kappa|$. It is seen that more rapid convergence and greater stability is obtained when the basis functions have the appropriate behavior at the origin. In this case PM give a result of -9368.5224 a.u. obtained using a tempered basis of 50 Gaussian orbitals.

Table 2 gives results analogous to those of Table 1 but including p and d orbitals centered at each nucleus. Again, $n_{\max}$ is the highest power of r in the basis so that results are given for basis functions going up to quadratic terms in x, y, z (apart from the non-integer relativistic correction. Two comments concerning the $\kappa > 0$ basis functions are important. In the non-relativistic limit, the lowest $p_{1/2}$ orbital behaves like a constant at the origin. Therefore $n_{\max} = 2$ for the lowest dimensional calculation and is similarly incremented for the larger calculations. Because of the problem of spurious solutions that can arise when functions with $\kappa > 0$ are included, one more small component basis function is included; i.e. in the lowest dimensional calculation, $n_{\max} = 3$ in the small component $p_{1/2}$ basis. In two cases, minimax solutions could not be found for the calculations with $\gamma = |\kappa|$.

The results obtained by PM using 50 s and 41 p Gaussian orbitals is -9499.89 a.u. Using 50 s, 41 p and 32 d Gaussian orbitals the result is -9504.5712 a.u.

It is not feasible to carry out the minimax search procedure using larger basis sets. Therefore, to obtain more precise results, we expand the basis sets using fixed values $\alpha = \beta = 154.0$. This is chosen to give the correct asymptotic behavior at large r:

$$\alpha = c^{-1}[-E(-E + 2c^2)]^{1/2} .$$

In these calculations, $n_{\max}$ is the number of $s_{1/2}$ and $p_{1/2}$ large orbitals. The number of orbitals decreases by 1 when j increases by 1. As before, the number of small orbitals is the same as the number of large orbitals if $\kappa < 0$ and is 1 larger, if $\kappa > 0$.

Table 1. Minimax non-linear parameters and energies (in a.u.) for the case of s orbitals centered at each of the nuclei. Primed values are computed with $\gamma = |\kappa|$

$n_{\max}$	α	β	E	α'	β'	E'
1	107.74	103.70	−9342.8816	133.85	114.12	−9330.247
2	142.19	136.32	−9363.8107	131.55	167.88	−9278.578
3	176.62	164.67	−9367.0208	214.58	174.95	−9353.888
4	176.39	141.69	−9366.9352	211.82	248.53	−9333.519
5	144.37	180.90	−9368.0698	216.69	148.54	−9359.783
6	181.54	178.07	−9368.2617	268.00	309.26	−9346.6957
7	226.51	207.57	−9368.5095	283.14	221.36	−9365.3712
8	249.05	241.39	−9368.5177	282.34	190.76	−9365.1192
9	277.20	254.65	−9368.5221	346.16	281.68	−9366.6921
10	274.64	290.00	−9368.5166	342.92	244.22	−9366.5517

Table 2. Minimax non-linear parameters and energies (in a.u.) obtained including p and d orbitals in the calculation. Primed values are obtained with $\gamma = |\kappa|$

κ	l_j	n_{max}	α	β	E	α'	β'	E'
−1	$s_{1/2}$	2	137.90	134.10		132.94	170.21	
1	$p_{1/2}$	2	160.19	203.52		179.82	289.00	
−2	$p_{3/2}$	1	155.95	139.30	−9496.9410	171.78	154.28	−9410.3224
−1	$s_{1/2}$	3	156.82	147.97		205.43	163.71	
1	$p_{1/2}$	3	221.54	240.05		232.51	320.01	
−2	$p_{3/2}$	2	220.24	200.48	−9498.4119	231.50	210.04	−9479.4060
−1	$s_{1/2}$	4	155.23	175.00				
1	$p_{1/2}$	4	220.76	242.09				
−2	$p_{3/2}$	3	220.04	210.90	−9498.3076			
−1	$s_{1/2}$	3	151.25	143.34				
1	$p_{1/2}$	2	145.11	274.65				
−2	$p_{3/2}$	2	196.30	179.94				
2	$d_{3/2}$	2	161.49	224.82				
−3	$d_{5/2}$	1	229.20	190.49	−9503.9964			

Table 3. Energies obtained using s and p orbitals with various values of n_{max}

n_{max}	E
2	−9488.9386
3	−9497.2293
4	−9497.7088
5	−9499.3192
6	−9499.6129
7	−9499.5947
8	−9499.7141
9	−9499.7908
PM	−9499.8950

Table 4. Energies obtained using up to d orbitals with various values of n_{max}

n_{max}	E
3	−9503.2790
4	−9504.2202[a]
5	−9504.5126
6	−9504.5627
7	−9504.5338
8	−9504.5440
PM	−9504.5712

[a] $(N+2)$nd eigenvalue

Table 3 gives results including s and p orbitals up to $n_{max} = 9$. It is seen that these results essentially confirm that of PM.

Table 4 gives results including s, p, and d orbitals up to $n_{max} = 8$. It must be noted that in the case $n_{max} = 4$ a spurious root (at -15438.0) was obtained despite the precautions taken against it. In this case we give the value of the $(N+2)$nd eigenvalue. The result given by PM, adding 32 d orbitals, is −9504.5712 a.u., again essentially in agreement with the present results. Table 5 gives results including up to f orbitals. Again, in the case $n_{max} = 5$, a spurious root occurred. The result given by PM, adding 23 f orbitals, i.e. −9504.5712 a.u., is again in agreement with these. Results including up to g orbitals are given in Table 6. The result given by PM, adding 14 g orbitals, i.e. −9504.7562, agrees with the present result to 6 figures. Results essentially the same as those of PM have also been obtained by Franke [14] by solving a matrix approximation to the equations iteratively and by Düsterhöft and Kolb [15] using a finite element numerical method.

Table 5. Energies obtained using up to f orbitals with various values of n_{max}

n_{max}	E
4	−9504.9805
5	−9504.6595[a]
6	−9504.7068
7	−9504.7293
PM	−9504.7485

[a] $(N+2)$nd eigenvalue

Table 6. Energies obtained using up to g orbitals with various values of n_{max}

n_{max}	E
5	−9504.7211
6	−9504.7401
7	−9504.7497
PM	−9504.7562

5 Discussion

In our opinion, the present results confirm the values given by PM to at least 0.1 a.u. and probably 0.01 a.u. The results are obtained with a far smaller number of basis functions and show the importance of having the correct analytic behavior of the orbitals at the nucleus. The results given in Table 1 indicate the much more satisfactory convergence when the factor r^{γ} is included in the radial function; the importance of this was already suggested in [4].

Although the results confirm those of PM, the calculations lead to some disturbing observations. The basis sets used in the calculations with fixed α and β are essentially those recommended by the proponents of the "kinetic balance" principle. We note that the first entry in Table 5 is slightly below the apparently true result, and therefore is seemingly not a true upper bound. The occurrence of spurious solutions in two cases is much more troublesome; these should definitely not have occurred if the kinetic balance principle is valid.

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