Finite–Basis-Set Approach to the Dirac-Hartree-Fock Equations

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A variational Dirac-Hartree-Fock procedure is introduced, which does not exhibit problems of spurious roots, variational collapse, or continuum dissolution. The optimized eigenvalues converge uniformly from above to the numerical Dirac-Hartree-Fock results as the dimension of the basis set is increased. Results for the $1s^2$, $2s^2$, and $2p_{1/2}^2$ shells are presented as examples.

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The development of numerical techniques to integrate the Dirac-Hartree-Fock (DHF) equations has proven to be very successful in relativistic atomic physics calculations. Accurate calculations are now performed by use of relativistic DHF[1,2] and relativistic random-phase approximation[3] codes, in which the "Brown-Ravenhall disease" or "continuum dissolution"[4] of the Hamiltonian does not appear despite the fact that no *a priori* projection of the Hamiltonian into positive-energy states[5] is used.

An analytical approach to the problem, similar to the one introduced by Roothaan[6] in the nonrelativistic case, is important for two reasons: It simplifies complicated atomic calculations, and it provides a straightforward extension to relativistic calculations in molecules.

The first attempt at an analytical DHF procedure was made by Kim.[7] In it, a variation of the basis-set parameters does not yield an upper bound to the total energy. Instead, the relativistic virial theorem[2]

$$E=\langle \beta c^2\rangle ,\quad \beta=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}, \tag{1}$$

is used to find the correct solution. The results are unreliable, and indeed the ground-state energy quoted for helium falls below the value obtained numerically. The virial-theorem method has also been used by Kagawa,[8] although no discussion of bounds or spurious roots was given.

An analytical approach using Gaussian wave functions has been presented by Mark and Rosicky[9] and explored by Mark, Lischka, and Rosicky,[10] but the basis set it employs does not provide bounds in general. These methods fail to provide upper bounds to atomic energies because they use incomplete variational representations[11-13] of the one-electron relativistic spectrum. An alternative approach applying a partitioning technique is being investigated by Wood, Grant, and Wilson.[14]

In order to construct a complete variational representation of the DHF energy spectrum, we rewrite the DHF equations in the ϕ-θ representation which proved to be instrumental in understanding the Dirac-Coulomb problem. This representation is defined by the transformation[12]

$$\begin{aligned} g(r)&=A^{-1}[q\phi(r)+\theta(r)],\\ f(r)&=A^{-1}[\phi(r)-q\theta(r)], \end{aligned} \tag{2}$$

where

$$q=(\kappa-\gamma)/(\alpha Z),\quad \gamma=[\kappa^2-(\alpha Z)^2]^{1/2}, \tag{3}$$

$A=[1+q^2]^{1/2}$, $g(r)$ and $f(r)$ are the large and small radial components, κ is the Dirac quantum number, α is the fine-structure constant, and Z is the nuclear charge.

In terms of the upper and lower components $\phi(r)$ and $\theta(r)$,[12] the radial DHF equations for closed shells are (atomic units are used throughout)

$$\begin{aligned} &\alpha\theta_a'+\left(\frac{\alpha Z}{\kappa_a}+\frac{\alpha\gamma_a}{r}\right)\theta_a-\left(\frac{\gamma_a}{\kappa_a}+e_a-\alpha^2{\sum_b}'\mu_{ab}\right)\phi_a+\alpha^2{\sum_b}'\nu_{ab}\frac{A_a}{A_b}\phi_b=0,\\ &\alpha\phi_a'-\left(\frac{\alpha Z}{\kappa_a}+\frac{\alpha\gamma_a}{r}\right)\phi_a-\left(\frac{\gamma_a}{\kappa_a}-e_a-2\frac{\alpha^2 Z}{r}+\alpha^2{\sum_b}'\mu_{ab}\right)\theta_a-\alpha^2{\sum_b}'\nu_{ab}\frac{A_a}{A_b}\theta_b=0, \end{aligned} \tag{4}$$

where a and b denote the shells, e is the one-electron energy in units of its rest mass, and[2]

$$\mu_{ab}=(2j_b+1)r^{-1}Y_0(bb,r), \tag{5}$$

$$\begin{aligned} \nu_{ab}&={\sum_L}'-(2j_b+1)\begin{pmatrix} j_a & L & j_b\\ \frac{1}{2} & 0 & -\frac{1}{2}\end{pmatrix}^2\frac{1}{r}Y_L(ab,r)\ \text{if}\ l_a+l_b+L=\text{even},\\ &=0\ \text{otherwise}, \end{aligned} \tag{6}$$

$$Y_L(ab,r_2)=r_2\int(r_<^L/r_>^{L+1}[g_a(r_1)g_b(r_1)+f_a(r_1)f_b(r_1)]dr_1. \tag{7}$$

The basis set used in this work for each one-electron orbital with $\kappa < 0$ is

$$\begin{aligned} \phi_{i,k} &= e^{-\lambda^{(k)}r}r^{\gamma+i-1}, \quad i=1,2,\ldots,N_\gamma, \quad k=1,2,\ldots,N_\lambda, \\ \theta_{i,k} &= e^{-\lambda^{(k)}r}r^{\gamma+i-1}, \quad i=1,2,\ldots,N_\gamma, \quad k=1,2,\ldots,N_\lambda, \end{aligned} \tag{8}$$

where the $\lambda^{(k)}$ comprise a set of N_λ arbitrary exponential parameters and N_γ is the number of different powers per exponential parameter in the basis set. We follow the calculations for the Coulomb case,[12] and take the values of the exponential parameters and the number of powers per exponential parameter to be the same for the ϕ and θ functions. All the exponential parameters are varied to minimize the total energy E. Let Ψ_i be the eigenvector for the ith shell for a given value of the exponential parameters:

$$\Psi_j = \frac{1}{r}\begin{pmatrix} ig_j(r)\Omega_{\kappa m}(\hat{r}) \\ -f_j(r)\Omega_{-\kappa m}(\hat{r}) \end{pmatrix}, \tag{9}$$

where $\Omega_{\kappa m}$ are spherical spinors. Then the one-electron energy ϵ_i associated with the ith shell and the total energy E are given by

$$\epsilon_i = I_i + \textstyle\sum_j (J_{ij} - K_{ij}), \tag{10}$$

$$E = \textstyle\sum_i I_i + \frac{1}{2}\sum_{i,j}(J_{ij} - K_{ij}), \tag{11}$$

where J_{ij} and K_{ij} are the direct and exchange integrals, respectively, and $I = \langle\Psi|(H_\mathrm{D} - c^2)|\Psi\rangle$ with H_D the Dirac-Coulomb Hamiltonian.

A basis set of the form (8) with one exponential parameter was introduced by Drake and Goldman[11] for the one-electron Dirac-Coulomb case. The set satisfies all the right properties of bounds and completeness, although spurious roots do appear for $\kappa > 0$. It contains N_λ vectors more than is necessary to describe a Dirac-Coulomb electron in a state with $\kappa < 0$.[12] This basis set is used for the DHF case because the solution $\theta = 0$, describing the lowest positive-energy states with $\kappa < 0$ in the Coulomb case, does not exist for the HF potential. In other words, a finite set consisting of eigenfunctions of the Dirac-Coulomb Hamiltonian is incomplete and will not yield, in general, upper bounds in the DHF case. Ishikawa, Binning, and Sando[15] applied this basis set with one exponential parameter to the ground state of beryllium. This set, however, fails to provide bounds in the case $\kappa > 0$.[16]

In this work we have successfully applied a discrete variational representation to the DHF equations for a closed-shell system for any value of the quantum number κ. There are no spurious roots in the variational spectrum; the variational eigenvalues agree with the numerical results to machine accuracy and are always upper bounds. For $\kappa < 0$, the basis set (8) was used. For $\kappa > 0$ we followed the method of Ref. 12 for the Dirac-Coulomb case, in which the variational eigenvectors satisfy the correct nonrelativistic limit. This is achieved by our constraining the basis vectors to satisfy the following first-order condition at the origin:

$$\phi_1 + 2\alpha Z\theta_1 = (Z/\kappa)(\phi_0 - q\theta_0), \tag{12}$$

where

$$\begin{aligned} \phi &= r^\gamma(\phi_0 + \phi_1 r + \ldots), \\ \theta &= r^\gamma(\theta_0 + \theta_1 r + \ldots), \end{aligned} \tag{13}$$

TABLE I. Values of the one-electron energy (ϵ) and the total energy (E) for the $1s^2$ shell in He and Ne^{8+} for different sizes of the basis set (8). The results converge to the numerical DHF values listed in the last line. N_λ is the number of different exponential parameters in the basis set and N_γ is the number of powers per exponential parameter.

		$Z=2$		$Z=10$	
N_λ	N_γ	ϵ (a.u.)	E (a.u.)	ϵ (a.u.)	E (a.u.)
1	2	−0.896 525 24	−2.847 793 82	−43.951 8660	−93.969 473 08
1	3	−0.917 789 85	−2.861 723 41	−43.971 8575	−93.982 759 05
1	4	−0.917 789 93	−2.861 723 41	−43.971 8575	−93.982 759 05
1	5	−0.917 990 16	−2.861 813 02	−43.971 9148	−93.982 798 18
1	6	−0.917 990 16	−2.861 813 02	−43.971 9151	−93.982 798 43
1	7	−0.917 990 56	−2.861 813 11	−43.971 9151	−93.982 798 48
1	8	−0.917 990 62	−2.861 813 31	−43.971 9165	−93.982 799 53
2	2	−0.917 969 47	−2.861 805 55	−43.971 9131	−93.982 797 06
2	3	−0.917 990 30	−2.861 813 13	−43.971 9164	−93.982 799 41
2	4	−0.917 990 6827	−2.861 813 3376	−43.971 916 564	−93.982 799 545
2	5	−0.917 990 6881	−2.861 813 3424	−43.971 916 565	−93.982 799 545
Numerical		−0.917 990 6883	−2.861 813 3425	−43.971 916 565	−93.982 799 545

TABLE II. Values of the one-electron energies (ϵ_1, ϵ_2) and the total energy (E) for the $1s^2$ and $2s^2$ shells in Ne^{6+} for different sizes of the basis set (8).

N_λ	N_γ	ϵ_1 (a.u.)	ϵ_2 (a.u.)	E (a.u.)
1	2	−37.921 39	−6.163 410	−103.886 38
1	3	−40.012 49	−7.156 977	−109.224 76
1	4	−40.495 30	−7.459 443	−110.138 05
1	5	−40.568 03	−7.493 634	−110.236 63
1	6	−40.585 29	−7.500 468	−110.253 67
1	7	−40.587 71	−7.501 096	−110.255 51
1	8	−40.588 30	−7.501 307	−110.255 94
2	2	−40.582 3490	−7.500 960 41	−110.251 8459
2	3	−40.588 3703	−7.501 310 27	−110.255 9797
2	4	−40.588 4040	−7.501 339 44	−110.256 0060
2	5	−40.588 4051	−7.501 339 65	−110.256 0071
Numerical		−40.588 4059	−7.501 339 80	−110.256 0077

and q is defined in Eq. (3).

For states with $\kappa > 0$, the following basis set satisfying conditions (12) has been used to represent the solution

$$\Phi = \begin{pmatrix} \phi \\ \theta \end{pmatrix} \tag{14}$$

to Eqs. (4):

$$\Phi_{0,k} = e^{-\lambda^{(k)} r} r^{\gamma} \begin{pmatrix} q \\ 1 \end{pmatrix}, \tag{15a}$$

$$\Phi_{1,k} = e^{-\lambda^{(k)} r} r^{\gamma} \begin{pmatrix} \kappa q(1 + 2\kappa + 2\gamma) + q(Z + \kappa\lambda^{(k)}) r \\ (Z + \kappa\lambda^{(k)}) r \end{pmatrix}, \tag{15b}$$

$$\Phi^{*}_{1,k} = e^{-\lambda^{(k)} r} r^{\gamma} \begin{pmatrix} \kappa q(2\kappa - 2\gamma - 1) - (Z + \kappa\lambda^{(k)}) r \\ q(Z + \kappa\lambda^{(k)}) r \end{pmatrix},$$

$$\Phi_{i,k} = e^{-\lambda^{(k)} r} r^{\gamma + i} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \Phi^{*}_{i,k} = e^{-\lambda^{(k)} r} r^{\gamma + i} \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{15c}$$

where $i = 2, 3, \ldots, N_\gamma$, and $k = 1, 2, \ldots, N_\lambda$.

The DHF equations for a closed-shell system are solved to self-consistency in the finite basis set [(8),(15)]. Each step of the iteration process produces a set of $N_\lambda N_\gamma$ positive-energy eigenstates and a set of $N_\lambda N_\gamma$ negative-energy eigenstates, or $N_\lambda N_\gamma + 1$ for orbitals with $k > 0$, for the one-electron orbitals. The DHF procedure is repeated for different values of the nonlinear parameters in order to minimize the total energy.

The method has been applied to the $1s^2$, $2s^2$, and $2p^2_{1/2}$ shells. The total energy E is *always* an upper bound to the value obtained by use of the numerical DHF method. The one-electron energy ϵ for each shell is an upper bound to the numerical DHF value of ϵ when the total energy E is minimized for the finite basis set. There are no spurious roots. The identity (1) is satisfied for any size of the basis set at the variational minimum, implying that the virial-theorem condition is necessary but not sufficient to determine the DHF energies. Thus, the difference $E - \langle \beta c^2 \rangle$ gives an estimate of the accuracy of the result for a specific dimension of the basis set (i.e., how well the minimum was attained) but does not convey any information regarding the DHF value of the energy.

In Table I we illustrate the convergence of the results as the dimension of the basis set is increased, for He and heliumlike Ne. ϵ is the one-electron energy and E is the total energy of the $1s^2$ shell. In Table II we display results for the $1s^2$ and $2s^2$ shells in Ne^{6+}. ϵ_1 and ϵ_2 are the one-electron orbital energies, and E is the total energy. In Table III we display results for the $1s^2$, $2s^2$, and $2p^2_{1/2}$ shells in Ne^{4+}. $\epsilon_{-1,1}$, $\epsilon_{-1,2}$, and $\epsilon_{1,2}$ are the one-electron orbital energies for the $1s$, $2s$, and $2p_{1/2}$ states, respectively, and E is the total energy. In all cases the optimized values of the energy are upper bounds to the numerical DHF values towards which they converge uniformly.

In conclusion, we have successfully implemented a variational DHF procedure which is devoid of the problems of spurious roots, variational collapse, or continuum dissolution. The amount of computer time involved is longer than for a similar nonrelativistic calculation because twice as many vectors are needed and because, the powers of r in the basis set being real, the direct and exchange integrals in the DHF Hamiltonian involve hypergeometric functions with infinite numbers of terms. However, the computing power available should allow the advantageous use of this method in complex atomic and molecular calculations.

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TABLE III. Values of the one-electron energies for s states ($\epsilon_{-1,1}, \epsilon_{-1,2}$) and the $p_{1/2}$ state ($\epsilon_{1,2}$), and the total energy (E) in atomic units for the $1s^2$, $2s^2$, and $2p_{1/2}^2$ shells in Ne^{4+} for different sizes of the basis sets (8) and (15).

$N_{-1\lambda}$	$N_{-1\gamma}$	$\epsilon_{-1,1}$	$\epsilon_{-1,2}$	$N_{1\lambda}$	$N_{1\gamma}$	$\epsilon_{1,2}$	E
2	2	−37.280 21	−5.284 933	1	4	−4.542 993	−120.555 88
2	3	−37.298 24	−5.290 432	1	6	−4.556 660	−120.575 00
2	4	−37.299 36	−5.290 676	1	8	−4.557 226	−120.575 89
Numerical		−37.299 44	−5.290 706	1	6	−4.557 283	−120.575 92

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