

Single-Fock-operator method for matrix Dirac-Fock self-consistent-field calculations on open-shell atoms

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A generalized coupling operator method is employed to construct a single Fock operator for matrix Dirac-Fock self-consistent-field calculations on general open-shell multiplet states of atoms. The approach handles any number of open electronic shells. The matrix Dirac-Fock procedure is implemented with analytic basis sets of Gaussian-type functions for expansion of the large and small components of the Dirac four-spinors. Open-shell Dirac-Fock calculations in the single-Fock-operator formalism are performed on the ground and low-lying excited states of Li, B, Na, Al, K, Ga, and In.

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I. INTRODUCTION

Relativistic Dirac-Fock (DF) theory and many-body perturbation theory (MBPT), which account for relativistic and electron-correlation effects, were developed by several groups using discrete basis sets of “local” [1,2] and “global” [3–5] functions. Implementations based on expansion in analytic basis functions [1–5] have the advantage over those based on numerical finite-difference algorithms [6–8] of providing a compact representation of the complete Dirac spectrum. Further, they facilitate the evaluation of many-body diagrams by finite summation [3,4]. In a series of studies [4,9], we have developed matrix DF and relativistic MBPT for calculations on closed-shell systems employing “global” basis sets of Gaussian-type functions (GTF’s), and applied it to many-electron systems. Analytic basis-set expansion in GTF’s has yielded accurate results for closed-shell systems with no sign of the near-linear dependency problems reported with Slater-type orbital basis sets [10–12].

In the present study, we extend our closed-shell DF method to general open-shell systems. We employ the generalized coupling operator method [13,14] and construct a single Fock operator for open-shell DF SCF with which one can determine all closed- and open-shell spinors. Our interest in the single-Fock-operator method in matrix DF calculations on open-shell systems arises from the need for a state-specific relativistic MBPT for general open-shell systems. Since the pioneering work of Roothaan in nonrelativistic Hartree-Fock theory [15], a number of attempts have been made to construct a single Fock operator with which one can determine all the occupied orbitals for open-shell and multiconfiguration (MC) self-consistent field (SCF) wave functions

[13,14,16,17]. Construction of a single Fock operator for general SCF theory is important not only to simplify open-shell SCF calculations but also in formal applications; a single Fock operator is required when the Møller-Plesset-type separation of the N -electron Hamiltonian is used in the perturbation theory of electron correlation. Our aim is to develop a relativistic many-body perturbation theory based on the DF wave functions for open-shell systems. In a forthcoming study, we will report a state-specific relativistic MBPT for general open-shell systems in which our single-Fock-operator method is necessary for a Møller-Plesset-type separation of the relativistic many-electron Hamiltonian [18].

This paper presents an account of matrix DF SCF method which employs a single-Fock-operator formalism for general open-shell systems. We start with a general form for the total-energy expression which does not restrict the configurational form of the total wave function. Thus the formalism applies to excited as well as to ground states. Using projection operators, we decouple the set of Euler equations derived from the first-order variation of the energy with respect to the closed- and open-shell spinors, and transform them into a single pseudosecular equation. In the next section, we outline a single-Fock-operator method for matrix Dirac-Fock self-consistent field calculations for open-shell systems. In Sec. III, the results of matrix DF calculations on the ground and low-lying excited states of the atoms Li, B, Na, Al, K, Ga, and In are presented.

II. SINGLE FOCK OPERATOR FOR MATRIX DIRAC-FOCK CALCULATIONS

Kim pioneered the matrix DF SCF method, using basis sets of Slater-type functions to study the closed-shell atoms He, Be, and Ne [19]. His work revealed a tendency for calculated energies to fall below the variational limit. The failure of the matrix DF method can be avoided by constraining the global basis sets [3,4,9–12]. Goldman [10], Drake and Goldman [11], and Quiney, Grant, and Wilson [3,12] have implemented the matrix DF equa-

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tions by employing S spinors (S for Slater) which avoid variational failure and spurious solutions.

Kagawa has implemented the matrix DF SCF method for open shell [20] and MC wave functions [21] using the coupling operator method. Mohanty and Clementi [22] have applied the matrix DF formalism of Kagawa [20] to a number of closed- and open-shell atoms with so-called "kinetically balanced" basis sets of GTF [4,9]. Kagawa's algorithm [20], however, employs different DF operators for closed-shell and open-shell spinors and thus is not a suitable starting point for our relativistic MBPT method. As an alternative to our MBPT, which is based on open-shell DF wave functions, closed-shell DF SCF calculations may be done, followed by construction of a relativistic MBPT for open-shell systems based on a V^{N-1} potential. In a series of studies [1], Johnson and co-workers have employed local basis sets of spline functions to attain impressive accuracy in closed-shell DF SCF and relativistic MBPT calculations for open-shell systems employing such a method.

Our single-Fock-operator formalism for matrix Dirac-Fock SCF calculations is a generalization of our nonrelativistic coupling operator formalism [14] for open-shell and MC SCF wave functions. There is, however, an important difference between the nonrelativistic coupling operator formalism [14] and its relativistic generalization; proper relativistic generalization of the projection operators used to construct the Fock operator is key to success in the matrix DF SCF scheme for open-shell systems.

The approximate N -electron Hamiltonian for our open-shell DF calculations is the relativistic "no-pair" Dirac-Coulomb Hamiltonian [23,24],

$$H = \sum_i h_D(i) + \mathcal{L}_+ \left[\sum_{ij} 1/r_{ij} \right] \mathcal{L}_+, \quad (1)$$

where $h_D(i)$ is the Dirac one-electron Hamiltonian

$$h_D(i) = c\alpha_i \cdot \mathbf{p}_i + (\beta - 1)c^2 + V_{\text{nuc}}(r_i). \quad (2)$$

Here α and β are the Dirac matrices and \mathbf{p} is the momentum operator. $V_{\text{nuc}}(r)$ is the nuclear attraction term

$$V_{\text{nuc}}(r) = -Z/r \quad \text{for } r > R \\ = -(Z/2R)(3 - r^2/R^2) \quad \text{for } r \leq R.$$

The nucleus is modeled as a sphere of uniform proton-charge distribution. Z is the nuclear charge. R is the radius of the nucleus and is related to the atomic mass A by $R = 2.2677 \times 10^{-5} A^{1/3}$. $\mathcal{L}_+ = L_+(1)L_+(2) \cdots L_+(n)$, with $L_+(i)$ the projection operator onto the space spanned by the positive-energy eigenfunctions of the matrix DF SCF equation [23]. The projection operator \mathcal{L}_+ takes into account the field-theoretic condition that the negative-energy states are filled [23,24]. Throughout this study, atomic units are used and speed of light is taken to be 137.037.

In the central-field approximation, the solution of the Dirac equation is given by

$$\Psi_{n\kappa m}(r, \theta, \phi) = \frac{1}{r} \begin{bmatrix} P_{n\kappa}(r) X_{\kappa m}(\theta, \phi) \\ i Q_{n\kappa}(r) X_{-\kappa m}(\theta, \phi) \end{bmatrix}, \quad (3)$$

where $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small components of the radial wave function.

The radial functions are expanded in GTF,

$$P_{n\kappa}(r) = \sum C_{n\kappa i}^L g_{\kappa i}^L(r), \quad (4)$$

$$Q_{n\kappa}(r) = \sum C_{n\kappa i}^S g_{\kappa i}^S(r), \quad (5)$$

where $\{C_{n\kappa i}^L\}$ and $\{C_{n\kappa i}^S\}$ are expansion coefficients for spinors of symmetry κ . $\{g_{\kappa i}^L(r)\}$ and $\{g_{\kappa i}^S(r)\}$ are the large- and small-component basis sets, respectively. In order to obtain a matrix form of our single Fock operator, Eqs. (4) and (5) are combined into a row-column product;

$$\begin{bmatrix} P_{n\kappa}(r) \\ Q_{n\kappa}(r) \end{bmatrix} = |\underline{g}_\kappa\rangle \underline{C}_{n\kappa}, \quad (6)$$

where

$$|\underline{g}_\kappa\rangle = \begin{bmatrix} g_{\kappa 1}^L g_{\kappa 2}^L g_{\kappa 3}^L \cdots & 0 \\ 0 & g_{\kappa 1}^S g_{\kappa 2}^S g_{\kappa 3}^S \cdots \end{bmatrix}$$

and

$$\underline{C}_{n\kappa} = \begin{bmatrix} C_{n\kappa 1}^L \\ C_{n\kappa 2}^L \\ C_{n\kappa 3}^L \\ \vdots \\ C_{n\kappa 1}^S \\ C_{n\kappa 2}^S \\ C_{n\kappa 3}^S \\ \vdots \end{bmatrix}.$$

For the large component, the GTF's are of the form [4,9]

$$g_{\kappa i}^L(r) = A_{\kappa i}^L r^{n_\kappa} \exp(-\xi_{\kappa i} r^2),$$

with $n_\kappa = -\kappa$ for $\kappa < 0$ and $n_\kappa = \kappa + 1$ for $\kappa > 0$. $A_{\kappa i}^L$ is the normalization constant. The small component basis set $\{g_{\kappa i}^S(r)\}$ is constructed according to the kinetic balance condition [4,9]. With the uniformly charged finite-nucleus approximation, GTF's of integer power of r are appropriate basis functions because imposition of the finite nuclear boundary results in a solution which is Gaussian at the origin [9].

The total electronic energy of a general open-shell system can be expressed [20] as

$$E = \sum_{i \in (\mathcal{O})} N_i h_{ii} + \sum_{i, j \in (\mathcal{O})} N_i N_j (J_{ij} - K_{ij}) \\ + \sum_{k \in (\mathcal{O})} f_k \left[N_k h_{kk} + \sum_{i \in (\mathcal{O})} N_i N_k (J_{ik} - K_{ik}) \right] \\ + \sum_{k, l \in (\mathcal{O})} (a_{kl} J_{kl} - b_{kl} K_{kl}), \quad (7)$$

where f_k is the fractional occupation of k th open-shell. The h_i , J_{ij} , and K_{ij} represent core, Coulomb, and exchange integrals, respectively. The a_{kl} and b_{kl} are coupling constants, the value of which depend on the state

under study. The occupation number N_i , of the i th spinor shell is given by $N_i = 2j_i + 1$. \mathcal{C} and \mathcal{O} represent closed-shell and open-shell manifolds, respectively.

The first-order variation of the total energy in Eq. (7) gives a set of Euler equations

$$F_c|i\rangle = \sum_{j \in \mathcal{M}} \epsilon_{ji}|j\rangle, \quad i \in \mathcal{C} \quad (8)$$

$$F_k|k\rangle = \sum_{j \in \mathcal{M}} \epsilon_{jk}|j\rangle, \quad k \in \mathcal{O} \quad (9)$$

where

$$F_c = h + \sum_{j \in \mathcal{C}} N_j(J_j - K_j) + \sum_{k \in \mathcal{O}} f_k N_k(J_k - K_k) \quad (10)$$

$$F_k = f_k \left[h + \sum_{j \in \mathcal{C}} N_j(J_j - K_j) \right] + \sum_{l \in \mathcal{O}} (a_k J_l - b_{kl} K_l) \quad (11)$$

and a set of Lagrange multiplier Hermiticity conditions [13,14,17]

$$\langle i|F_k - F_c|k\rangle = 0, \quad i \in \mathcal{C}, \quad k \in \mathcal{O} \quad (12)$$

and

$$\langle k|F_l - F_k|l\rangle = 0, \quad k \in \mathcal{O}, \quad l \in \mathcal{O}. \quad (13)$$

\mathcal{M} is the manifold generated by a set of all the SCF occupied orbitals. The $\{\epsilon_{ij}\}$ are the Lagrange multipliers. h , J_i , and K_i are, respectively, the core, Coulomb, and exchange operators.

In order to construct a single Fock operator, one needs only introduce the projection operators in terms of the occupied and virtual SCF spinors

$$\Pi_c = P_c + P_v, \quad \Pi_k = P_k + P_v, \quad k \in \mathcal{O}, \quad c \in \mathcal{C} \quad (14)$$

with

$$P_c = \sum_{i \in \mathcal{C}} |i\rangle\langle i|, \quad P_k = |k\rangle\langle k| \quad (15)$$

and

$$P_v = \sum_{v \in \mathcal{V}_-} |v\rangle\langle v| + \sum_{v \in \mathcal{V}_+} |v\rangle\langle v|, \quad (16)$$

where \mathcal{V}_- and \mathcal{V}_+ are, respectively, manifolds generated by the negative- and the unoccupied positive-energy branches of the DF spectrum. A matrix form of the projection operators in Eq. (14) is defined by

$$\underline{\Pi}_c = \underline{P}_c + \underline{P}_v, \quad \underline{\Pi}_k = \underline{P}_k + \underline{P}_v,$$

where

$$\underline{P}_c = \sum_{i \in \mathcal{C}} \underline{C}_i \underline{C}_i^+, \quad \underline{P}_k = \underline{C}_k \underline{C}_k^+$$

and

$$\underline{P}_v = \sum_{v \in \mathcal{V}_-} \underline{C}_v \underline{C}_v^+ + \sum_{v \in \mathcal{V}_+} \underline{C}_v \underline{C}_v^+.$$

The crucial difference between the nonrelativistic formalism [13,14] and its relativistic generalization is the definition of the projection operator P_v , which projects

the spinors onto the virtual space. In the relativistic generalization of the coupling operator formalism, it is essential that the projection operator P_v be constructed in terms of both the negative- and unoccupied positive-energy branches of the DF spectrum to satisfy completeness:

$$P_c + \sum_{k \in \mathcal{O}} P_k + P_v = 1. \quad (17)$$

Using the projection operator introduced in Eqs. (14)–(16), the single Fock operator that satisfies the correct variational condition can be derived [14]:

$$R = R_0 + T, \quad (18)$$

where

$$R_0 = \Pi_c F_c \Pi_c + \sum_{k \in \mathcal{O}} \Pi_k F_k \Pi_k \quad (19)$$

and

$$T = \sum_{k \in \mathcal{O}} [(\lambda_{ck} - \lambda_{kc}) P_c (F_k - F_c) P_k + (\lambda_{kc} - \lambda_{ck}) P_k (F_c - F_k) P_c] + \sum_{k \in \mathcal{O}} \sum_{l \in \mathcal{O}(k \neq l)} (\lambda_{lk} - \lambda_{kl}) P_l (F_k - F_l) P_k. \quad (20)$$

Here the $\{\lambda_{ij}\}$ are arbitrary nonzero numbers satisfying the conditions $\lambda_{ij} \neq \lambda_{ji}$. The operator T ensures the Hermiticity of the Lagrange multipliers during the iterative DF SCF procedure. Matrix elements of the operator T become identically zero at SCF convergence. Thus only matrix elements of the operator R_0 enter the MBPT calculations. With the coupling operator given above, the DF equations for a general class of open-shell systems are reduced to single pseudosecular equation form from which all closed- and open-shell spinors can be determined:

$$R|i\rangle = \epsilon_i|i\rangle. \quad (21)$$

In matrix DF calculations, the SCF equation in Eq. (21) takes the form

$$\underline{S} \underline{R} \underline{S} \underline{C}_i = \epsilon_i \underline{S} \underline{C}_i. \quad (22)$$

Here \underline{S} is the overlap matrix given by $\underline{S} = \langle \mathbf{g} | \mathbf{g} \rangle$ and

$$\underline{R} = \underline{R}_0 + \underline{T}$$

with

$$\underline{R}_0 = \underline{\Pi}_c \underline{F}_c \underline{\Pi}_c + \sum_{k \in \mathcal{O}} \underline{\Pi}_k \underline{F}_k \underline{\Pi}_k$$

and

$$\underline{T} = \sum_{k \in \mathcal{O}} [(\lambda_{ck} - \lambda_{kc}) \underline{P}_c (\underline{F}_k - \underline{F}_c) \underline{P}_k + (\lambda_{kc} - \lambda_{ck}) \underline{P}_k (\underline{F}_c - \underline{F}_k) \underline{P}_c] + \sum_{k \in \mathcal{O}} \sum_{l \in \mathcal{O}(k \neq l)} (\lambda_{lk} - \lambda_{kl}) \underline{P}_l (\underline{F}_k - \underline{F}_l) \underline{P}_k.$$

TABLE I. Total DF SCF energy of the $^2S_{1/2}$ ground state Li (in a.u.).

Basis set ^a	Total energy
6s	-7.415 622 543
8s	-7.430 211 140
10s	-7.432 917 191
12s	-7.433 373 434
16s	-7.433 522 930
20s	-7.433 532 399
32s ^b	-7.433 533 788
Numerical limit	-7.433 533 6 ^c

^aGeometric basis set of Schmidt and Ruedenberg (Ref. [25]).

^bGeometric basis set with $\alpha=0.0080$ and $\beta=1.755 188$ (present work).

^cDF limit obtained by using the numerical finite difference DF SCF program of Desclaux (Ref. [27]).

III. RESULTS AND DISCUSSION

A series of matrix DF calculations on the ground and low-lying excited states of the Li and Al atoms were performed with geometric GTF basis sets which were progressively enlarged. The exponents of a geometric basis set [25,26] $\{\xi_{\kappa i}\}$ are generated by a geometric series $\xi_{\kappa i} = \alpha\beta^{i-1}$, $i=1, 2, \dots, N$, with α and β parameters. Table I contains seven representative sets of total DF energies for ground-state Li along with the total DF energy obtained with the numerical finite difference DF program of Desclaux [27]. Geometrical basis sets of 6–20 GTF's were taken from the work of Schmidt and Ruedenberg [25]. The 32-GTF basis set was constructed for this work. A basis of at least 12 GTF is needed to obtain mhartree accuracy in the total energy. The total DF energy computed with the 20-GTF expansion agrees well with that from the finite-difference calculation. Basis-set

TABLE II. The DF energies of the ground $^2P_{1/2}$ state and excited $^2P_{3/2}$ state of the Al atom (in a.u.).

State	Basis set ^a	Total energy
$^2P_{1/2}$	20s20p	-242.319 306
	22s20p	-242.329 417
	24s20p	-242.330 856
	26s24p	-242.331 084
	28s26p	-242.331 125
	31s29p	-242.331 133
	Numerical limit ^b	-242.331 143
$^2P_{3/2}$	20s20p	-242.318 762
	22s20p	-242.328 873
	24s20p	-242.330 311
	26s24p	-242.330 540
	28s26p	-242.330 580
	31s29p	-242.330 588
	Numerical limit ^b	-242.330 598

^aGeometric basis set ($\alpha=0.014 49$ and $\beta=2.061$).

^bDF limit obtained by using the numerical finite-difference DF SCF program of Desclaux (Ref. [27]).

truncation error is on the order of $1 \mu\text{hartree}$. The 32-GTF basis gives a total energy accurate to better than a $\mu\text{hartree}$. The computed energy is about $0.2 \mu\text{hartree}$ lower than that obtained via numerical DF because of the difficulty the numerical finite-difference method has in accurately integrating across the boundary of the finite nucleus. Matrix DF calculations with GTF basis sets can, therefore, be more accurate and provide better upper bounds to total DF energies than can other methods because GTF's are able to accurately represent the solution near the finite nucleus.

Table II displays six representative sets of DF energies for the ground $^2P_{1/2}$ and excited $^2P_{3/2}$ states of aluminum. In both the ground and excited states, the same geometric basis functions were used, with $\alpha=0.014 49$ and $\beta=2.061$ but varying basis-set size. The results demonstrate the convergence patterns of the total DF energies. As expansion size increases, total energy approaches the numerical limit smoothly from above. The accuracy and reliability of our matrix DF calculations on open-shell multiplets are confirmed by the excellent agreement between our results and those obtained by the numerical method of Desclaux [27]. For both ground and excited states, use of the large 31s29p basis set gives a total DF energy accurate to $10 \mu\text{hartree}$. The fine-structure separation between the $^2P_{1/2}$ and $^2P_{3/2}$ states computed by the matrix DF calculations is 119.507 cm^{-1} , in excellent agreement with the value 119.51 cm^{-1}

TABLE III. Total DF energies of the ground and low-lying excited states (in a.u.).

Atom	Basis set	State	Matrix DFC	Finite difference ^a
Li	32s ^b	$^2S_{1/2}$	-7.433 533 79	-7.433 533 6
Li		$^2P_{1/2}$	-7.365 862 32	-7.365 861 7
Li		$^2P_{3/2}$	-7.365 859 76	-7.365 859 1
B	23s23p ^c	$^2P_{1/2}$	-24.536 616 2	-24.536 616 9
B		$^2P_{3/2}$	-24.536 523 2	-24.536 523 9
Na	30s28p ^d	$^2S_{1/2}$	-162.078 095	-162.078 101
Al	31s29p ^e	$^2P_{1/2}$	-242.331 133	-242.331 143
Al		$^2P_{3/2}$	-242.330 588	-242.330 598
K	31s29p ^f	$^2S_{1/2}$	-601.526 020	-601.526 058
Ga	32s29p24d ^g	$^2P_{1/2}$	-1942.566 70	-1942.566 82
Ga		$^2P_{3/2}$	-1942.563 06	-1942.563 18
In	32s29p24d ^h	$^2P_{1/2}$	-5880.441 26	-5880.442 19
In		$^2P_{3/2}$	-5880.431 50	-5880.432 43

^aDF energies obtained by using the finite difference program of Desclaux (Ref. [27]).

^b $\alpha=0.0080$ and $\beta=1.755 188$.

^c $\alpha=0.035 92$ and $\beta=2.1034$.

^d $\alpha=0.0080$ and $\beta=2.010 510$.

^e $\alpha=0.014 49$ and $\beta=2.061$.

^f $\alpha=0.018 22$ and $\beta=2.027 15$.

^g $\alpha=0.015$ and $\beta=2.010 902$.

^h $\alpha=0.012$ and $\beta=2.040 705$.

computed with the finite-difference program [27].

Table III displays the total DF energies of the ground and low-lying excited states of Li($Z=3$), B($Z=5$), Na($Z=11$), Al($Z=13$), K($Z=19$), Ga($Z=31$), and In($Z=49$). These open-shell systems have been chosen because we can assess the accuracy of our open-shell matrix DF algorithm by comparing the results of our calculations to those obtained numerically [27]. The atomic masses used were, respectively, 6.94, 10.81, 22.99, 26.98, 39.098, 69.72, and 114.82 for Li, B, Na, Al, K, Ga, and In. The size of the geometric basis set appears in the second column, accompanied by the parameters α and β in the footnote. In the fifth column, the total finite-difference DF energies are tabulated for comparison. For all the systems examined, both the ground and low-lying excited states were computed with the same basis set. In each case, the DF SCF process converged in about 40 iterations to within 1.0×10^{-9} hartree in total energy. For all systems except In, the total DF energies agree with the corresponding numerical limit to one part in 10^7 . Basis-set truncation error for In is on the order of 1 mhartree. The fine-structure interval computed for Ga and In are, respectively, 800.30 and 2141.9 cm^{-1} , in excellent agreement with the finite-difference values of 800.24 and 2142.2 cm^{-1} .

IV. CONCLUSIONS

The aim of this study has been to develop the matrix DF SCF scheme for general open-shell systems using a single-Fock-operator formalism. We have developed reliable procedures for accurate matrix DF calculations on the ground and excited multiplet states. The single Fock operator constructed in the present study can be employed in a straightforward manner in relativistic MBPT for a general class of open-shell systems if one employs a Møller-Plesset-type separation of the many-electron Hamiltonian. The DF algorithm has been successfully applied to a number of open-shell systems and it has proven to be capable of accuracy comparable to that of finite-difference numerical methods.

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