PHYSICAL REVIEW E VOLUME 58, NUMBER 4 OCTOBER 1998

Quadratically convergent multiconfiguration Dirac-Fock and multireference relativistic configuration-interaction calculations for many-electron systems

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(Received 10 December 1997; revised manuscript received 29 April 1998)

A quadratically convergent Newton-Raphson algorithm for a relativistic multiconfiguration Dirac-Fock self-consistent-field calculations is developed and implemented with analytic basis sets of Gaussian spinors. A procedure to perform second-order energy optimization for a general class of multiconfiguration wave functions constructed from one-particle Dirac spinors is described. We report the results of relativistic multiconfiguration Dirac-Fock self-consistent-field calculations and relativistic multireference configuration-interaction calculations based on the multiconfiguration Dirac-Fock wave functions for the lowest $^3P_0$, $^3P_1$, and $^3P_2$ states of oxygenlike iron (Fe^{18+}), ground $J=0$ and excited $J=1$ states of beryllium, and ground-state berylliumlike neon (Ne^{6+}), species that exhibit the near degeneracy characteristic of a manifold of strongly interacting configurations. [S1063-651X(98)11309-0]

PACS number(s): 02.70.−c, 31.15.−p, 31.25.Eb, 31.25.Jf

I. INTRODUCTION

The importance of electron correlation in the accurate description of light elements and molecules that contain light elements is well established. In heavy-atom systems and highly ionized high-Z ions, the effects of relativity become important in addition to electron correlation. Further, the effects of relativity and electron correlation in these systems are strongly intertwined. Thus, an intense effort in the last decade has been directed toward developing relativistic many-body theories to accurately account for both relativistic and electron correlation effects in heavy-atom systems and highly ionized high-Z ions. Among the relativistic many-body techniques developed recently are numerical finite-difference and matrix multiconfiguration (MC) Dirac-Fock self-consistent field (DF SCF) theory [1–3], relativistic many-body perturbation theory [4–9], relativistic coupled cluster theory [10–13], and relativistic configuration interaction (CI) [14–17]. Discrete basis sets of both ''local'' [4,5,10,12,15] and ''global'' functions [3,6–8,11,14,16] as well as numerical finite-difference algorithms [1,2,9,13,17] have been used. Implementations based on expansion in analytic basis functions [3–8,10–12,14–16] have an advantage over those based on numerical finite-difference algorithms [1,2,9,17] in providing a compact representation of the complete Dirac spectrum.

We recently [18] employed the generalized coupling operator method [19] to construct a single Fock operator for open-shell DF SCF theory, and showed that with such an operator all closed- and open-shell four-component Dirac spinors can be determined. We reported a state-specific relativistic many-body perturbation theory for open-shell systems in which our single Fock operator method is employed to obtain a Møller-Plesset-type separation of the relativistic many-electron Hamiltonian [8]. Calculations which have employed ''global'' basis sets of G spinors (G for ''Gaussian'' after Grant [20]) have been done on a number of many-electron systems [8]. State-specific many-body perturbation theory involves a full implementation of generalized Møller-Plesset perturbation theory applied to general open-shell reference wave functions, and, in low order, yields a large fraction of the dynamic correlation [21]. The spinors used in these relativistic many-body perturbation theory calculations were obtained in single-configuration DF SCF calculations, and most contemporary implementations rely on a single-configuration reference.

Single-reference many-body perturbation theory is effective in describing dynamic correlation, but fails to account for nondynamic correlation (i.e., near-degeneracy effects). Dynamic correlation is a short-range effect that arises from electron-electron interaction and is the major correction to the Dirac-Fock independent particle model, while nondynamic correlation is a consequence of the existence of nearly degenerate excited states that interact strongly with the reference state [21,22]. Nondynamic correlation is accounted for by including in the reference state sufficient configuration state functions (CSF's) to describe all near degeneracies. Systems in which only dynamic correlation is important are well represented by single-configuration Dirac-Fock wave functions, whereas systems in which nondynamic correlation is important cannot be correctly described by single-configuration Dirac-Fock wave functions. Near degeneracy of the valence spinors gives rise to a manifold of strongly interacting configurations, i.e., strong configuration mixing within a relativistic complex due to asymptotic degeneracy [22], and makes a relativistic multiconfiguration treatment mandatory. The classic examples are the near-degeneracy effects in the beryllium and carbon isoelectronic sequences, and in general all open-shell atoms with two or more valence electrons. For most reactive and excited-state energy surfaces of molecules, single-configuration self-consistent field theory also fails to properly describe the separated fragments because of the near degeneracy involved in those processes. While slow convergence in iterative first-order MC DF SCF procedures has been a significant barrier, it can be practically solved in many cases by employing the quadratically convergent Newton-Raphson technique [23]. Once near-degeneracy effects are accounted for by relativistic MC DF SCF theory, the remaining dynamic correlation may be treated by multireference generalized Møller-Plesset perturbation theory [21] or relativistic multireference CI based on the MC DF SCF reference wave function [17].

In the present study, we extend our single-configuration open-shell DF SCF [18] to a general MC DF SCF in order to treat the systems with significant nondynamic correlation effects. Numerical finite-difference and matrix MC DF SCF algorithms based on a first-order energy variation define only a stationary point on the energy surface, and thus their iterative solutions often exhibit slow convergence for the ground states of atoms and molecules, and are often nonconvergent for excited states. To optimize even relatively simple MC wave functions with respect to spinor variations, it is necessary to know the curvature of the energy surface with respect to variations in spinors and CI coefficients. This requires knowing the second derivatives. Second-order optimization of Dirac four-spinors and CI mixing coefficients in MC DF SCF theory is thus mandatory in order to guarantee well-controlled convergence in relatively few iterations. The essential feature of MC DF SCF theory is the multireference approach to treating nondynamic correlation.

Here we report a successful implementation by expansion in G spinor basis sets of the second-order MC DF SCF and multireference configuration interaction with single and double excitations (CI-SD) formalisms. We develop the MC variational energy up to second order in the unitary rotation parameters, and seek an energy extremum by employing a quadratic approximation on the energy surface. The approach parallels the second-order algorithms developed in nonrelativistic multiconfiguration Hartree-Fock calculations [23], and provides excellent convergence once a quadratic basin on the energy surface is entered. In Sec. II, the quadratically convergent relativistic MC DF SCF and multireference CI-SD algorithms are formulated. In Sec. III, the results of matrix MC DF SCF and multireference CI-SD calculations on the the lowest $^3P_0$, $^3P_1$, and $^3P_2$ states of oxygenlike iron (Fe^{18+}), ground $J=0$ and excited $J=1$ states of beryllium, and the ground $J=0$ state of beryllium-like neon (Ne^{6+}) are presented.

II. THEORY

The effective N-electron Hamiltonian (in atomic units) for the development of our matrix MC DF SCF algorithm is taken to be the relativistic ‘‘no-pair’’ Dirac-Coulomb (DC) Hamiltonian [24,25],

$$H_{\mathrm{DC}}^{+}=\sum_i h_D(i)+\mathcal{L}_{+}\left(\sum_{i>j}\frac{1}{r_{ij}}\right)\mathcal{L}_{+}\,, \tag{1}$$

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

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

Here α and β are the 4×4 Dirac vector and scalar matrices, respectively. $V_{\mathrm{nuc}}(r)$ is the nuclear attraction term. The nucleus is modeled as a sphere of uniform proton-charge distribution (Z is the nuclear charge, and R the radius of the sphere),

$$V_{\mathrm{nuc}}(r)=\begin{cases}-\dfrac{Z}{r} & \text{for}\quad r>R\\[2ex] -\dfrac{Z}{2R}\left(3-\dfrac{r^2}{R^2}\right) & \text{for}\quad r\leqslant R.\end{cases} \tag{3}$$

The total projection operator $\mathcal{L}_{+}=L_{+}(1)L_{+}(2)\cdots L_{+}(n)$, where $L_{+}(i)$ is the projection operator onto the space spanned by the positive- eigenfunctions of the MC DF SCF equation [18,25] for the individual electrons. The operator $\mathcal{L}_{+}$ formally takes into account the field-theoretic condition that the negative-energy states are filled [24,25]. The eigenfunctions of the matrix DF SCF equations clearly separate into two discrete manifolds of positive- and negative-energy states. As a result, the positive-energy projection operators can be accommodated easily in many-body calculations. The formal conditions on the projection are automatically satisfied when only the positive-energy spinors are employed.

Adding the frequency-independent Breit interaction,

$$B_{12}=-\tfrac{1}{2}[\alpha_1\alpha_2+(\alpha_1\cdot\mathbf{r}12)(\alpha_2\cdot\mathbf{r}_{12})/r_{12}^2]/r_{12} \tag{4}$$

to the instantaneous electron-electron Coulomb interaction, in Coulomb gauge, results in the Coulomb-Breit potential, which is correct to order α^2 (α being the fine-structure constant) [24]. Addition of the Breit term yields the no-pair Dirac-Coulomb-Breit (DCB) Hamiltonian [24,25]

$$H_{\mathrm{DCB}}^{+}=\sum_i h_D(i)+\mathcal{L}_{+}\left(\sum_{i>j}\left(\frac{1}{r_{ij}}+B_{ij}\right)\right)\mathcal{L}_{+}\,, \tag{5}$$

which is covariant to first order and increases the accuracy of calculated fine-structure splittings and inner-shell binding energies. Higher-order QED effects appear first in order α^3. Studies have appeared that go beyond the no-pair approximation where negative-energy states are needed to evaluate the higher-order QED effects [26,27].

Eigenfunctions of the no-pair DC Hamiltonian are approximated by a linear combination of N-electron CSF's.

$$\Psi_{\mathrm{MCDFC}}(\gamma\mathcal{J}\pi)=\sum_{I}^{N_{\mathrm{CSF}}}C_I^{\gamma\mathcal{J}\pi}\Phi_I(\gamma_I\mathcal{J}\pi). \tag{6}$$

Here the MC Dirac-Fock-Coulomb self-consistent-field (DFC SCF) wave function $\Psi_{\mathrm{MCDFC}}(\gamma\mathcal{J}\pi)$ is an eigenfunction of the angular momentum and parity operators with total angular momentum $\mathcal{J}$ and parity π, and $\Phi_I(\gamma_I\mathcal{J}\pi)$ the CSF's. γ denotes a set of quantum numbers other than $\mathcal{J}$ and π necessary to specify the state uniquely. In the following, $C_I^{\gamma\mathcal{J}\pi}$ is abbreviated as C_I^{γ}.

The total DC energy of the general electronic state $\Psi_{\mathrm{MCDFC}}(\gamma\mathcal{J}\pi)$ can be expressed as

$$\begin{aligned}E^{\gamma\mathcal{J}\pi}&=\langle\Psi_{\mathrm{MCDFC}}(\gamma\mathcal{J}\pi)|H_{\mathrm{DC}}^{+}|\Psi_{\mathrm{MCDFC}}(\gamma\mathcal{J}\pi)\rangle\\&=\sum_{I\geqslant J}^{N_{\mathrm{CSF}}}C_I^{\gamma}C_J^{\gamma}\langle\Phi_I(\gamma_I\mathcal{J}\pi)|H_{\mathrm{DC}}^{+}|\Phi_J(\gamma_J\mathcal{J}\pi)\rangle(2-\delta_{IJ}).\end{aligned} \tag{7}$$

Here it is assumed that $\Psi_{\mathrm{MCDFC}}(\gamma\mathcal{J}\pi)$ and $\Phi_J(\gamma_J\mathcal{J}\pi)$ are normalized, and the hermiticity of the Hamiltonian has been employed to reduce the number of terms in the summation. The total energy can be conveniently expressed in terms of the unique elements of the one- and two-particle radial integrals,

$$E^{\gamma\mathcal{J}\pi}=\sum_{\alpha=1}^{N_t} t_\alpha I(a_\alpha b_\alpha)+\sum_{\beta=1}^{N_V} V_\beta R^{\nu\beta}(a_\beta b_\beta,c_\beta d_\beta), \tag{8}$$

where N_t and N_V are the numbers of nonzero t_α and V_β coefficients. The short notation for the radial integrals has been used:

$$I(ab)=I(n_a\kappa_a n_b\kappa_b)=(\phi_{n_a\kappa_a}(r)|h_D(r)|\phi_{n_b\kappa_b}(r)\rangle, \tag{9}$$

$$\begin{aligned}R^\nu(ab,cd)&=R^\nu(n_a\kappa_a n_b\kappa_b,n_c\kappa_c n_d\kappa_d)\\&=\left\langle \phi_{n_a\kappa_a}(r_1)\phi_{n_b\kappa_b}(r_2)\left|\frac{r_<^\nu}{r_>^{\nu+1}}\right|\right.\\&\qquad\left.\times\phi_{n_c\kappa_c}(r_1)\phi_{n_d\kappa_d}(r_2)\right\rangle,\end{aligned} \tag{10}$$

where $\{\phi_{n_a\kappa_a}(r)\}$ is an orthonormal set of Dirac one-electron radial spinors of symmetry κ. The symmetry κ is related to spinor angular momentum j by $\kappa=\mp(j+\frac{1}{2})$ for $l=j\mp\frac{1}{2}$, where l is orbital angular momentum quantum number of the large component spinor. The generalized coefficients t_α and V_β are expressed in terms of nonzero angular coefficients t_α^{IJ} and V_β^{IJ}:

$$t_\alpha=\sum_{\alpha'=1}^{N_t'} t_{\alpha'}^{IJ}\delta(\alpha,\alpha')\{2-\delta_{IJ}\},C_I^\gamma C_J^\gamma, \tag{11}$$

$$V_\beta=\sum_{\beta'=1}^{N_V'} V_{\beta'}^{IJ}\delta(\beta,\beta')\{2-\delta_{IJ}\}C_I^\gamma C_J^\gamma. \tag{12}$$

The angular coefficients t_α^{IJ} and V_β^{IJ} account for the symmetries of the radial integrals $I(a_\alpha b_\alpha)$ and $R^\nu(a_\beta b_\beta,c_\beta d_\beta)$, and the notations $\alpha=\{a_\alpha b_\alpha\}$ and $\beta=\{\nu_\beta,a_\beta b_\beta,c_\beta d_\beta\}$ have been used.

Throughout the section, the following notations are used: The indices e and f denote occupied spinors; the indices p, q, r, and s denote any of the occupied or virtual spinors (both positive and negative energy spinors); the indices I, J, and K denote CI coefficients; and the indices a, b, c, d, and ν are reserved for the sets α and β describing unique radial integrals.

A. Second-order MC DFC SCF energy optimization by spinor rotations

Given a trial orthonormal set of one-electron radial spinors $\{\phi_{n_p\kappa_p}(r)\}$, the optimum occupied radial spinors $\{\phi_{n_e\kappa_e}^{\mathrm{opt}}\}$ can be found by a unitary transformation $\mathbf{U}=\mathbf{1}+\mathbf{T}$ via

$$\begin{aligned}\phi_{n_e\kappa_e}^{\mathrm{opt}}(r)&=\frac{1}{r}\begin{pmatrix}P_{n_e\kappa_e}^{\mathrm{opt}}(r)\\Q_{n_e\kappa_e}^{\mathrm{opt}}(r)\end{pmatrix}=\sum_p^{2N_\kappa}\phi_{n_p\kappa_p}(r)U_{pe}\\&=\sum_p^{2N_\kappa}\phi_{n_p\kappa_p}(r)(T_{pe}+\delta_{pe}).\end{aligned} \tag{13}$$

Here, the summation extends over both negative and positive energy spinors. $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large (L) and small (S) radial components and are expanded in N_κ Gaussian-type functions, $\{\chi_{\kappa i}^L\}$ and $\{\chi_{\kappa i}^S\}$, that satisfy the boundary conditions associated with the finite nucleus [7,18,28]:

$$P_{n\kappa}(r)=\sum_i \chi_{\kappa i}^L\xi_{n\kappa i}^L, \tag{14}$$

$$Q_{n\kappa}(r)=\sum_i \chi_{\kappa i}^S\xi_{n\kappa i}^S. \tag{15}$$

Here $\{\xi_{n\kappa i}^L\}$ and $\{\xi_{n\kappa i}^S\}$ are linear variation parameters.

In terms of the powers of the spinor variation parameters $\mathbf{T}=\{T_{pe}\}$, the energy $E^{\gamma\mathcal{J}\pi}$ in Eq. (8) can be expanded in the following way:

$$E^{\gamma\mathcal{J}\pi}=E^{(0)}+\Delta E^{(1)}(\mathbf{T})+\Delta E^{(2)}(\mathbf{T})+\cdots. \tag{16}$$

Here $\Delta E^{(i)}(\mathbf{T})=E^{(i)}(\mathbf{T})-E^{(i-1)}(\mathbf{T})$ is the ith-order energy correction proportional to the term $(\mathbf{T})^i$. The energy $E^{\gamma\mathcal{J}\pi}$ is a fourth-order function of rotation matrix elements T_{pe}. Inserting the optimum spinor expression (13) into Eq. (8) and collecting the terms of the same power of $\mathbf{T}$, the energy expression to second-order $E^{(2)}(\mathbf{T})$ in T_{pe} is obtained,

$$E^{(2)}(\mathbf{T})=E^{(0)}+\Delta E^{(1)}(\mathbf{T})+\Delta E^{(2)}(\mathbf{T}), \tag{17}$$

where $E^{(0)}$ is given in Eq. (8),

$$\begin{aligned}\Delta E^{(1)}(\mathbf{T})=\sum_{e=1}^{N_w}\sum_{p=1}^{2N_\kappa}T_{pe}\Bigg[&\sum_{\alpha=1}^{N_t}t_\alpha\{I(pb_\alpha)\delta(e,a_\alpha)+I(a_\alpha p)\delta(e,b_\alpha)\}+\sum_{\beta=1}^{N_V}V_\beta\{R^{\nu\beta}(pb_\beta,c_\beta d_\beta)\delta(e,a_\beta)\\&+R^{\nu\beta}(a_\beta p,c_\beta d_\beta)\delta(e,b_\beta)+R^{\nu\beta}(a_\beta b_\beta,pd_\beta)\delta(e,c_\beta)+R^{\nu\beta}(a_\beta b_\beta,c_\beta p)\delta(e,d_\beta)\}\Bigg]\end{aligned} \tag{18}$$

and

$$\begin{aligned}\Delta E^{(2)}(\mathbf{T})=\sum_{e=1}^{N_w}\sum_{f=1}^{N_w}\sum_{p=1}^{2N_\kappa}\sum_{q=1}^{2N_\kappa} T_{pe}T_{qf}\Bigg[&\sum_{\alpha=1}^{N_t} t_\alpha I(pq)\,\delta(e,a_\alpha)\,\delta(f,b_\alpha)+\sum_{\beta=1}^{N_V} V_\beta\{R^{\nu\beta}(pq,c_\beta d_\beta)\,\delta(e,a_\beta)\,\delta(f,b_\beta)\\&+R^{\nu\beta}(pb_\beta,qd_\beta)\,\delta(e,a_\beta)\,\delta(f,c_\beta)+R^{\nu\beta}(pb_\beta,c_\beta q)\,\delta(e,a_\beta)\,\delta(f,d_\beta)+R^{\nu\beta}(a_\beta p,qd_\beta)\,\delta(e,b_\beta)\,\delta(f,c_\beta)\\&+R^{\nu\beta}(a_\beta p,c_\beta q)\,\delta(e,b_\beta)\,\delta(f,d_\beta)+R^{\nu\beta}(a_\beta b_\beta,pq)\,\delta(e,c_\beta)\,\delta(f,d_\beta)\}\Bigg].\end{aligned}\tag{19}$$

Here the index N_w represents the number of occupied electronic shells.

Variation of the approximate energy $E^{(2)}(\mathbf{T})$ with respect to parameters T_{pe} leads to the Newton-Raphson equations,

$$\frac{\partial E^{(2)}(\mathbf{T})}{\partial T_{pe}}=g^{o}_{pe}+\sum_{qf} h^{oo}_{pe,qf}T_{qf}=0,\tag{20}$$

where the gradient with respect to T_{pe} is

$$\begin{aligned}g^{o}_{pe}=\frac{\partial \Delta E^{(1)}(\mathbf{T})}{\partial T_{pe}}=&\sum_{\alpha=1}^{N_t} t_\alpha[I(pb_\alpha)\,\delta(e,a_\alpha)+I(a_\alpha p)\,\delta(e,b_\alpha)]+\sum_{\beta=1}^{N_V} V_\beta\{R^{\nu\beta}(pb_\beta,c_\beta d_\beta)\,\delta(e,a_\beta)\\&+R^{\nu\beta}(a_\beta p,c_\beta d_\beta)\,\delta(e,b_\beta)+R^{\nu\beta}(a_\beta b_\beta,pd_\beta)\,\delta(e,c_\beta)+R^{\nu\beta}(a_\beta b_\beta,c_\beta p)\,\delta(e,d_\beta)\},\end{aligned}\tag{21}$$

and the Hessian matrix with respect to T_{pe} is

$$\begin{aligned}h^{oo}_{pe,qf}=\frac{\partial^2 \Delta E^{(2)}(\mathbf{T})}{\partial T_{pe}\partial T_{qf}}=&\sum_{\alpha=1}^{N_t} t_\alpha[I(pq)\,\delta(e,a_\alpha)\,\delta(f,b_\alpha)+I(qp)\,\delta(e,b_\alpha)\,\delta(f,a_\alpha)]+\sum_{\beta=1}^{N_V} V_\beta\{R^{\nu\beta}(pq,c_\beta d_\beta)\,\delta(e,a_\beta)\,\delta(f,b_\beta)\\&+R^{\nu\beta}(pb_\beta,qd_\beta)\,\delta(e,a_\beta)\,\delta(f,c_\beta)+R^{\nu\beta}(pb_\beta,c_\beta q)\,\delta(e,a_\beta)\,\delta(f,d_\beta)+R^{\nu\beta}(a_\beta p,qd_\beta)\,\delta(e,b_\beta)\,\delta(f,c_\beta)\\&+R^{\nu\beta}(a_\beta p,c_\beta q)\,\delta(e,b_\beta)\,\delta(f,d_\beta)+R^{\nu\beta}(a_\beta b_\beta,pq)\,\delta(e,c_\beta)\,\delta(f,d_\beta)+R^{\nu\beta}(qp,c_\beta d_\beta)\,\delta(f,a_\beta)\,\delta(e,b_\beta)\\&+R^{\nu\beta}(qb_\beta,pd_\beta)\,\delta(f,a_\beta)\,\delta(e,c_\beta)+R^{\nu\beta}(qb_\beta,c_\beta p)\,\delta(f,a_\beta)\,\delta(e,d_\beta)+R^{\nu\beta}(a_\beta q,pd_\beta)\,\delta(f,b_\beta)\,\delta(e,c_\beta)\\&+R^{\nu\beta}(a_\beta q,c_\beta p)\,\delta(f,b_\beta)\,\delta(e,d_\beta)+R^{\nu\beta}(a_\beta b_\beta,qp)\,\delta(f,c_\beta)\,\delta(e,d_\beta)\}.\end{aligned}\tag{22}$$

To account for the orthogonality constraints, terms involving Lagrange multipliers must be added to the energy functional:

$$W=E^{(2)}(\mathbf{T})+\sum_{ef}^{N_w}\omega_{ef}(\delta_{ef}-S_{ef}),\tag{23}$$

where $S_{ef}=\langle\ \phi_{n_e\kappa_e}(r)|\phi_{n_f\kappa_f}(r)\rangle$ is the overlap between spinors e and f. $\{\omega_{ef}\}$ are the Lagrange multipliers and the diagonal elements ω_{ee} are related to the fractional occupations q_{ee} and orbital energies ϵ_e by $\omega_{ee}=q_{ee}\epsilon_e$. Since an orthonormal trial set of radial spinors was assumed,

$$S_{ef}=S^{LL}_{ef}+S^{SS}_{ef}=\delta_{ef}.$$

Finally, the variation of the total energy functional leads to the equation

$$\frac{\partial W}{\partial T_{pe}}=\tilde{g}^{o}_{pe}+\sum_{qf}\tilde{h}^{oo}_{pe,qf}T_{qf}=0,\tag{24}$$

where the new gradient is

$$\tilde{g}^{o}_{pe}=g^{o}_{pe}-2\sum_{f}\omega_{ef}S_{fp}=g^{o}_{pe}-2\,\omega_{ep},\tag{25}$$

and the new Hessian is

$$\tilde{h}_{pe,qf}=h_{pe,qf}-2\,\omega_{ef}S_{pq}=h_{pe,qf}-2\,\omega_{ef}\delta_{pq}.\tag{26}$$

B. Simultaneous optimization of the spinor rotations and CI coefficients

The CI coefficients C_I^γ [Eq. (7)] are not constant, and variations over them must also be incorporated in the second-order energy. Consider two sets of CI coefficients—$\mathbf{C}^\gamma=\{C_I^\gamma\}$ (optimum) and $\mathbf{C}^{(0)\gamma}=\{C_I^{(0)\gamma}\}$(approximate). A Taylor expansion of the energy yields

$$\begin{aligned}E^{\gamma\mathcal{J}\pi}(\mathbf{T},\mathbf{C}^\gamma=\mathbf{C}^{(0)\gamma}+\Delta\mathbf{C}^\gamma)&=E^{\gamma\mathcal{J}\pi}(\mathbf{T},\mathbf{C}^{(0)\gamma})+\sum_I\left.\frac{\partial E^{\gamma\mathcal{J}\pi}(\mathbf{T},\mathbf{C}^\gamma)}{\partial C_I^\gamma}\right|_{C^{(0)\gamma}}\Delta C_I^\gamma\\&+\frac{1}{2}\sum_{IJ}\left.\frac{\partial^2 E^{\gamma\mathcal{J}\pi}(\mathbf{T},\mathbf{C}^\gamma)}{\partial C_I^\gamma\partial C_J^\gamma}\right|_{C^{(0)\gamma}}\Delta C_I^\gamma\Delta C_J^\gamma+\cdots.\end{aligned}\tag{27}$$

ΔC_I^γ may be expanded in terms of the CI vectors $\{C_I^{(0)\gamma'}\}$:

$$\Delta C_I^\gamma = C_I^\gamma - C_I^{(0)\gamma} = \sum_{\gamma'=1}^{N_{\rm CSF}} A_{\gamma'} C_I^{(0)\gamma'} - C_I^{(0)\gamma}$$
$$= \sum_{\gamma'=1}^{N_{\rm CSF}} (A_{\gamma'} - \delta_{\gamma'\gamma}) C_I^{(0)\gamma'}$$
$$= \sum_{\gamma'=1}^{N_{\rm CSF}} B_{\gamma'} C_I^{(0)\gamma'}. \qquad (28)$$

Now the second-order energy can be expressed in terms of ΔC_I^γ or $B_{\gamma'}$. Inserting the expression for $E^{\gamma\mathcal{J}\pi}$ [Eq. (16)] into Eq. (27) and collecting terms with up to second order in $\Delta \mathbf{C}^\gamma$ and $\mathbf{T}$, we obtain:

$$E^{(2)}(\mathbf{T},\Delta\mathbf{C}^\gamma) = E^{(2)}(\mathbf{T}) + \sum_I \left. \frac{\partial E^{(1)}(\mathbf{T})}{\partial C_I^\gamma} \right|_{C^{(0)\gamma}} \Delta C_I^\gamma$$
$$+ \frac{1}{2}\sum_{IJ} \left. \frac{\partial^2 E^{(0)}}{\partial C_I^\gamma \partial C_J^\gamma} \right|_{C^{(0)\gamma}} \Delta C_I^\gamma \Delta C_J^\gamma, \qquad (29)$$

where the abbreviated notation $E^{(i)}(\mathbf{T},\mathbf{C}^{(0)\gamma}) = E^{(i)}(\mathbf{T})$ is used. After collecting terms in Eq. (29) order by order in both $\Delta\mathbf{C}^\gamma$ and $\mathbf{T}$, we obtain

$$E^{(2)}(\mathbf{T},\Delta\mathbf{C}^\gamma) = E^{(0)} + \Delta E^{(1)}(\mathbf{T},\Delta\mathbf{C}^\gamma) + \Delta E^{(2)}(\mathbf{T},\Delta\mathbf{C}^\gamma), \qquad (30)$$

where $\Delta E^{(1)}(\mathbf{T},\Delta\mathbf{C}^\gamma)$ is given by

$$\Delta E^{(1)}(\mathbf{T},\Delta\mathbf{C}^\gamma) = \Delta E^{c(1)} + \Delta E^{o(1)}.$$

$\Delta E^{o(1)}$ is defined in equation (18), and upper indices c and o represent the CI and orbital variations, respectively:

$$\Delta E^{c(1)} = 2\sum_{IJ} C_J^{(0)\gamma} H_{IJ} \Delta C_I^\gamma = 2\sum_{IJ}\sum_{\gamma'} C_J^{(0)\gamma} H_{IJ} C_I^{(0)\gamma'} B_{\gamma'}$$
$$= 2\sum_{\gamma'} E^{(0)\gamma'} B_{\gamma'} \delta_{\gamma'\gamma} = 2E^{(0)\gamma} B_\gamma. \qquad (31)$$

Second-order energy correction is more complex and it includes mixed terms:

$$\Delta E^{(2)}(\mathbf{T},\Delta\mathbf{C}^\gamma) = \Delta E^{cc(2)} + \Delta E^{oo(2)} + \Delta E^{oc(2)},$$

where

$$\Delta E^{cc(2)} = \frac{1}{2}\sum_{IJ} \left. \frac{\partial^2 E^{(0)}(\mathbf{T})}{\partial C_I^\gamma \partial C_J^\gamma} \right|_{C^{(0)\gamma}} \Delta C_I^\gamma \Delta C_J^\gamma = \sum_{IJ} H_{IJ} \Delta C_I^\gamma \Delta C_J^\gamma$$
$$= \sum_{\gamma'} E^{(0)\gamma'} B_{\gamma'}^2, \qquad (32)$$

$$\Delta E^{co(2)} = \Delta E^{oc(2)} = \sum_I \left. \frac{\partial \Delta E^{(1)}(\mathbf{T})}{\partial C_I^\gamma} \right|_{C^{(0)\gamma}} \Delta C_I^\gamma$$
$$= \sum_{\gamma'} \left(\sum_I \left. \frac{\partial \Delta E^{(1)}(\mathbf{T})}{\partial C_I^\gamma} \right|_{C^{(0)\gamma}} C_I^{(0)\gamma'} \right) B_{\gamma'}. \qquad (33)$$

The terms with the upper index o arise only from $E^{(2)}(\mathbf{T})$. There are additional terms in the self-consistent field procedure due to changes in CI coefficients. Inserting $\partial \Delta E^{(1)}(\mathbf{T})/\partial T_{pe}$ from Eq. (21) gives us

$$\frac{\partial \Delta E^{co(2)}}{\partial T_{pe}} = \sum_{\gamma'} \left(\sum_I \left. \frac{\partial^2 \Delta E^{(1)}(\mathbf{T})}{\partial C_I^\gamma \partial T_{pe}} \right|_{C^{(0)\gamma}} C_I^{(0)\gamma'} \right) B_{\gamma'}$$
$$= \sum_{\gamma'} \sum_I \left[\sum_\alpha^{N_t} t_\alpha^I \{ I(pb_\alpha)\,\delta(e,a_\alpha) + I(a_\alpha p)\,\delta(e,b_\alpha)\} + \sum_{\beta=1}^{N_V} V_\beta^I \{ R^{\nu\beta}(pb_\beta,c_\beta d_\beta)\,\delta(e,a_\beta) \right.$$
$$\left. + R^{\nu\beta}(a_\beta p,c_\beta d_\beta)\,\delta(e,b_\beta) + R^{\nu\beta}(a_\beta b_\beta,pd_\beta)\,\delta(e,c_\beta) + R^{\nu\beta}(a_\beta b_\beta,c_\beta p)\,\delta(e,d_\beta)\} \right] C_I^{(0)\gamma'} B_{\gamma'}. \qquad (34)$$

If we define

$$h_{\gamma',pe}^{co} = h_{pe,\gamma'}^{oc} = \sum_I^{N_{\rm CSF}} \left[\sum_\alpha^{N_t} t_\alpha^I \{ I(pb_\alpha)\,\delta(e,a_\alpha) + I(a_\alpha p)\,\delta(e,b_\alpha)\} + \sum_{\beta=1}^{N_V} V_\beta^I \{ R^{\nu\beta}(pb_\beta,c_\beta d_\beta)\,\delta(e,a_\beta) + R^{\nu\beta}(a_\beta p,c_\beta d_\beta)\,\delta(e,b_\beta) \right.$$
$$\left. + R^{\nu\beta}(a_\beta b_\beta,pd_\beta)\,\delta(e,c_\beta) + R^{\nu\beta}(a_\beta b_\beta,c_\beta p)\,\delta(e,d_\beta)\} \right] C_I^{(0)\gamma'}, \qquad (35)$$

with

$$t_{\alpha}^{K}=\left.\frac{\partial t_{\alpha}}{\partial C_{K}^{\gamma}}\right|_{C^{(0)\gamma}}$$

$$=\sum_{\alpha'=1}^{N_t} t_{\alpha'}^{IJ}\delta(\alpha,\alpha')\{C_J^{(0)\gamma}\delta(I,K)+C_I^{(0)\gamma}\delta(J,K)\},\tag{36}$$

$$V_{\beta}^{K}=\left.\frac{\partial V_{\beta}}{\partial C_{K}^{\gamma}}\right|_{C^{(0)\gamma}}$$

$$=\sum_{\beta'=1}^{N_V} V_{\beta'}^{IJ}\delta(\beta,\beta')\{C_J^{(0)\gamma}\delta(I,K)+C_I^{(0)\gamma}\delta(J,K)\},\tag{37}$$

then

$$\frac{\partial\Delta E^{co(2)}}{\partial T_{pe}}=\sum_{\gamma'}^{N_c} h_{pe,\gamma'}^{oc}B_{\gamma'}\,.\tag{38}$$

The minimum of $E^{(2)}(\mathbf{T},\Delta\mathbf{C}^{\gamma})$ with respect to $B_{\gamma'}$ can be obtained easily using Eqs. (31) and (32):

$$\frac{\partial\Delta E^{c(1)}}{\partial B_{\gamma'}}=g_{\gamma'}^{c}=2E^{(0)\gamma}\delta_{\gamma'\gamma},\tag{39}$$

$$\frac{\partial\Delta E^{cc(2)}}{\partial B_{\gamma'}}=2E^{(0)\gamma'}B_{\gamma'}\,,\tag{40}$$

$$\frac{\partial\Delta E^{cc(2)}}{\partial B_{\gamma'}\partial B_{\gamma''}}=h_{\gamma',\gamma''=}^{cc}2E^{\gamma'}\delta_{\gamma'\gamma''}\,,\tag{41}$$

$$\frac{\partial\Delta E^{co(2)}}{\partial B_{\gamma'}}=\sum_{qf} h_{\gamma',qf}^{oc}T_{qf}\,.\tag{42}$$

Finally,

$$\frac{\partial E^{(2)}(\mathbf{T},\Delta\mathbf{C}^{\gamma})}{\partial B_{\gamma'}}=2E^{\gamma'}(\delta_{\gamma'\gamma}+B_{\gamma'})+\sum_{qf} h_{\gamma',qf}^{co}T_{qf}.\tag{43}$$

The mixed terms are more complicated, because here the variations of spinors and CI coefficients mix. In order to have a quadratically convergent MC method we must include these terms.

If we add $B_{\gamma'}$ to our set of variational parameters,

$$\tilde{g}_{pe}^{o}+\sum_{qf}\tilde{h}_{pe,qf}^{oo}T_{qf}+\sum_{\gamma'} h_{pe,\gamma'}^{oc}B_{\gamma'}=0\tag{44}$$

and

$$g_{\gamma'}^{c}+\sum_{qf} h_{\gamma',qf}^{co}T_{qf}+\sum_{\gamma''} h_{\gamma',\gamma''}^{cc}B_{\gamma''}=0.\tag{45}$$

As with the spinor orthogonality constraints, the normalization condition $\Sigma_{\gamma'}A_{\gamma'}A_{\gamma'}=1$ of the CI vectors must be incorporated:

$$W=E^{(2)}(\mathbf{T},\Delta\mathbf{C}^{\gamma})+\sum_{ef}\omega_{ef}(\delta_{ef}-S_{ef})$$

$$+\lambda\left(1-\sum_{\gamma'}A_{\gamma'}A_{\gamma'}\right).\tag{46}$$

The orthogonality constraints contribute to the CI gradient and Hessian matrix in the following way: $\tilde{g}_{\gamma'}^{c}=g_{\gamma'}^{c}-2\lambda$ and $\tilde{h}_{\gamma',\gamma''}^{cc}=h_{\gamma',\gamma''}^{cc}-2\lambda\,\delta(\gamma',\gamma'')$. The off-diagonal mixed Hessian matrix elements $h_{nm,\gamma'}^{oc}$ and $h_{\gamma',g\xi}^{co}$ remain the same. Using Eqs. (44)–(46), we obtain the second-order Newton-Raphson equation

$$\begin{pmatrix}\tilde{g}_{pe}^{o}\\ \tilde{g}_{\gamma'}^{c}\end{pmatrix}+\sum_{qf\gamma''}\begin{pmatrix}\tilde{h}_{pe,qf}^{oo} & h_{pe,\gamma''}^{oc}\\ h_{\gamma',qf}^{co} & \tilde{h}_{\gamma',\gamma''}^{cc}\end{pmatrix}\begin{pmatrix}T_{qf}\\ B_{\gamma''}\end{pmatrix}=\begin{pmatrix}0\\ 0\end{pmatrix}.\tag{47}$$

The Hessian matrix possesses N_{κ} positive and N_{κ} negative eigenvalues corresponding to a minimum and a maximum, respectively, in the space of large and small component parameters. Therefore, the energy functional is minimized with respect to spinor rotations between the occupied electronic spinors and the positive-energy virtual spinors, and it is maximized with respect to spinor rotations between the occupied electronic spinors and the negative-energy spinors.

C. Relativistic multireference configuration interaction

In Sec. II B, we derived a Newton-Raphson equation to determine optimum MC DFC SCF wave functions based on the DC Hamiltonian. The effects of the frequency-independent Breit interaction may be excluded or included in the multireference CI-SD step. These correspond to multireference CI-SD calculations based, respectively, on the no-pair DC and DCB Hamiltonians. In the following, they will be referred to as the DC multireference CI-SD and DCB multireference CI-SD schemes. In our DC and DCB multireference CI-SD schemes, the eigenfunctions of the DC and DCB Hamiltonians are constructed as linear combinations of CSF's generated by single and double excitations out of the reference CSF's $\Phi_I(\gamma_I\mathcal{J}\pi)$ involved in Eq. (6),

$$\Psi_{\mathrm{CI}}(\gamma\mathcal{J}\pi)=\sum_{I}^{N_{\mathrm{CSF}}}\left(C_{I0}^{\gamma}\Phi_I(\gamma_i\mathcal{J}\pi)+\sum_{i}^{n_I^S} C_{Ii}^{\gamma S}\Phi_{I;e}^{r}(\gamma_i\mathcal{J}\pi)\right.$$

$$\left.+\sum_{i}^{n_I^D} C_{Ii}^{\gamma D}\Phi_{I;ef}^{rs}(\gamma_i\mathcal{J}\pi)\right),\tag{48}$$

where n_I^S (n_I^D) is the total number of singly excited CSF's $\Phi_{I;e}^{r}$ (doubly excited $\Phi_{I;ef}^{rs}$) constructed by single (double) excitations from the reference CSF's Φ_I. $C_{Ii}^{\gamma S}$ and $C_{Ii}^{\gamma D}$ are CI-SD coefficients, which are determined variationally. Since multiconfiguration self-consistent-field calculations provide only occupied and virtual spinors of the same symmetries, virtual spinors of other symmetries are generated via a Fock operator [21] with fractionally occupied multiconfiguration self-consistent-field spinors.

In expansion (48), some of the CSF's coming from different reference states Φ_A may be identical. For example,

$$\Phi^{rs}_{A;ef} = \Phi^{r}_{B;e} \quad \text{for} \quad A \neq B.$$

In such a case, the expansion coefficients may be factorized, $(C_{Ai}\Phi^{rs}_{A;ef} + C_{Bj}\Phi^{r}_{B;e})$, and replaced by $(C_{Ai}+C_{Bj})\Phi^{r}_{B;e}$ leading to summation in Eq. (48) only over nonredundant CSF's. If the reference MC DFC SCF wave function includes the most important double excitations from the dominant CSF's, the multireference CI-SD wave function will contain important triple and quadruple excitations.

D. Computational method

All G-spinor basis set expansion calculations were done with a finite nucleus of uniform proton charge distribution. The atomic masses used for Be, Ne^{6+}, and Fe^{18+} are, respectively, 9.0, 20.0, and 55.847 amu. The large radial components of the Dirac spinors of symmetry κ are expanded in sets of Gaussian-type functions,

$$\chi^{L}_{\kappa i} = N^{L}_{\kappa i} r^{n_\kappa} \exp(-\zeta_{\kappa i} r^2), \tag{49}$$

with $n_\kappa = -\kappa$ for $\kappa < 0$, and $n_\kappa = \kappa + 1$ for $\kappa > 0$. $N^{L}_{\kappa i}$ is the normalization constant. The small component basis set $\{\chi^{S}_{\kappa i}\}$ is constructed to satisfy the boundary conditions associated with the finite nucleus [28] . The basis sets were composed of even-tempered Gaussian-type functions. The basis set exponents $\{\zeta_{\kappa i}\}$in even-tempered Gaussian-type functions are given in terms of the parameters α and β by the geometric series $\xi_{\kappa i} = \alpha\beta^{i-1}; i = 1,2,\ldots,N_\kappa$. The speed of light is taken to be 137.035 989 5 a.u. throughout this study.

The Gaussian-type functions that satisfy the boundary conditions associated with the finite nucleus automatically satisfy the so-called kinetic balance condition [29]. Basis sets of G and S spinors (S for Slater) that satisfy the boundary conditions have been shown to possess a minimum in the electronic energy surface in the basis set exponent space [30]. Dyall and Faegri recently argued [31] that, using kinetic balance to define the small component basis set in terms of the large component set implies that there is only one exponent parameter space for both components. Imposition of relativistic boundary conditions at the origin (kinetic balance in more restricted terms) is an implicit projection onto the positive-energy states in exponent space. The energy-minimum property and positive definiteness of the Hessian matrix in the exponent space of a kinetically balanced basis was demonstrated earlier in single-configuration matrix DF SCF calculations [30].

III. RESULTS AND DISCUSSION

Single-configuration DFC SCF and MC DFC SCF calculations, employing the no-pair DC Hamiltonian, were performed on ground-state Be. In the MC DFC SCF calculations, the 1s spinors are kept doubly occupied, and the remaining two electrons are distributed in the $n=2$ and 3 shells to generate various CSF's. Table I contains the results in increasing number of configurations (N_{CSF}), up to $N_{\mathrm{CSF}} = 11$. An even-tempered $25s20pG$-spinor basis set was used. The parameters α and β for the even-tempered basis set are, respectively, 0.021 967 and 2.140. For comparison, the results of numerical finite-difference three-configuration MC DFC SCF calculations made with GRASP [2] are included. The GRASP results were obtained in the point nucleus approximation. The results of our second-order three-configuration MC DFC calculations are in excellent agreement with the GRASP results. The discrepancies between the two calculations are on the order of 10 μhartree. In the default mode, the GRASP calculations with a five-configuration MC DFC failed to converge, although our second-order MC DFC calculations converged smoothly. Numerical finite-difference codes [1,2], based on first-order variation, tend to experience convergence difficulties as the number of CSF's increases, and also for heavy atoms in which there are many occupied spinors to be treated self-consistently [32].

For the five-, nine-, and 11-configuration MC DFC SCF calculations, the CI coefficients, $C_{1s^2 2s3s}$, $C_{1s^2 2p_{1/2} 3p_{1/2}}$, and $C_{1s^2 2p_{3/2} 3p_{3/2}}$, are small but nonzero. The $2s$ and $3s$ spinors are not uniquely determined because we have included all three CSF''s that arise from the electronic configurations, $1s^2 2s^2$, $1s^2 2s3s$, and $1s^2 3s^2$ and the total MC DFC energy is invariant to unitary rotations between the $2s$ and $3s$ spinors. The pairs of spinors $(2p_{1/2}, 3p_{1/2})$ and $(2p_{3/2}, 3p_{3/2})$, are not uniquely defined for the same reason. Thus, upon convergence of the Newton-Raphson iterative process, the first-order density matrix was diagonalized to obtain natural spinors. In Table I, the CI coefficients in the natural spinor representation are presented. The nonzero CI coefficients in parentheses are those for nonunique spinors at convergence. Our nine- and 11-configuration MC DFC SCF wave functions account for, respectively, -0.04533 and -0.04575 a.u., of DC correlation energy, both dynamic and nondynamic.

Lindroth *et al.* [33] combined several experimental and theoretical studies [35–40] to estimate nonrelativistic and relativistic energies as well as higher-order QED effects for Be^{2+} and Be^{0}. Based on their study, the best ''experimental'' estimate of the DC correlation energy of Be is -0.09433 a.u. [33]. Thus our nine- and 11-configuration MC DFC SCF calculations recover roughly 50% of the overall DC correlation energy of the system. The remaining dynamic correlation energy may be accounted for by multireference CI-SD based on the MC DFC wave functions. The CI coefficients displayed in Table I clearly indicate that multiconfiguration treatment is needed to account for nondynamic correlation in Be. Three configurations contribute significantly to the wave function.

The convergence pattern of our second-order three-configuration MC DFC SCF energy for ground-state Be is demonstrated in Table II. In the table, $|T+B|$ represents the norm of spinor and CI rotation parameters and ΔE the energy difference between successive Newton-Raphson iterations. The spinor variation parameters T and the off-diagonal elements of the unitary rotation matrix for CI coefficients B have been introduced, respectively, in Eqs. (16) and (28). Nonscreened hydrogenic spinors were used as initial guesses. Although the initial guesses are very poor, quadratic convergence with respect to spinor rotation and CI rotation param-

TABLE I. Computed MC DFC energies E_{MCDFC} (a.u.) and configuration mixing coefficients C for ground-state Be^0 in increasing CSF expansion length. The values in square brackets represent factors of powers of 10. The CI coefficients in parentheses are for nonunique spinors at MC DFC convergence.

N_{CSF}	1	3		5	9	11
	this work	this work	GRASP	this work	this work	this work
E_{MCDFC}	−14.575 892 [a]	−14.619 547	−14.619 563	−14.621 145	−14.621 223	−14.621 644
$C_{1s^2 2s^2}$	1.0	0.949 94	0.949 95	0.950 80	0.951 09	0.953 04
				(0.950 73)	(0.950 99)	(0.952 99)
$C_{1s^2 2p_{1/2}^2}$		0.180 40	0.180 39	0.177 33	0.176 82	0.172 98
				(0.177 33)	(0.176 80)	(0.172 93)
$C_{1s^2 2p_{3/2}^2}$		0.255 08	0.255 07	0.250 73	0.250 02	0.244 59
				(0.250 73)	(0.250 15)	(0.244 57)
$C_{1s^2 2s 3s}$				0.0	0.0	0.0
				(−0.011 52)	(−0.011 34)	(−0.011 32)
$C_{1s^2 3s^2}$				−0.040 84	−0.040 28	−0.040 22
				(−0.040 78)	(−0.040 20)	(−0.040 17)
$C_{1s^2 2p_{1/2} 3p_{1/2}}$					0.0	0.0
					(6.6[−5])	(1.5[−5])
$C_{1s^2 3p_{1/2}^2}$					0.003 60	0.003 52
					(0.003 54)	(0.003 45)
$C_{1s^2 2p_{3/2} 3p_{3/2}}$					0.0	0.0
					(2.3[−4])	(9.5[−5])
$C_{1s^2 3p_{3/2}^2}$					0.005 11	0.004 98
					(0.005 31)	(0.004 90)
$C_{1s^2 3d_{3/2}^2}$						−0.011 08
						(−0.011 08)
$C_{1s^2 3d_{5/2}^2}$						−0.013 57
						(−0.013 57)

[a] The single-configuration DFB energy is −14.575 189 a.u.

TABLE II. Convergence of the three-configuration MC DFC SCF energy E_{MCDFC} (a.u.), and nine-configuration complete active space DFC SCF energy E_{CAS} (a.u.), for $J=0$ ground state Be^0. Nonscreened hydrogenic spinors were used as initial guesses. The values in square brackets represent factors of powers of 10.

Iteration	$\lvert T+B \rvert$	ΔE	E_{MCDFC}	$\lvert T+B \rvert$	ΔE	E_{CAS}
0			−13.765 211			−13.766 510
1	2.61[−1]	−4.05[−1]	−14.170 616	9.75[−1]	−6.63[−1]	−14.429 424
2	3.82[−1]	−3.16[−1]	−14.486 122	6.16[−1]	−1.88[−1]	−14.617 453
3	4.20[−1]	−1.32[−1]	−14.618 161	1.36[−1]	−2.25[−3]	−14.619 703
4	5.13[−2]	−1.38[−3]	−14.619 545	1.32[−2]	−1.40[−5]	−14.619 717
5	2.02[−3]	−2.15[−6]	−14.619 547	8.70[−4]	−6.45[−8]	−14.619 717
6	1.74[−4]	−2.54[−9]	−14.619 547			

TABLE III. Computed MC DFC energies E_{MCDFC} (a.u.) and configuration mixing coefficients C for the lowest odd-parity $J=1$ state of Be^0 in increasing CSF expansion length. The values in square brackets represent factors of powers of 10.

	$N_{\mathrm{CSF}}=1$	$N_{\mathrm{CSF}}=2$	$N_{\mathrm{CSF}}=8$	$N_{\mathrm{CSF}}=14$
E_{MCDFC}	−14.337 744	−14.514 307	−14.515 871	−14.521 093
$C_{2s2p_{1/2}}$	1.0	0.816 54	0.815 74	0.812 15
$C_{2s2p_{3/2}}$		−0.577 29	−0.576 73	−0.573 48
$C_{2s3p_{1/2}}$			1.5[−4]	−3.7[−4]
$C_{2s3p_{3/2}}$			5.2[−5]	2.9[−3]
$C_{2p_{1/2}3s}$			−5.6[−5]	1.3[−4]
$C_{2p_{1/2}3d_{3/2}}$				−0.039 49
$C_{2p_{3/2}3s}$			−5.2[−5]	−7.0[−6]
$C_{2p_{3/2}3d_{3/2}}$				−0.070 52
$C_{2p_{3/2}3d_{5/2}}$				0.05 281
$C_{3s3p_{1/2}}$			−0.036 05	−0.034 68
$C_{3s3p_{3/2}}$			0.025 48	0.024 54
$C_{3p_{1/2}3d_{3/2}}$				−0.007 15
$C_{3p_{3/2}3d_{3/2}}$				−0.015 04
$C_{3p_{3/2}3d_{5/2}}$				0.011 22

eters becomes apparent in the values of ΔE after the first few Newton-Raphson iterations. In the table, the convergence pattern of the second-order complete active space DFC SCF energy E_{CAS} is also demonstrated. The nine-configuration complete active space DFC SCF wave function contains all the CSF's generated by distributing the four electrons over the spinor set $\{1s,2s,2p_{1/2},2p_{3/2}\}$. Here again, we observe quadratic convergence in the values of ΔE after the first few Newton-Raphson iterations, even though the initial guesses, nonscreened hydrogenic spinors, are poor.

Single-configuration DFC SCF and MC DFC SCF calculations were also performed on the lowest odd-parity $J=1$ state of beryllium. To our knowledge, relativistic multiconfiguration self-consistent-field calculations have never been reported on the odd-parity $J=1$ state of beryllium, presumably owing to convergence difficulties in first-order multiconfigurational self-consistent-field methods. In the MC DFC SCF calculations, 1s spinors are kept doubly occupied, and the remaining two electrons are distributed in the $n=2$ and 3 shells to generate various CSF's. Table III contains the results in increasing number of configurations up to $N_{\mathrm{CSF}}=14$. The lowest odd-parity $J=1$ state exhibits the near degeneracy characteristic of several strongly interacting configurations. For example, the configuration mixing coefficients of the strongly interacting $2s2p_{1/2}\ {}^3P_1$ and $2s2p_{3/2}\ {}^1P_1$ CSF's are, respectively, 0.812 15 and −0.573 48, for the expansion length $N_{\mathrm{CSF}}=14$.

TABLE IV. Convergence of the 14-configuration MC DFC SCF energy E_{MCDFC} (a.u.) for the lowest odd-parity $J=1$ state of Be^0. Nonscreened hydrogenic spinors were used as initial guesses. The values in square brackets represent factors of powers of 10.

NR iteration	$\lvert T+B\rvert$	ΔE	E_{MCDFC}
0			−14.393 733
1	5.58[−1]	−1.12[−1]	−14.505 729
2	1.13[0]	−1.14[−2]	−14.517 135
3	5.57[−1]	−3.50[−3]	−14.520 639
4	1.15[−1]	−4.58[−4]	−14.521 091
5	1.52[−2]	−1.68[−6]	−14.521 093
6	2.52[−3]	−4.44[−8]	−14.521 093

The convergence pattern of the second-order 14-configuration MC DFC SCF is demonstrated in Table IV. Nonscreened hydrogenic spinors were used as initial guesses. Although the initial guesses are very poor, quadratic convergence with respect to spinor rotation and CI rotation parameters becomes apparent after the first few Newton-Raphson iterations. In iteration 0, a number of CSF's possess configuration mixing coefficients comparable in magnitude ($C_{2s2p_{1/2}}=-0.438\ 50$, $C_{2s2p_{3/2}}=0.310\ 06$, $C_{2s3p_{1/2}}=0.465\ 66$, $C_{2s3p_{3/2}}=-0.329\ 21$, etc.) due to the poor trial spinors. In the next iteration, however, the coefficients of only the two strongly interacting CSF's, $2s2p_{1/2}\ {}^3P_1$ and $2s2p_{3/2}\ {}^1P_1$ become dominant and nearly convergent, $C_{2s2p_{1/2}}=0.812\ 62$ $C_{2s2p_{3/2}}=-0.574\ 98$. Convergence to the lowest odd-parity $J=1$ state is nearly as rapid as to the ground $J=0$ state primarily because the second-order energy variation, in which all active and core electrons are simultaneously subjected to unitary mixing [Eq. (13)], induces quadratic convergence even when the gradient norm is large.

Table V displays the energy separation between the ground $J=0$ and excited $J=1$ states computed by taking the difference in MC DFC SCF energies. The energy interval 21 976 cm^{-1} computed by 11-configurational MC DFC SCF for the ground $J=0$ state and 14-configurational MC DFC SCF for the odd-parity $J=1$ state agrees well with experiment [34] (21 979 cm^{-1}), although the remaining dynamical correlation is not recovered.

MC DF SCF effectively describes nondynamic correlation due to near degeneracy, but fails to account for a large fraction of dynamic correlation. To account for the remaining dynamic correlation, DC and DCB multireference CI-SD calculations based on an 11-configuration MC DFC wave-

TABLE V. MC DFC energy separation ΔE (in cm^{-1}) between the ground $J=0$ and odd-parity $J=1$ states of Be^0 in increasing CSF expansion length.

$N_{\mathrm{CSF}}^{J=0}-N_{\mathrm{CSF}}^{J=1}$	1-1	3-2	9-8	11-14	Experiment [a]
ΔE	52 267	17 651	23 122	21 976	21 979

[a] Reference [34].

TABLE VI. DC multireference CI energies $E_{\mathrm{CI}}^{\mathrm{DC}}$, and DCB multireference CI energies $E_{\mathrm{CI}}^{\mathrm{DCB}}$ (a.u.), based on an eleven-configuration MC DFC wave function and l-limit DC and DCB correlation energies $E_{\mathrm{corr}}^{\mathrm{DC}}(l)$ and $E_{\mathrm{corr}}^{\mathrm{DCB}}(l)$ for ground-state Be^0.

	f limit	g limit	h limit	extrapolated $l\rightarrow\infty$[a]
$E_{\mathrm{CI}}^{\mathrm{DC}}$	$-14.669\,402$	$-14.669\,763$	$-14.669\,921$	$-14.670\,127$
$E_{\mathrm{corr}}^{\mathrm{DC}}(l)$	$-0.093\,510$	$-0.093\,871$	$-0.094\,029$	$-0.094\,237$
$E_{\mathrm{CI}}^{\mathrm{DCB}}$	$-14.668\,884$	$-14.669\,254$	$-14.669\,411$	$-14.669\,623$
$E_{\mathrm{corr}}^{\mathrm{DCB}}(l)$	$-0.093\,695$	$-0.094\,065$	$-0.094\,222$	$-0.094\,434$

[a] Extrapolation was carried out using the formula $\Delta E(l)=E(l)-E(l-1)=A(l+1/2)^{-B}$.

function were performed on ground-state Be in increasing order of partial-wave expansion. The results are displayed in Table VI. All electrons were included in the calculations. The total DC ($E_{\mathrm{CI}}^{\mathrm{DC}}$) and DCB ($E_{\mathrm{CI}}^{\mathrm{DCB}}$) energies of the ground state were calculated, respectively, by excluding and including the frequency-independent Breit interaction in the effective electron-electron interaction. A moderately large G-spinor basis set of $25s20p17d16f14g14h$ functions was used. The total DC energy, $-14.669\,921$ a.u., obtained by relativistic multireference CI-SD calculations based on the

TABLE VII. MC DFC energies E_{MCDFC} (a.u.) and configuration mixing coefficients C for ground-state Ne^{6+} in increasing CSF expansion length. The values in square brackets represent factors of powers of 10. The CI coefficients in parentheses are for nonunique spinors at MC DFC energy convergence.

N_{SCF}	1	3		5	9	11
	this work	this work	GRASP	this work	this work	this work
E_{MCDFC}	$-110.255\,974^{a}$	$-110.377\,196$	$-110.378\,145$	$-110.378\,671$	$-110.378\,614$	$-110.380\,100$
$C_{1s^22s^2}$	1.0	0.967 59	0.967 71	0.967 80	0.967 86	0.968 56
				(0.967 80)	(0.967 86)	(0.968 56)
$C_{1s^22p_{1/2}^2}$		0.146 83	0.146 54	0.146 25	0.146 11	0.144 44
				(0.146 25)	(0.146 11)	(0.144 44)
$C_{1s^22p_{3/2}^2}$		0.205 47	0.205 10	0.204 65	0.204 47	0.202 12
				(0.204 65)	(0.204 47)	(0.202 12)
C_{1s^22s3s}				0.0	0.0	0.0
				(4.1[−4])	(4.1[−5])	(4.1[−5])
$C_{1s^23s^2}$				−0.009 62	−0.009 57	−0.009 56
				(−0.009 62)	(−0.009 57)	(−0.009 56)
$C_{1s^22p_{1/2}3p_{1/2}}$					0.0	0.0
					(1.2[−5])	(1.3[−5])
$C_{1s^23p_{1/2}^2}$					0.001 24	0.001 22
					(0.001 24)	(0.001 22)
$C_{1s^22p_{3/2}3p_{3/2}}$					0.0	0.0
					(1.5[−5])	(1.7[−5])
$C_{1s^23p_{3/2}^2}$					0.001 75	0.001 73
					(0.001 75)	(0.001 73)
$C_{1s^23d_{3/2}^2}$						−0.005 97
						(−0.005 97)
$C_{1s^23d_{5/2}^2}$						−0.007 34
						(−0.007 34)

[a] The single-configuration DFB energy is $-110.242\,103$ a.u.

TABLE VIII. DC multireference CI energies $E_{\mathrm{CI}}^{\mathrm{DC}}$ and DCB multireference CI energies $E_{\mathrm{CI}}^{\mathrm{DCB}}$ (a.u.), based on a five-configuration MC DFC wave function and l-limit DC and DCB correlation energies $E_{\mathrm{corr}}^{\mathrm{DC}}(l)$ and $E_{\mathrm{corr}}^{\mathrm{DCB}}(l)$ for ground-state Ne^{6+}.

	f limit	g limit	h limit	extrapolated ($l\to\infty$) [a]
$E_{\mathrm{CI}}^{\mathrm{DC}}$	−110.433 605	−110.434 187	−110.434 443	−110.434 789
$E_{\mathrm{corr}}^{\mathrm{DC}}(l)$	−0.177 631	−0.178 213	−0.178 469	−0.178 814
$E_{\mathrm{CI}}^{\mathrm{DCB}}$	−110.421 239	−110.421 862	−110.422 143	−110.422 540
$E_{\mathrm{corr}}^{\mathrm{DCB}}(l)$	−0.179 136	−0.179 759	−0.180 040	−0.180 437

[a] Extrapolation was carried out using the formula $\Delta E(l)=E(l)-E(l-1)=A(l+1/2)^{-B}$.

11-configuration MC DFC SCF wave function in a partial-wave expansion of $l_{\max}=5$, yields a DC correlation energy of $-0.094\,03$ a.u. The computed DC correlation energy thus accounts for 99.7% of the ''experimental'' estimate of $-0.094\,31$ a.u.. The total energies computed in increasing order of partial-wave expansion, up to $l_{\max}=5$ (h spinors), have been extrapolated to $l_{\max}\to\infty$. The extrapolated DC correlation energy $-0.094\,24$ a.u. accounts for 99.93% of the estimated DC correlation energy. The total extrapolated DC energy is $-14.670\,127$ a.u., whereas the ''experimental'' estimate of the relativistic DC and nonrelativistic energies of Be are, respectively, $-14.670\,20$ and $-14.667\,35$ a.u.[33]. The total DCB energy $-14.669\,623$ a.u. obtained by extrapolating to $l_{\max}\to\infty$ yields a correction due to the Breit interaction of $+0.000\,504$ a.u., in good agreement with $+0.000\,490$ a.u. estimated by Lindroth et al. [33].

Table VII contains the results of single-configuration and MC DFC SCF calculations on berylliumlike neon (Ne^{6+}) with as many as 11 configurations ($N_{\mathrm{CSF}}=11$). An even-tempered basis set of $26s22p$ G spinors was used. The parameters α and β for the even-tempered basis set are 0.592 446 and 1.955 56, respectively. Comparison of the Be and Ne^{6+} results shows that the CI coefficients for the dominant $1s^2 2s^2$ CSF ($C_{1s^2 2s^2}$) in Ne^{6+} is slightly larger than that in Be in every instance. The difference arises from the fact that the $2p_{3/2}$ spinor energy in Ne^{6+} is farther from the $2s_{1/2}$ energy than in Be, an increase which is due to the larger nuclear attraction in berylliumlike neon. However, as the nuclear charge Z increases further in the beryllium isoelectronic sequence, the $2s_{1/2}$ and $2p_{1/2}$ states become asymptotically degenerate [22]. The degeneracy is thus relativistic in origin. At least a two-configuration MC DFC SCF treatment ($1s_{1/2}^2 2s_{1/2}^2$ and $1s_{1/2}^2 2p_{1/2}^2$ CSF's), is necessary in the Be isoelectronic sequence because of this asymptotic degeneracy.

Table VIII displays the results of DC and DCB multireference CI-SD calculations on Ne^{6+} in increasing order of partial-wave expansion. A moderately large G-spinor basis set of $26s22p18d16f14g14h$ functions was used. The total DC energy $E_{\mathrm{DCCI}}=-110.434\,443$ a.u. obtained by multireference CI-SD based on a five-configuration MC DFC SCF wave function in a partial-wave expansion of $l_{\max}=5$, yields a DC correlation energy of $E_{\mathrm{corr}}^{\mathrm{DC}}=-0.178\,47$ a.u. The total energies computed in increasing order of partial-wave expansion, up to $l_{\max}=5$, are extrapolated to $l_{\max}\to\infty$. Although no experimental estimate is available for the berylliumlike ion, we believe that the extrapolated DC correlation energy $-0.178\,82$ a.u. accounts for at least 99.9% of the overall DC correlation energy of Ne^{6+} based on the accuracy obtained with neutral beryllium. The total DC energy obtained by extrapolation is $-110.434\,789$ a.u. The difference between the extrapolated total DC and DCB energies, 0.012 249 a.u., represents the relativistic many-body shift

TABLE IX. Computed total MC DFC and MC DFB energies (a.u.) for the lowest $J=0$, 1, and 2 states of Fe^{18+} in increasing CSF expansion length.

	$2s^2 2p_{1/2}^2 2p_{3/2}^2$	$+2s^2 2p_{1/2} 2p_{3/2}^3$	$+2s^2 2p_{3/2}^4$	$+2p_{1/2}^2 2p_{3/2}^4$	$(+3s)$	$(+3s3p_{1/2})$	$(+3s3p_{1/2}3p_{3/2})$
$J=2$							
N_{CSF}	1	2			11	45	232
DFC	−1052.185 501	−1052.252 739			−1052.259 307	−1052.267 952	−1052.284 373
DFB	−1051.797 145	−1051.866 694			−1051.873 403	−1051.882 125	−1051.898 743
J=0							
N_{CSF}	1		2	3	10	29	109
DFC	−1051.562 777		−1051.886 361	−1051.917 272	−1051.923 587	−1051.934 197	−1051.948 194
DFB	−1051.163 890		−1051.498 691	−1051.528 368	−1051.534 810	−1051.545 390	−1051.559 561
$J=1$							
N_{CSF}		1			9	43	208
DFC		−1051.841 571			−1051.848 576	−1051.852 567	−1051.873 536
DFB		−1051.461 367			−1051.468 438	−1051.472 482	−1051.493 674

TABLE X. The DC correlation energy $E_{\mathrm{corr}}^{\mathrm{DC}}$ and DCB correlation energy $E_{\mathrm{corr}}^{\mathrm{DCB}}$ (a.u.), for Fe^{18+} in increasing CSF expansion length.

	$+2s^2 2p_{1/2} 2p_{3/2}^3$	$+2s^2 2p_{3/2}^4$	$+2p_{1/2}^2 2p_{3/2}^4$	$(+3s)$	$(+3s3p_{1/2})$	$(+3s3p_{1/2}3p_{3/2})$
$J=2$						
DC	−0.067 238	−0.067 238	−0.067 238	−0.073 806	−0.082 451	−0.098 872
DCB	−0.069 549	−0.069 549	−0.069 549	−0.076 258	−0.084 950	−0.101 598
$J=0$						
DC		−0.323 584	−0.354 495	−0.360 810	−0.371 420	−0.385 417
DCB		−0.334 801	−0.364 478	−0.370 920	−0.381 500	−0.395 671
$J=1$						
DC				−0.007 005	−0.010 996	−0.031 962
DCB				−0.007 071	−0.011 115	−0.032 307

due to inclusion of the frequency-independent Breit interaction in the effective electron-electron interaction. The level shift in berylliumlike Ne^{6+} due to the Breit interaction is over 20 times larger in magnitude than that in neutral Be. For highly ionized systems, the Breit interaction significantly modifies the relativistic many-body effects.

As with berylliumlike ions, oxygenlike ions exhibit the near degeneracy characteristic of a manifold of strongly interacting configurations. Table IX displays the computed MC DFC SCF energies (E_{MCDFC}) of the lowest $J=0$ $(^3P_0)$, $J=1$ $(^3P_1)$, and $J=2$ $(^3P_2)$ even-parity states of oxygenlike iron Fe^{18+} in an increasing number of configurations. In each entry in the table, the number of CSF's (N_{CSF}) that arises from the electronic configurations displayed on the top row is given. MC Dirac-Fock-Breit (DFB) SCF calculations including the Breit interaction in the configuration-mixing step of the MC SCF algorithm have also been performed to study the effect of the Breit interaction on fine-structure term energies. The computed MC DFB SCF energies (E_{MCDFB}) for the $J=0$, 1, and 2 states are also displayed in the table. An even-tempered basis set of $24s20pG$ spinors was used. The parameters α and β for the even-tempered basis set are 0.035 944 and 2.205 10, respectively. In the MC DF SCF calculations, the $1s$ spinor was kept doubly occupied throughout and the remaining six electrons were treated as active electrons to generate various CSF's.

Within the $n=2$ complex, each of the electronic configurations $2s^2 2p_{1/2}^2 2p_{3/2}^2$ and $2s^2 2p_{1/2}^1 2p_{3/2}^3$ gives rise to a $J=2$, even-parity CSF, and these interact strongly. Two-configuration MC DFC SCF calculations for the two $J=2$ CSF's yield configuration mixing coefficients of 0.9565 and 0.2917. The $n=2$ complex gives rise to only one CSF for the $J=1$, even-parity state, which arises from the electronic configuration $2s^2 2p_{1/2}^1 2p_{3/2}^3$. Thus the $J=1$ state has no near degeneracy. On the other hand, each of the electronic configurations $2s^2 2p_{1/2}^2 2p_{3/2}^2$, $2s^2 2p_{3/2}^4$, and $2p_{1/2}^2 2p_{3/2}^4$ gives rise to a $J=0$ state, and they interact strongly. Three-configuration MC DFC SCF calculations for the three $J=0$ CSF's in the $n=2$ complex yield the configuration mixing coefficients 0.8865, −0.4604, and 0.0603, showing near degeneracy with especially strong interaction between the two CSF's arising from $2s^2 2p_{1/2}^2 2p_{3/2}^2$ and $2s^2 2p_{3/2}^4$.

The MC DFC and DFB SCF calculations displayed in the last three columns of Table IX include CSF's arising from the $n=3$ complex. The largest MC DFC and DFB SCF calculations include 232, 109, and 208 CSF's, respectively, for $J=2$, 0, and 1 even-parity states. Table X displays DC and DCB correlation energies for the $J=2$, 0, and 1 states computed in increasing CSF expansion lengths. The DC (or DCB) correlation energies were computed by subtracting the single-configuration DFC (or DFB) SCF energies from the MC DFC (or DFB) SCF energies. Because of near degeneracy and strong configuration mixing of CSF's, the $J=0$ state yields the largest correlation energy in each MC expansion. At $N_{\mathrm{CSF}}=3$ (within the $n=2$ complex), the $J=0$ state yields a DC correlation energy of −0.354 495 a.u., the bulk of which is nondynamic correlation energy. Table XI displays the MC DFC and DFB SCF energies of $J=0$ and 1 states relative to the ground $J=2$ state, i.e., the fine-structure

TABLE XI. MC DFC and MC DFB energies (a.u.) of $J=0$ and 1 states relative to the $J=2$ ground state for Fe^{18+} in increasing CSF expansion length.

	$2s^2 2p_{1/2}^2 2p_{3/2}^2$	$+2s^2 2p_{1/2} 2p_{3/2}^3$	$+2s^2 2p_{3/2}^4$	$+2p_{1/2}^2 2p_{3/2}^4$	$(+3s)$	$(+3s3p_{1/2})$	$(+3s3p_{1/2}3p_{3/2})$
$J=0$							
DC	0.622 724	0.689 962	0.366 378	0.335 467	0.335 720	0.333 755	0.336 179
DCB	0.633 255	0.702 804	0.368 003	0.338 326	0.338 593	0.336 735	0.339 182
$J=1$							
DC		0.411 168			0.410 731	0.415 385	0.410 837
DCB		0.405 327			0.404 965	0.409 643	0.405 069

TABLE XII. l-limit and extrapolated ($l_{\max}\rightarrow\infty$) DC and DCB multireference CI energies (a.u.), for the $J=2$, 0, and 1 states of Fe^{18+} based, respectively, on two-, three-, and one-reference configuration MC DFC wave functions.

	$J=2$		$J=0$		$J=1$	
	DC	DCB	DC	DCB	DC	DCB
d-limit [a]	−1052.422 699	−1052.038 799	−1052.082 711	−1051.696 386	−1052.010 543	−1051.632 509
f limit [b]	−1052.450 525	−1052.067 057	−1052.110 280	−1051.724 465	−1052.038 054	−1051.660 463
g limit [c]	−1052.458 548	−1052.075 206	−1052.118 564	−1051.732 959	−1052.046 013	−1051.668 633
h limit [d]	−1052.461 445	−1052.078 295	−1052.121 597	−1051.736 107	−1052.048 922	−1051.671 624
$l_{\max}\rightarrow\infty$ [e]	−1052.466 466	−1052.083 507	−1052.126 760	−1051.741 411	−1052.053 943	−1051.676 763

[a] Basis set $24s20p16d$.

[b] Basis set $24s20p16d14f$.

[c] Basis set $24s20p16d14f14g$.

[d] Basis set $24s20p16d14f14g14h$.

[e] Extrapolation was carried out using the formula $\Delta E(l)=E(l)-E(l-1)=A(l+1/2)^{-B}$.

term energies, in increasing CSF expansion lengths. The bulk of the experimentally determined fine-structure term energies are reproduced by the MC DFC or DFB SCF calculations within the $n=2$ complex: $J=0$ and 1 state energies computed by the three-configuration MC DFB SCF and one-configuration DFB SCF calculations are 0.338 326 a.u. and 0.405 327 a.u., respectively, above the ground $J=2$ state, while experimental values are 0.34268 ± 0.00047 and 0.40752 ± 0.00002 a.u., respectively. However, the agreement of the computed and experimental fine-structure splittings between $J=1$ and 2 states deteriorates when the size of MC DF SCF is increased by adding CSF's generated from the $n=3$ complex. Partially accounting for dynamic correlation by including the $n=3$ complex in multiconfiguration self-consistent-field calculations simply causes an imbalance in the recovery of dynamic correlation for each J state. More accurate treatment of dynamic correlation is necessary to calculate the fine-structure separations accurately.

To account accurately for dynamic correlation, DC and DCB multireference CI-SD calculations were performed for all three fine-structure states in increasing partial-wave expansion up to $l_{\max}=5$. For $J=2$, 0, and 1 even-parity states, the numbers of reference CSF's for multireference CI-SD calculations were 2, 3, and 1, respectively; these account for all the CSF's arising from the n=2 complex. The $1s_{1/2}$ electrons were excluded (frozen), and the remaining six electrons were correlated in the multireference CI-SD calculations. The results are displayed in Table XII. The l-limit ($l\leqslant5$) results were extrapolated to $l_{\max}\rightarrow\infty$ using the formula $\Delta E(l)=A(l+1/2)^{-B}$, where A and B are fitting parameters. The extrapolated energies for the three states were used to calculate the term energies of the $J=0$ and 1 states relative to the $J=2$ state. The results are summarized in Table XIII. The DCB multireference CI-SD calculations, which include the Breit interaction in the effective electron-electron interaction, result in close agreement between the calculated and experimental term energy separations, while the DC multireference CI-SD calculation does not. The relativistic many-body shift due to the Breit interaction is essential in predicting the fine-structure separations.

Table XIV summarizes the fine-structure splittings (in cm^{-1}) relative to the ground $J=2$ ($^3P_2$) state computed with our MC DF SCF and DCB multireference CI-SD methods. The table also contains the term splittings obtained by previous relativistic correlated methods and by experiment for comparison. Critical compilations of the available experimental data along the oxygen isoelectronic sequence have been carried out by Edlén [41,42] . The most extensive correlated calculations on oxygenlike iron were done by finite-difference multiconfiguration Hartree-Fock and relativistic MC DF SCF. Froese Fischer and Saha [43] applied the nonrelativistic multiconfiguration Hartree-Fock method to calculate correlation corrections for the $n=2$ complex, as well as the $n=3$ and 4 complexes. Relativistic corrections were included via the Breit-Pauli approximation. The $^3P_2$-$^3P_0$ splitting they obtained agrees well with experiment, the discrepancy between the computed value and experiment being $\approx$ 200 cm^{-1}. Cheng, Kim, and Desclaux [44] performed MC DF calculations with the CSF's generated within the $n=2$ complex. The remaining correlation correction from outside the $n=2$ complex was estimated [45] using an expansion of the nonrelativistic limit of the MC DF energy in powers of Z and the hydrogenic perturbation theory Z-expansion. As with our MC DFB SCF results in Table XI, the bulk of the fine-structure splittings are reproduced in their MC DF calculations by employing a small number of

TABLE XIII. Fine-structure term energies (a.u.) relative to the $J=2$ ground state of Fe^{18+} computed by DC multireference CI and DCB multireference CI in increasing partial-wave expansion.

	f limit		g limit		h limit		Extrapolated		
	DC	DCB	DC	DCB	DC	DCB	DC	DCB	Experiment [a]
$J=0$	0.340 25	0.342 59	0.339 98	0.342 25	0.339 85	0.342 19	0.339 70	0.342 09	0.342 68(47)
$J=1$	0.412 47	0.406 59	0.412 54	0.406 57	0.412 52	0.406 67	0.412 53	0.406 74	0.407 52(2)

[a] Reference [42]. The values in parentheses are experimental errors.

TABLE XIV. Comparison of the fine-structure term splittings (cm^{-1}) in Fe^{18+}.

Method	${}^3P_2$-${}^3P_0$	${}^3P_2$-${}^3P_1$
MC DFB SCF [a] (this work)	74 442	88 902
MCDF ($n=2$)[b]	74 232	88 950
MC Hartree-Fock ($n=2$)[c]	73 827	87 476
MC Hartree-Fock ($n=2,3,4$)[d]	75 428	90 486
MCDF+HPT[e]	76 106	89 033
DC multireference CI[f] (this work)	75 080	89 269
DC multireference CI+L.S.[g] (this work)	75 087	89 484
Experiment[h]	75 209(104)	89 440(4)

[a] Values taken from Table XI.
[b] Reference [44], $n=2$ complex MCDF calculations.
[c] Froese Fischer and Saha [43], $n=2$ complex multiconfiguration Hartree-Fock calculations.
[d] Froese Fischer and Saha [43], $n=2$, 3, and 4 complex multiconfiguration Hartree-Fock calculations.
[e] Reference [45], MCDF calculations with second-order hydrogenic many-body perturbation theory corrections.
[f] Extrapolated values taken from Table XIII.
[g] Lamb shift (L.S.) estimated by GRASP [2] is added to the DC multireference CI value.
[h] References [41,42]. The values in parentheses are experimental errors.

CSFs generated within the $n=2$ complex. Our ${}^3P_2$-${}^3P_0$ and ${}^3P_2$-${}^3P_1$ DCB multireference CI splittings are 130 and 170 cm^{-1} shy of experimental values, respectively. To account for higher-order QED effects, the Lamb shift for each fine-structure level was estimated in GRASP [2] calculations. When the Lamb shift for each fine-structure level is accounted for, the discrepancies between the computed and experimental values are further reduced, respectively, to ≈ 120 and 40 cm^{-1}.

IV. CONCLUSIONS

Here we have reported on the successful implementation and application of a second-order relativistic multiconfiguration Dirac-Fock self-consistent-field method for relativistic quantum mechanical calculations on many-electron systems. A quadratically convergent Newton-Raphson algorithm for multiconfiguration Dirac-Fock self-consistent-field calculations has been successfully developed and implemented with analytic basis sets of G spinors. Relativistic multiconfiguration Dirac-Fock self-consistent-field calculations, followed by multireference configuration-interaction calculations based on multiconfiguration self-consistent-field wave functions, have been applied to beryllium, berylliumlike neon, and oxygenlike iron, species which exhibit the near degeneracy characteristic of a manifold of strongly interacting configurations. The present formalism treats the electrons relativistically, and treats the effects of relativity and electron correlation (both dynamic and nondynamic) variationally.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation. The authors thank Dr. H. M. Quiney, Oxford University, and Dr. Y.-K. Kim, National Institute of Standards and Technology, for valuable discussions.

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