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Relativistic many-body perturbation theory for general open-shell multiplet states of atoms

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A relativistic many-body perturbation theory, which accounts for relativistic and electron-correlation effects for general open-shell multiplet states of atoms and molecules, is developed and implemented with analytic basis sets of Gaussian spinors. The theory retains the essential aspects of Møller-Plesset perturbation theory by employing the relativistic single-Fock-operator method of Koc and Ishikawa [Phys. Rev. A **49**, 794 (1994)] for general open-shell systems. Open-shell Dirac-Fock and relativistic many-body perturbation calculations are reported for the ground and low-lying excited states of Li, B^{2+}, Ne^{7+}, and Ca^{11+}. [S1050-2947(96)05006-8]

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I. INTRODUCTION

In recent years, a great deal of effort has been directed toward developing a relativistic many-body theory which accurately accounts for relativistic, electron-correlation, and quantum electrodynamic (QED) effects. Relativistic Dirac-Fock (DF) self-consistent field (SCF) and many-body perturbation theories (MBPT), which do account for relativistic and electron-correlation effects, have been developed by several groups. Discrete basis sets of both ''local'' [1–3] and ''global'' [4,5] functions as well as numerical finite-difference algorithms [6–8] have been used. 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 [1–5].

In a series of studies [1], Johnson and co-workers have employed ''local'' basis sets of spline functions to attain impressive accuracy in relativistic MBPT calculations for alkali-metal atoms and their isoelectronic sequences employing $V^{N\text{-}1}$ potentials. In the V^{N-1} potential approach, a DF SCF calculation is done on the closed-shell core, followed by a relativistic MBPT calculation constructed for the open-shell system. They have recently [2] extended the formalism to excited-state multiplets of closed-shell atoms. Ishikawa and co-workers [5,9] have developed matrix DF and relativistic MBPT for closed-shell atoms. Calculations which have employed ''global'' basis sets of G spinors (G for ''Gaussian'' after Grant [10]) have been done on a number of many-electron systems. Analytic basis set expansion in G spinors has yielded accurate results for closed-shell systems with no sign of the near-linear dependency problems reported with S-spinor (S for ''Slater'') basis sets [4,11,12]. In the present study we address the problem of applying perturbation theory to determining the effects of relativity and electron correlation in the general open-shell states of atoms and molecules.

We recently [13] employed the generalized coupling operator method [14–16] to construct a single Fock operator for open-shell DF SCF, and showed that with such an operator all closed- and open-shell spinors can be determined. 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. 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 [17] separation of the N-electron Hamiltonian is used in the perturbation theory of electron correlation. In this paper, we report a state-specific relativistic MBPT for general open-shell systems in which our single-Fock-operator method is employed for a Møller-Plesset-type separation of the relativistic many-electron Hamiltonian. The state-specific MBPT 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 dynamical correlation. The relativistic MBPT is a size-consistent theory of electron-correlation effects in atoms and molecules, a theory which leads to expressions that are directly proportional to the number of electrons in the system. We start with a general form for the total DF SCF energy expression which does not restrict the configurational form of the DF wave function, a formalism which thus applies to excited as well as to ground states.

In the next section, we outline the relativistic MBPT based on our single Fock operator for open-shell systems. In the third section, the results of matrix DF and relativistic MBPT calculations on the ground and low-lying excited states of neutral lithium, lithiumlike boron, lithiumlike neon, and fluorinelike calcium are presented.

II. STATE-SPECIFIC PERTURBATION THEORY WITH MØLLER-PLESSET PARTITIONING

The starting point for our development of state-specific MBPT is the relativistic ''no-pair'' Dirac-Coulomb (DC) Hamiltonian [18,19]:

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

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

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

Here $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are the Dirac matrices. $V_{\mathrm{nuc}}(r)$ is the nuclear attraction term,

$$V_{\mathrm{nuc}}(r) = \begin{cases} -Z/r & \text{for } r > R \\ -(Z/2R)(3 - r^2/R^2) & \text{for } r \leqslant R. \end{cases} \tag{3}$$

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 $R = (2.2677 \times 10^{-5}) A^{1/3}$. $\mathscr{L}_+ = L_+(1) L_+(2), \ldots, L_+(n)$, with $L_+(i)$ the projection operator onto the space spanned by the positive-energy eigenfunctions of the matrix DF SCF equation [19]. The projection operator $\mathscr{L}_+$ takes into account the field-theoretic condition that the negative-energy states are filled [18,19]. Throughout this study, atomic units are used and the speed of light is taken to be 137.035 989 5 a.u.

A. Single-Fock-operator method for matrix Dirac-Fock calculations

We first outline how to optimize the energy of the reference open-shell configuration state function (CSF), $\Phi_0(\gamma_0 JP)$, by the open-shell DF SCF procedure. The reference CSF is an eigenfunction of the total angular momentum and parity operators. J and P represent the total angular momentum and parity quantum numbers, respectively. γ denotes a set of quantum numbers other than J and P needed to specify the state uniquely. In general, the reference CSF is given by a linear combination of antisymmetrized products of positive-energy eigenspinors of the matrix DF SCF equation. In our single-Fock-operator method, the virtual spinors and their energies are calculated in the field of the nucleus and all electrons (V^N potential) at the DF SCF stage.

The total energy of a general open-shell reference state $|\Phi_0(\gamma_0 JP)\rangle$ can be expressed [20] as

$$E_{\mathrm{SCF}} = \langle \Phi_0(\gamma_0 JP) | H_+^{\mathrm{DC}} | \Phi_0(\gamma_0 JP) \rangle ,$$

where

$$\begin{aligned} \langle \Phi_0(\gamma_0 JP) | H_+^{\mathrm{DC}} | \Phi_0(\gamma_0 JP) \rangle \\ = \sum_{i(\in \mathscr{C})} N_i h_{Dii} + \sum_{i,j(\in \mathscr{C})} N_i N_j (J_{ij} - K_{ij}) \\ + \sum_{k(\in \mathscr{O})} f_k \left(N_k h_{Dkk} + \sum_{i(\in \mathscr{C})} N_i N_k (J_{ik} - K_{ik}) \right) \\ + \sum_{k,m(\in \mathscr{O})} (a_{km} J_{km} - b_{km} K_{km}) \end{aligned} \tag{4}$$

and where f_k is the fractional occupation of the kth open shell. The h_{Dii}, J_{ij}, and K_{ij} represent Dirac one-electron integrals, direct, and exchange integrals of the electron-electron interaction, respectively. The a_{km} and b_{km} are coupling constants, the values of which depend on the state under study. The occupation number N of the ith spinor shell is given by $N_i = 2J_i + 1$. $\mathscr{C}$ and $\mathscr{O}$ represent closed-shell and open-shell manifolds, respectively. The energy expression in Eq. (4) is not general enough to handle all multiconfigurational DF wave functions. It is restricted to single-configuration open-shell DF wave functions as well as some classes of multiconfiguration DF wave functions. Consequently the open-shell DF SCF formalism is applicable to single-configuration reference functions and to some classes of multireference model spaces [e.g., a multiconfiguration wave function for the beryllium isoelectronic sequence formed from $(1s_{1/2})^2(2s_{1/2})^2$, $(1s_{1/2})^2(2p_{1/2})^2$, and $(1s_{1/2})^2(2p_{3/2})^2$ CSFs]. The first-order variation of the total energy in Eq. (4) gives a set of Euler equations and a set of Lagrange multiplier Hermiticity conditions [14,15].

To construct a single Fock operator, one need only introduce projection operators in terms of the occupied and virtual SCF spinors,

$$\Pi_c = \mathscr{P}_c + \mathscr{P}_v, \quad \Pi_k = \mathscr{P}_k + \mathscr{P}_v, \quad k \in \mathscr{O}, \quad c \in \mathscr{C}, \tag{5}$$

with

$$\mathscr{P}_c = \sum_{i(\in \mathscr{C})} |i\rangle\langle i|, \quad \mathscr{P}_k = |k\rangle\langle k|, \tag{6}$$

and

$$\mathscr{P}_v = \sum_{v(\in \mathscr{V}_-)} |v\rangle\langle v| + \sum_{v(\in \mathscr{V}_+)} |v\rangle\langle v|, \tag{7}$$

where $\mathscr{V}_-$ and $\mathscr{V}_+$ are manifolds generated by the negative and unoccupied positive-energy branches of the DF spectrum, respectively.

The crucial difference between the nonrelativistic coupling operator formalism [14–16] and its relativistic generalization is the definition of the projection operator $\mathscr{P}_v$, which projects the spinors onto the virtual space. In the relativistic generalization, the projection operator $\mathscr{P}_v$ must be constructed from both the negative and unoccupied positive-energy branches of the DF spectrum in order to guarantee completeness [13].

$$\mathscr{P}_c + \sum_{k(\in \mathscr{O})} \mathscr{P}_k + \mathscr{P}_v = 1. \tag{8}$$

Using the projection operators introduced in Eqs. (5)–(7), a single Fock operator which satisfies the correct variational condition can be derived [13–16]. With the single Fock operator, the DF equations for a general class of open-shell systems are reduced to single pseudosecular equation form,

$$R|i\rangle = \varepsilon_i |i\rangle. \tag{9}$$

Here the single Fock operator R is given by

$$R = R_0 + T, \tag{10}$$

where

$$R_0 = \Pi_c F_c \Pi_c + \sum_{k(\in \mathscr{O})} \Pi_k F_k \Pi_k , \tag{11}$$

with

$$F_c = h_D + \sum_{j(\in\mathscr{C})} N_j(J_j - K_j) + \sum_{k(\in\mathscr{O})} f_k N_k (J_k - K_k),$$

$$F_k = f_k\left(h_D + \sum_{j(\in\mathscr{C})} N_j(J_j - K_j) \right) + \sum_{m(\in\mathscr{O})} (a_{km} J_m - b_{km} K_m),$$

and

$$\begin{aligned} T = \sum_{k(\in\mathscr{O})} & [(\lambda_{ck} - \lambda_{kc}) \mathscr{P}_c (F_k - F_c) \mathscr{P}_k \\ & + (\lambda_{kc} - \lambda_{ck}) \mathscr{P}_k (F_c - F_k) \mathscr{P}_c] \\ & + \sum_{k(\in\mathscr{O})} \sum_{m[\in\mathscr{O}(k\neq m)]} (\lambda_{mk} - \lambda_{km}) \mathscr{P}_m (F_k - F_m) \mathscr{P}_k . \end{aligned} \tag{12}$$

Here the $\{\lambda_{ij}\}$ are arbitrary, nonzero numbers satisfying the conditions $\lambda_{ij} \neq \lambda_{ji}$. We have shown that these constants can be optimized to improve SCF convergence [16]. The operator T ensures Hermiticity of the Lagrange multipliers during the iterative DF SCF procedure. It is a formal device that enables one to remove the off-diagonal multipliers and reexpress the DF equations as a pseudoeigenvalue equation involving a single Fock operator, R of Eq. (9). At convergence, the total SCF energy is identical to that computed by single-configurational or multiconfigurational jj-coupled DF equations with off-diagonal Lagrange multipliers. Matrix elements of the operator T become identically zero at SCF convergence [13], and thus only the operator R_0 enters the MBPT calculations. Because the cross terms $\mathscr{P}_v F_c \mathscr{P}_c$, $\mathscr{P}_c F_c \mathscr{P}_v$, $\mathscr{P}_v F_k \mathscr{P}_k$, and $\mathscr{P}_k F_k \mathscr{P}_v$ are identically zero at SCF convergence, the SCF spinors satisfy the eigenvalue equation

$$R_0 |i\rangle = \varepsilon_i |i\rangle, \tag{13}$$

where the Fock operator R_0 now has the following reduced form in terms of the SCF spinors:

$$\begin{aligned} R_0 = & \mathscr{P}_c F_c \mathscr{P}_c + \sum_{k(\in\mathscr{O})} \mathscr{P}_k F_k \mathscr{P}_k + \mathscr{P}_v F_c \mathscr{P}_v \\ & + \mathscr{P}_v \left(\sum_{k(\in\mathscr{O})} F_k \right) \mathscr{P}_v . \end{aligned} \tag{14}$$

The last two terms in Eq. (14) are responsible for generating the virtual spinors and their energy levels. In our relativistic MBPT calculations, we modify the virtual spinors generated in this manner by neglecting the last term. This is achieved by diagonalizing the matrix form of the operator,

$$R_0 = \mathscr{P}_c F_c \mathscr{P}_c + \sum_{k(\in\mathscr{O})} \mathscr{P}_k F_k \mathscr{P}_k + \mathscr{P}_v F_c \mathscr{P}_v . \tag{15}$$

In this form, the virtual spinors and their energy levels are generated solely by the mean-field operator F_c for the closed-shell electrons. There is an arbitrariness with the choice of virtual spinors and their energy levels, and they are usually chosen to improve convergence in low order of MBPT. The matrix form of the operators of Eqs. (5)–(13) has been presented in a previous work [13]. The SCF spinors obtained from the single-Fock-operator algorithm are automatically orthogonal to one another and are ideally suited to relativistic MBPT based on open-shell reference wave functions.

B. Relativistic many-body perturbation theory for open-shell systems

In relativistic MBPT, the N-electron Hamiltonian H_+^{DC} is partitioned into a model Hamiltonian H_0 and a perturbation V such that $H_+^{\mathrm{DC}} = H_0 + V$ [1–9]. The zero-order Hamiltonian H_0 is arbitrary but should be chosen as close to the full Hamiltonian H_+^{DC} as possible so that the perturbation series converges rapidly in low order. In practice, the zero-order Hamiltonian is most commonly chosen to be a sum of the one-electron DF operators [4,5] (i.e., Møller-Plesset partitioning) because, in such a formulation, all the perturbation corrections describe electron-correlation effects. For closed-shell systems, the best results have been obtained with the Møller-Plesset partitioning. We choose H_0 to be the sum of the single Fock operators R_0 [13] for the open-shell reference state and fully implement generalized Møller-Plesset perturbation theory applied to general open-shell reference wave functions. The generalized Møller-Plesset perturbation theory provides a hierarchy of well-defined algorithms that allow one to calculate relativistic correlation corrections in noniterative steps and, in low order, yields a large fraction of the dynamical correlation.

The N-electron Dirac-Coulomb Hamiltonian H_+^{DC} is partitioned into an unperturbed Hamiltonian and a perturbation term following Møller and Plesset [17],

$$H_+^{\mathrm{DC}} = H_0 + V, \tag{16}$$

where the unperturbed Hamiltonian H_0 is a sum of the single Fock operators R_0 [Eq. (15)],

$$H_0 = \sum_i R_0(i) \quad \text{and} \quad V = H_+^{\mathrm{DC}} - \sum_i R_0(i). \tag{17}$$

We generate the CSFs $\{\Phi_i(\gamma_i JP);\ i=1,2,...\}$ by single, double, triple,... excitations from the reference CSF, $\Phi_0(\gamma_0 JP)$, in order to expand the exact many-electron wave functions. The individual CSFs are constructed as eigenfunctions of the total angular momentum and parity operators and, in general, are expressed as linear combinations of antisymmetrized products of positive-energy SCF spinors. The SCF spinors are solutions of the single pseudoeigenvalue equation (9), and thus are mutually orthogonal. Consequently, all the CSFs $\{\Phi_i(\gamma_i JP);\ i=0,1,2,...\}$ are orthogonal to one another. The unperturbed Hamiltonian is diagonal in this space;

$$H_0 = \sum_i |\Phi_i(\gamma_i JP)\rangle E_i^{(0)} \langle \Phi_i(\gamma_i JP)| \tag{18}$$

so that

$$H_0 |\Phi_i(\gamma_i JP)\rangle = E_i^{(0)} |\Phi_i(\gamma_i JP)\rangle \quad (i=0,1,2,\ldots). \tag{19}$$

$E_i^{(0)}$ is a sum of the SCF one-electron energies $\{\varepsilon_q\}$,

$$E_i^{(0)}=\sum_q \varepsilon_q N_q n_q[\Phi_i], \tag{20}$$

where $n_q[\Phi_i]$ is the occupancy of the qth spinor in $\Phi_i(\gamma_i JP)$.

A straightforward application of Rayleigh-Schrödinger perturbation theory [17] provides the order-by-order expressions for the perturbation series for the state approximated by $|\Phi_0(\gamma_0 JP)\rangle$,

$$\Psi=\Phi_0(\gamma_0 JP)+\Phi^{(1)}(JP)+\cdots, \tag{21}$$

$$E=E_0^{(0)}+E^{(1)}+E^{(2)}+E^{(3)}+\cdots, \tag{22}$$

where

$$\Phi^{(1)}(JP)=\sum_{i=1}\Phi_i(\gamma_i JP)\{V_{i0}(E_0-E_i)^{-1}\}, \tag{23}$$

$$E_0^{(0)}+E^{(1)}=E_{\mathrm{SCF}}, \tag{24}$$

$$E^{(2)}=\sum_{i=1}V_{0i}V_{i0}(E_0-E_i)^{-1}, \tag{25}$$

$$E^{(3)}=\sum_{i,j=1}V_{0i}W_{ij}V_{j0}(E_0-E_i)^{-1}(E_0-E_j)^{-1}. \tag{26}$$

Here

$$V_{ij}=\langle\Phi_i(\gamma_i JP)|V|\Phi_j(\gamma_j JP)\rangle$$

and

$$W_{ij}=\langle\Phi_i(\gamma_i JP)|W|\Phi_j(\gamma_j JP)\rangle \quad \text{with} \quad W=V-E^{(1)}.$$

The matrix elements $\{V_{ij}\}$ and $\{W_{ij}\}$ are evaluated using the angular momentum recoupling scheme described in Ref. [20]. In our generalized Møller-Plesset formalism, the CSFs $\{\Phi_i(\gamma_i JP);\ i\neq 0\}$ generated by single excitations relative to the reference CSF do not contribute to the second- and third-order energies because the singly excited CSFs, $\Phi_i(\gamma_i JP)$, generated by the SCF spinors satisfy the generalized Brillouin theorem [21], $\langle\Phi_i(\gamma_i JP)|H_+^{\mathrm{DC}}|\Phi_0(\gamma_0 JP)\rangle=0$. Therefore $V_{i0}=0$. The CSFs generated by excitations higher than double, relative to the reference CSF, $\Phi_0(\gamma_0 JP)$, also do not contribute to the second- and third-order because for them $V_{i0}=0$ and $H_{i0}=0$.

C. Computation

In the central field approximation, the solution of the pseudosecular equation (9) takes the form

$$\phi_{n\kappa}(r)=\begin{bmatrix}P_{n\kappa}(r)\\ Q_{n\kappa}(r)\end{bmatrix}, \tag{27}$$

where $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small components of the radial wave function. In the matrix DF scheme, the radial functions are expanded in basis sets of analytic functions,

$$P_{n\kappa}(r)=\sum_i C_{n\kappa i}^L g_{\kappa i}^L(r) \tag{28}$$

and

$$Q_{n\kappa}(r)=\sum_i C_{n\kappa i}^S g_{\kappa i}^S(r), \tag{29}$$

where $\{C_{n\kappa i}^L\}$ and $\{C_{n\kappa i}^S\}$ are expansion coefficients for spinors of symmetry κ, and $\{g_{\kappa i}^L(r)\}$ and $\{g_{\kappa i}^S(r)\}$ are the large and small component basis sets, respectively. Kim [22] and Kagawa [20] pioneered the matrix DF SCF method, using basis sets of Slater-type functions to study closed- and open-shell atoms. Their work revealed a tendency for calculated energies to fall below the variational limit. This failure of the matrix DF method can be avoided by constraining ‘‘global’’ basis sets [4,5,9,11,12]. Goldman and Dalgarno [11], Drake and Goldman [12], and Quiney, Grant, and Wilson [4] have implemented the matrix DF equations by employing S spinors which avoid variational failure [4,11,12] and spurious solutions [4]. B-spline ‘‘local’’ basis sets employed by Johnson and co-workers [1] also lead to matrix Dirac-Fock equations. Instead of constraining basis sets, proper boundary conditions based on the MIT bag model are imposed to avoid variational failure in the local basis expansion DF scheme [1]. In the present study, we employ basis sets of G spinors with a representation of the nucleus as a body of finite extent [5,9].

For the large component, the basis functions are of the form [9]

$$g_{\kappa i}^L(r)=A_{\kappa i}^L r^{n_\kappa}\exp(-\zeta_{\kappa i}r^2), \tag{30}$$

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 to satisfy the boundary condition associated with the finite nucleus of uniform proton-charge distribution [9]. With the uniformly charged finite nucleus approximation, G spinors 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 G-spinor basis functions which satisfy the boundary conditions associated with the finite nucleus [5,9] automatically satisfy the so-called ‘‘kinetic balance’’ criterion [23–25] for a finite value of c.

For all the lithiumlike systems studied, even-tempered basis sets [26] of $24s22p14d12f10g10h$ G spinors were used. In basis sets of even-tempered G spinors, the exponents $\{\zeta_{\kappa i}\}$ are given in terms of the parameters α and β, according to the geometric series,

$$\zeta_{\kappa i}=\alpha\beta^{i-1}, \quad i=1,2,\ldots,N_\kappa. \tag{31}$$

In DF calculations on lithiumlike and fluorinelike species, the parameters α and β are optimized until a minimum in the DF total energy is found [27]. The optimal α and β values thus determined for, e.g., lithium are, respectively, 0.002 484 5 and 2.059 68. For lithiumlike boron, the optimal α and β values are 0.006 093 5 and 2.151 02. The radial functions that possess a different κ quantum number but the same quantum number l are expanded in the same set of basis functions (e.g., the radial functions of $p_{1/2}$ and $p_{3/2}$

TABLE I. Calculated DF and MBPT energies of Li and Li-like ions (a.u.).

	$E^{(0)}_{\mathrm{SCF}}$	$E^{(2)}_{\mathrm{DC}}$	$E^{(3)}_{\mathrm{DC}}$	$B^{(1)}$	$B^{(2)}$	Total
			Li ($Z=3$)			
$^2S_{1/2}$	−7.433 533	−0.041 517	−0.003 121	0.000 262	−0.000 102	−7.478 011
$^2P_{1/2}$	−7.365 861	−0.041 241	−0.003 278	0.000 260	−0.000 101	−7.410 221
			Li^+			
$^1S_0$	−7.237 204	−0.039 931	−0.002 966	0.000 258	−0.000 101	−7.279 944
			B^{2+} ($Z=5$)			
$^2S_{1/2}$	−23.383 328	−0.045 938	−0.002 194	0.001 433	−0.000 332	−23.430 359
$^2P_{1/2}$	−23.160 832	−0.047 811	−0.002 295	0.001 451	−0.000 325	−23.209 812
			B^{3+}			
$^1S_0$	−21.993 147	−0.042 358	−0.001 973	0.001 369	−0.000 321	−22.036 429
			Ne^{7+} ($Z=10$)			
$^2S_{1/2}$	−102.765 444	−0.049 452	−0.001 264	0.012 982	−0.001 478	−102.804 65
$^2P_{1/2}$	−102.177 510	−0.053 299	−0.001 408	0.013 630	−0.001 449	−102.220 03
			Ne^{8+}			
$^1S_0$	−93.982 747	−0.044 238	−0.001 137	0.012 110	−0.001 400	−94.017 406

symmetries are expanded in the same set of p-type radial Gaussian-type functions). The nuclei were modeled as spheres of uniform proton charge in every calculation. The model has been discussed in Ref. [9]. Atomic masses for the Li, B, Ne, and Ca atoms are, respectively, 6.94, 10.81, 20.18, and 40.08.

Virtual spinors used in the MBPT calculations were generated in the field of the nucleus and all electrons (V^N potential). The order of the partial-wave expansion (L_{max}), the highest angular momentum of the spinors included in the virtual space, is $L_{\mathrm{max}}=5$ throughout this study. The effects on the transition energies of radiative corrections, mass polarization, and reduced mass are non-negligible. In the present study, however, we neglect these effects.

III. RESULTS AND DISCUSSION

DF and MBPT calculations have been performed on the ground $^2S_{1/2}(1s^2_{1/2}2S^1_{1/2})$ and excited $^2P_{1/2}(1s^2_{1/2}2p^1_{1/2})$ states of lithium and lithiumlike ions with moderately large basis sets of $24s22p14d12f10g10h$ G spinors. The three-electron open-shell states have been chosen to assess the accuracy of our MBPT algorithm by comparing results with the high-accuracy B-spline calculations of Johnson, Blundell, and Sapirstein [1]. Table I displays the DF and MBPT energies of the $Z=3,5,10$ ions computed in the present study. In the second column of Table I, we present the open-shell DF SCF energies $E^{(0)}_{\mathrm{SCF}}$ for the ground $^2S_{1/2}$ and excited $^2P_{1/2}$ states. The third column of the table gives the second-order Dirac-Couloumb correlation energies $E^{(2)}_{\mathrm{DC}}$. The third-order Dirac-Coulomb correlation corrections $E^{(3)}_{\mathrm{DC}}$ are given in the fourth column. The second- and third-order energies are necessarily approximate due to the truncation of the partial-wave expansion ($L_{\mathrm{max}}=5$). The MBPT calculations were also performed with the frequency-independent Breit interaction included. The Breit interaction is introduced into the no-pair DC Hamiltonian H^{DC}_+ by adding the term [1,2,28–30]

$$B_{ij}=-(1/2r_{ij})\{\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j+[(\boldsymbol{\alpha}_i\cdot\mathbf{r}_{ij})(\boldsymbol{\alpha}_j\cdot\mathbf{r}_{ij})/r^2_{ij}]\} \quad (32)$$

to the instantaneous Coulomb interaction $1/r_{ij}$. In the fifth column we present the first-order Breit interaction energies $B^{(1)}$. In the sixth column the second-order correlation corrections to the Breit interaction, $B^{(2)}$, are given. $B^{(2)}$ is the difference between the second-order correlation correction evaluated with the inclusion of B_{ij} in the electron-electron interaction and the second-order DC correlation correction, $E^{(2)}_{\mathrm{DC}}$. $B^{(2)}$ in correlation energies is the relativistic many-body shift that arises from incorporation of the frequency-independent Breit interaction into the effective two-body interaction.

For all the systems considered, the DF energies for the reference $^2S_{1/2}$ and $^2P_{1/2}$ states are in excellent agreement with the numerical finite-difference DF energies. For the neutral Li atom, the DF energies −7.433 532 8 a.u. and −7.365 861 2 a.u., respectively, for the $^2S_{1/2}$ and $^2P_{1/2}$ states computed with a basis of $24s22p$ G spinors agree with the corresponding numerical DF limits −7.433 533 2 a.u. and −7.365 861 7 a.u. obtained with the numerical finite-difference DF program of Desclaux [28]. The results in Table I clearly indicate that the Dirac-Coulomb correlation correction converges rapidly as nuclear charge Z increases for the Li isoelectronic sequence; the nuclear Coulomb field becomes increasingly dominant as Z increases. While $E^{(2)}_{\mathrm{DC}}$ remains almost constant, with a slight increase in magnitude as Z increases, $E^{(3)}_{\mathrm{DC}}$ decreases in magnitude, undergoing a threefold decrease as Z increases from 3 to 10. As the nuclear charge increases, the first- and second-order Breit interaction energies increase dramatically.

In a recent MBPT study [1], Johnson, Blundell, and Sapirstein computed the contributions to the energies of the $n=2$ states for lithiumlike ions in the range $Z=3$–92 using the no-pair DC Hamiltonian with Breit and mass-polarization corrections. The starting point of their calculations was a frozen-core DF description of a three-electron ion. The high-precision MBPT calculations employed at least 40 B-spline basis functions and $L_{\mathrm{max}}=8$. The corresponding lowest-order contribution, $E^{(0)}_i$, to the energy of a valence electron is the DF eigenvalue. They computed MBPT corrections to the lowest-order energy. It is of interest to compare the rate of

TABLE II. Contributions to the energies of $2s_{1/2}$ and $2p_{1/2}$ states of Li and Li-like ions (a.u.).

	$\Delta E^{(0)}$	$\Delta E^{(2)}_{\rm DC}$	$\Delta E^{(3)}_{\rm DC}$	$\Delta B^{(1)}$	$\Delta B^{(2)}$	Total
Li (Z=3)						
$2s_{1/2}$ state						
	−0.196 329	−0.001 586	−0.000 155	0.000 004	−0.000 001	−0.198 067
		(−0.001 598)			(−0.000 001)	(−0.198 079)
Ref. [1]	−0.196 320	−0.001 649	−0.000 125	0.000 005	−0.000 002	−0.198 091
$2p_{1/2}$ state						
	−0.128 657	−0.001 310	−0.000 312	0.000 002	−0.000 000	−0.130 277
		(−0.001 312)			(−0.000 000)	(−0.130 279)
Ref. [1]	−0.128 638	−0.001 375	−0.000 145	0.000 003	−0.000 001	−0.130 156
B^{2+} (Z=5)						
$2s_{1/2}$ state						
	−1.390 181	−0.003 580	−0.000 221	0.000 064	−0.000 011	−1.393 929
		(−0.003 607)			(−0.000 013)	(−1.393 958)
Ref. [1]	−1.390 126	−0.003 719	−0.000 164	0.000 069	−0.000 018	−1.393 958
$2p_{1/2}$ state						
	−1.167 685	−0.005 453	−0.000 322	0.000 082	−0.000 004	−1.173 382
		(−0.005 479)			(−0.000 004)	(−1.173 408)
Ref. [1]	−1.167 352	−0.005 904	−0.000 335	0.000 092	−0.000 016	−1.173 515
Ne^{7+} (Z=10)						
$2s_{1/2}$ state						
	−8.782 697	−0.005 214	−0.000 127	0.000 872	−0.000 078	−8.787 244
		(−0.005 236)			(−0.000 080)	(−8.787 268)
Ref. [1]	−8.782 576	−0.005 424	−0.000 127	0.000 904	−0.000 111	−8.787 334
$2p_{1/2}$ state						
	−8.194 763	−0.009 061	−0.000 271	0.001 520	−0.000 049	−8.202 624
		(−0.009 106)			(−0.000 050)	(−8.202 670)
Ref. [1]	−8.193 839	−0.010 117	−0.000 277	0.001 601	−0.000 139	−8.202 771

convergence of the perturbation series obtained by the $V_{N\text{-}1}$ method of Johnson, Blundell, and Sapirstein [1] with that obtained by our generalized MP method based on a V^N potential. Each order of perturbation theory should be somewhat different between the two perturbation series since the N-electron Hamiltonian is partitioned differently. In order to compare the convergence pattern of our MBPT energies with those of Johnson, Blundell, and Sapirstein [1], we have evaluated, in each order of perturbation theory, the contributions to the valence electron energy by taking the differences in energies ($\Delta E^{(0)}$,$\Delta E^{(2)}_{\rm DC}$,$\Delta E^{(3)}_{\rm DC}$,$\Delta B^{(1)}$,$\Delta B^{(2)}$) between the three-electron systems and the $^1S_0$ ground-state energies of the corresponding heliumlike ions.

Table II displays the convergence patterns of the two perturbation series. Contributions to the valence electron energy computed in the present study with $L_{\rm max}$=5 are given in the first row. In the second row, the second-order correlation contributions to the valence electron energy ($\Delta E^{(2)}_{\rm DC}$ and $\Delta B^{(2)}$) extrapolated to $L_{\rm max}$=8 are given in parentheses for comparative purposes. Second-order correlation energies were computed in partial-wave expansions of $L_{\rm max}$=3, 4, and 5, and extrapolated to $L_{\rm max}$=8 assuming that the energy increments decrease as $A(L_{\rm max}+\frac{1}{2})^{-n}$, where A and n are, respectively, a proportionality constant and an exponent. In the third row, the contributions to the valence electron energy taken from Table I of Ref. [1] are presented for comparison. For all the lithiumlike ions considered, our $\Delta E^{(0)}$ are consistently larger in magnitude than those obtained by Johnson, Blundell, and Sapirstein [1]. The difference between the two zero-order energies increases dramatically as Z increases. The zero-order energies $\Delta E^{(0)}$ computed in the V^{N-1} method are a frozen-core description of the three-electron ions whereas our zero-order energies are determined self-consistently by our open-shell DF scheme in which the Coulomb one-photon diagrams are summed through all orders. The second-order corrections obtained by Johnson, Blundell, and Sapirstein are consistently larger in magnitude than those computed by our generalized MP method and offset the difference in zero-order energies. In our MBPT scheme, the zero-order Hamiltonian is chosen to be a sum of the open-shell DF operators, and thus all the perturbation corrections describe electron-correlation effects.

We have summarized in Table III the ionization potentials for the ground $^2S_{1/2}$ states and $^2P_{1/2}$-$^2S_{1/2}$ transition energies of the lithiumlike ions. The computed ionization energies, including corrections due to reduced mass taken from Table I of Ref. [1], are listed in the second column of Table III. For comparative purposes, we also list in the second column the ionization potentials of Johnson, Blundell, and Sapirstein [1], and experimental values [31] as well. The ionization potentials computed in the present study are in excellent agreement both with those obtained by Johnson, Blundell, and Sapirstein and with experimental values.

The third column of Table III shows the $^2P_{1/2}$-$^2S_{1/2}$ transition energies computed by our MBPT method along with the available experimental data [31] and the values computed

TABLE III. Ionization potentials and transition energies of Li and Li-like ions (a.u.).

		Ionization potential	$^2P_{1/2}$-$^2S_{1/2}$ transition energy
Li ($Z=3$)	This work	0.198 05	0.067 783
		(0.198 06)[a]	(0.067 793)[a]
	Ref. [1]	0.198 08	0.067 928
	Experiment[b]	0.198 14	0.067 906
B^{2+} ($Z=5$)	This work	1.393 86	0.220 51
		(1.393 89)[a]	(0.220 51)[a]
	Ref. [1]	1.393 89	0.220 41
	Experiment[b]	1.393 93	0.220 34
Ne^{7+} ($Z=10$)	This work	8.787 00	0.584 48
		(8.787 03)[a]	(0.584 46)[a]
	Ref. [1]	8.787 09	0.584 42
	Experiment[b]	8.786 72	0.583 90

[a] Ionization and transition energies computed by using the extrapolated second-order energies.

[b] Reference [31].

by the B-spline MBPT method including the Breit interaction and mass-polarization corrections [1]. The transition energies obtained in the present study with the no-pair Hamiltonian agree well with those reported by Johnson, Blundell, and Sapirstein [1] as well as with experimental values. For the lithium atom in particular the transition energies obtained by Johnson, Blundell, and Sapirstein using $L_{\max}=8$ along with the Breit and mass-polarization corrections [1] are in very good agreement with the experimental data.

Table IV shows the DF SCF energies, second-order Dirac-Coulomb correlation energies, and the first- and second-order Breit interaction energies for the lowest $^2P_{1/2}$ and $^2S_{1/2}$ states of fluorinelike calcium in increasing order of partial-wave expansion. The third-order correlation corrections for fluorinelike calcium are much more computationally demanding than those for second order, and are therefore neglected in the present study. We have also neglected the effect of radiative corrections. The DF and MBPT calculations on the $^2P_{1/2}$ and $^2S_{1/2}$ states have been performed with a moderately large basis set of $22s20p14d12f10g10h$ G spinors. In each entry in Table IV, the order of partial-wave, DF SCF, and correlation corrections for the $^2P_{1/2}$ state are given in the first row. In the second row, the DF SCF and correlation corrections for the $^2S_{1/2}$ state are given. The third row gives the $^2P_{1/2}$-$^2S_{1/2}$ excitation energy computed as the difference between the total energies of the $^2P_{1/2}$ and $^2S_{1/2}$ states. In the third column of the table, we present the open-shell DF SCF energies. The fourth column of the table gives the second-order Dirac-Coulomb correlation energies $E_{\mathrm{DC}}^{(2)}$. In the fifth and sixth columns, we present the first- and second-order Breit interaction energies $B^{(1)}$ and $B^{(2)}$. As for the lithiumlike ions, the second-order energies are necessarily approximate due to truncation of the partial-wave expansion. As the order of partial-wave expansion increases, the computed excitation energy smoothly converges to about 3.085 a.u. This value is to be compared with the experimental value 3.0937 a.u. [32]. A crude estimate of the QED effects employing the one-electron formula indicates that the effect of the Lamb shift on the excitation energy will be of the order of 0.001 a.u. The residual discrepancy between theory and experiment is attributed to the effects of third-

TABLE IV. Calcualted DF and MBPT energies of F-like calcium in increasing partial-wave expansion (a.u.).

		DF SCF	$E_{\mathrm{DC}}^{(2)}$	$B^{(1)}$	$B^{(2)}$	Total
$L_{\max}=2$	$^2P_{1/2}$	−621.429 63	−0.276 54	0.170 17	−0.007 74	−621.543 74
	$^2S_{1/2}$	−618.250 83	−0.367 78	0.163 59	−0.008 01	−618.463 02
	EE[a]	3.080 7				
$L_{\max}=3$	$^2P_{1/2}$	−621.429 63	−0.316 61	0.170 17	−0.008 52	−621.584 59
	$^2S_{1/2}$	−618.250 83	−0.402 12	0.163 59	−0.008 78	−618.498 13
	EE[a]	3.086 5				
$L_{\max}=4$	$^2P_{1/2}$	−621.429 63	−0.330 23	0.170 17	−0.008 91	−621.598 60
	$^2S_{1/2}$	−618.250 83	−0.416 69	0.163 59	−0.009 19	−618.513 11
	EE[a]	3.085 5				
$L_{\max}=5$	$^2P_{1/2}$	−621.429 63	−0.335 37	0.170 17	−0.009 13	−621.603 97
	$^2S_{1/2}$	−618.250 83	−0.422 09	0.163 59	−0.009 43	−618.518 75
	EE[a]	3.085 2				
	EE[b]	3.093 7	(experiment)			

[a] Computed $^2P_{1/2}$-$^2S_{1/2}$ excitation energy.

[b] Experimental excitation energy: Ref. [32].

order correlation corrections and Lamb shifts neglected in the present study.

IV. CONCLUSIONS

We have implemented a reliable procedure for performing relativistic MBPT calculations on ground and excited multiplet states of atoms and ions. We have chosen the zero-order Hamiltonian to be the sum of single Fock operators for the open-shell reference state and developed a relativistic MBPT method which employs a full implementation of generalized Møller-Plesset perturbation theory applied to a general class of open-shell systems. The generalized Møller-Plesset perturbation theory provides a hierarchy of well-defined algorithms that allow one to calculate relativistic correlation corrections in noniterative steps and, in low order, yields a large fraction of the dynamical correlation. The state-specific MBPT algorithm has been applied to both closed- and open-shell systems and has proven to be capable of accuracy comparable to that of the best MBPT calculations [1] on the $n=2$ states of lithiumlike ions.

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