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Relativistic many-body perturbation-theory calculations based on Dirac-Fock-Breit wave functions

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A relativistic many-body perturbation theory based on the Dirac-Fock-Breit wave functions has been developed and implemented by employing analytic basis sets of Gaussian-type functions. The instantaneous Coulomb and low-frequency Breit interactions are treated using a unified formalism in both the construction of the Dirac-Fock-Breit self-consistent-field atomic potential and in the evaluation of many-body perturbation-theory diagrams. The relativistic many-body perturbation-theory calculations have been performed on the helium atom and ions of the helium isoelectronic sequence up to $Z = 50$. The contribution of the low-frequency Breit interaction to the relativistic correlation energy is examined for the helium isoelectronic sequence.

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I. INTRODUCTION

In recent years, accurate experimental studies on relativistic and quantum electrodynamic effects have been extended beyond one-electron systems by using newly developed advanced ion sources to produce highly ionized high-Z species. These experimental studies, in turn, have prompted increasingly accurate theoretical calculations on many-electron systems.

Accurate treatment of many-electron systems makes it necessary to go beyond the independent-particle-level approach to include electron correlation as well as relativistic and quantum-electrodynamical effects. In high-Z systems, relativistic and electron-correlation effects are strongly intertwined. Therefore, approaches that simultaneously take into account both relativistic and correlation effects are desirable as they can deal with the nonadditive interplay of these effects in atoms and molecules [1–14]. Relativistic many-body perturbation theory (MBPT), which simultaneously accounts for both relativistic and electron-correlation effects, was developed by a number of groups using discrete basis sets of "local" [2,8,9] and "global" [4,7,13] functions.

The MBPT, introduced in atomic physics by Kelly [15], provides a powerful and systematic approach to the calculation of atomic and molecular properties. Atomic MBPT calculations using the finite-difference method [1,6,14], however, can be very laborious because the construction of sufficiently complete sets of functions for correlated calculations is difficult. The relativistic MBPT algorithm, based on the algebraic approximation [2,4,7–9,13], i.e., an expansion in analytic basis sets, has the distinct advantage over those based on a numerical finite-difference approach in that it provides the compact representation of the Dirac spectrum, and facilitates the evaluation of the many-body diagrams by using finite summations. The discrete-basis-set-expansion approach has been shown to be comparable in accuracy with numerical finite-difference calculations [2,7,13,16].

The low-frequency Breit interaction has traditionally been treated as a first-order perturbation correction to finite-difference Dirac-Fock calculations based on the no-pair Dirac-Coulomb Hamiltonian. In fact, many successful calculations have been performed in this manner to predict fine-structure separations [11,17–19]. In their multiconfigurational finite-difference Dirac-Fock calculations on He-like ions, Gorceix *et al.* [12] have included the magnetic interaction in the multiconfigurational self-consistent-field (SCF) step and found that, in the region $Z \approx 50$, the magnetic correlation between the inner-shell electrons becomes as important as the electrostatic correlation. In the local B-spline basis-set-expansion DF and MBPT calculations on lithium-like ions, Johnson, Blundell, and Sapirstein included the lowest- and second-order correlation corrections to the Breit interaction [2]. In their approach, the retardation part was evaluated exactly in the lowest order. For these systems, the Breit interaction can have significant effects on the inner-shell orbitals and energies.

In order to study the electron correlation induced by the Breit interaction, the instantaneous Coulomb and low-frequency Breit interactions may be treated as an integral part of the effective two-electron interaction in relativistic Dirac-Fock-Breit (DFB) SCF and MBPT calculations [4,13,16]. By employing S spinors (S for "Slater" basis functions), Quiney, Grant, and Wilson have recently developed a relativistic MBPT starting from the DFB SCF wave functions [13]. Their calculations on the argon atom [13] and Ne^{8+} ion [20] revealed that the terms in the perturbation expansion corresponding to the self-consistent modification of the one-electron orbitals due to the Breit interaction, result in the most significant relativistic many-body effect.

We have recently developed a matrix DFB SCF scheme by employing analytic basis sets of even- and well-tempered Gaussian-type functions [16,21]. In this approach, the instantaneous Coulomb and low-frequency Breit interactions were treated on an equal footing as an integral part of the effective electron-electron interaction. Basis sets of G spinors (G for "Gaussian" functions) have a number of advantages in relativistic many-body calculations on atoms and molecules [7]. Basis sets of G spinors show none of the signs of near-linear-dependence difficulties reported with the basis sets of S spinors [4,22,23]. The use of large basis sets of G spinors has been shown to yield accurate results comparable to numerical finite-difference methods for highly ionized high-Z ions, as well as for neutral heavy-atom systems [7,16,21]. Although Gaussian basis sets are at a disadvantage with respect to the Slater basis in nonrelativistic calculations, because they behave improperly near a point nucleus, the advantage of the S-spinor basis [22–25] dissipates in heavy-atom systems when a finite nucleus is employed. In fact, when the nucleus is modeled as a finite body of uniform proton-charge distribution, the wave function near the origin is Gaussian [7,21]. The purpose of the present paper is to provide a description of our recently developed relativistic MBPT calculations based on our DFB wave functions computed by expansion in basis sets of G spinors. The results of the matrix DFB and relativistic MBPT calculations on He and He-like ions up to $Z=50$ are presented and relativistic correlation energies are analyzed.

II. RELATIVISTIC MBPT BASED ON DIRAC-FOCK-BREIT WAVE FUNCTIONS

For many-electron systems, the relativistic Hamiltonian cannot be expressed in closed potential form. In order to develop a relativistic many-body calculation, however, it is desirable to have an effective N-electron Hamiltonian to a desired degree of accuracy. The effective N-electron Hamiltonian approach is attractive because it translates the idea that atoms and molecules are weakly bound inhomogeneous many-electron systems in which the electron-positron pair productions are absent and particle number is conserved.

A. The relativistic no-pair Dirac-Coulomb-Breit Hamiltonian

The effective N-electron Hamiltonian for our development of matrix DFB and relativistic MBPT calculations is the so-called "no-pair" Dirac-Coulomb-Breit (DCB) Hamiltonian (in a.u.) [26,27].

$$H_+=H_0+H' , \tag{1a}$$

where

$$H_0=\sum_i F_{(i)} , \tag{1b}$$

$$F=c\boldsymbol{\alpha}\cdot\mathbf{p}+\beta c^2+V_N(r)+U(r) , \tag{1c}$$

and

$$H'=\sum_{i>j}\mathcal{L}_+V_{ij}\mathcal{L}_+-\sum_i\mathcal{L}_+U(r_i)\mathcal{L}_+ . \tag{1d}$$

Here the no-pair DCB Hamiltonian H_+ is partitioned into an unperturbed Hamiltonian H_0 and a perturbation term H' following Moller and Plesset. In Eq. (1c), F is the effective one-electron Hamiltonian for the DFB SCF pseudoeigenvalue equation, which is solved self-consistently:

$$F_\kappa\phi_{n\kappa}=\varepsilon_{n\kappa}\phi_{n\kappa} . \tag{2}$$

The effective one-electron Hamiltonian F_κ for the κth symmetry takes the form

$$F_\kappa=\begin{bmatrix} U^{LL} & c\Pi_\kappa+U^{LS} \\ c\Pi_\kappa^+ +U^{SL} & U^{SS}-2c^2 \end{bmatrix} \tag{3}$$

with

$$\Pi_\kappa=-\frac{d}{dr}+\frac{\kappa}{r}$$

and

$$\Pi_\kappa^+=\frac{d}{dr}+\frac{\kappa}{r} .$$

Here,

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

where $P(r)$ and $Q(r)$ are referred to as the large- and small-component radial functions, respectively. $V_N(r)$ is the nuclear attraction term,

$$V_N(r)=\begin{cases} -Z/r \quad \text{for } r>R , & \text{(4a)} \\ -(Z/2R)(3-r^2/R^2) \quad \text{for } r\le R . & \text{(4b)} \end{cases}$$

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 the relationship $R=2.2677\times10^{-5}\ A^{1/3}$. $U(r)$ in Eq. (1c) is the one-body mean-field potential to account approximately for the electron-electron interaction. $\mathcal{L}_+=L_+(1)L_+(2)\times\cdots\times L_+(n)$, with $L_+(i)$ the projection operator onto the space spanned by the positive-energy eigenfunctions of the DFB equations in Eq. (2). In c-number theory, the projection operator takes into account the field-theoretic condition that the negative-energy states are filled [26,27].

In Eq. (1d) the effective electron-electron interaction V_{ij} is given by the sum of the instantaneous Coulomb interaction plus the low-frequency form of the Coulomb-gauge Breit interaction operators,

$$V_{ij}=1/r_{ij}+B_{ij} , \tag{5a}$$

where

$$B_{ij}=-(1/2r_{ij})\{\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j+[(\boldsymbol{\alpha}_i\cdot\mathbf{r}_{ij})(\boldsymbol{\alpha}_j\cdot\mathbf{r}_{ij})/r_{ij}^2]\} . \tag{5b}$$

Many-body corrections evaluated numerically in terms of the low-frequency forms of the Coulomb- and Feynman-gauge interactions may be sufficiently different in no-pair theory. There is justification for choosing the Coulomb-gauge Breit operator in the "no-pair" N-electron Hamiltonian rather than the simpler Gaunt interaction in the present study. In a recent study, Sucher [28] analyzed the apparent gauge dependence of the effective potentials between electrons derived in the Coulomb and Feynman gauges, and indicated that the Feynman-gauge form of the interaction should not be used in no-virtual-pair calculations because the leading-order relativistic effects are incompletely determined.

Addition of the low-frequency Breit interaction to the instantaneous Coulomb interaction partially remedies the noncovariance of the DC Hamiltonian. Inclusion of the Breit interaction results in an effective N-electron Hamiltonian that contains all effects through order α^2. Sucher [28] argues that the no-pair DCB Hamiltonian provides a satisfactory starting point for calculations on many-electron atoms in the sense that it treats the electrons relativistically, treats the most important part of electron-electron interaction nonperturbatively, and puts the instantaneous Coulomb and low-frequency Breit interactions on the same footing in relativistic DFB SCF and MBPT calculations.

B. Matrix Dirac-Fock-Breit SCF method

Early studies claimed that a perturbative treatment of the low-frequency Breit interaction was mandatory. A number of recent studies, however, have demonstrated that this is not the case [4,13,16,21,29–31]. The no-pair DCB Hamiltonian in Eq. (1a) may be used in the variational calculations in place of the time-honored Dirac-Coulomb Hamiltonian. It is usually assumed that Breit-energy contributions are small, but even for moderate nuclear charge the Breit interaction is now known to contribute a substantial part of the correction to the total DFB SCF energy [13,21,29–31]. The low-frequency Breit interaction, which gives the leading correction to the instantaneous Coulomb interaction in quantum electrodynamics, is a two-body potential of the same general form as the instantaneous Coulomb interaction, and this term may be easily incorporated in the matrix DFB self-consistent-field procedure [4,13,16,21].

In our matrix DFB SCF calculations, both $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are expanded in terms of a set of Gaussian-type functions, $\{X^L_{\kappa i}\}$ and $\{X^S_{\kappa i}\}$ [7,16,21,32]:

$$P_{n\kappa}(r) = \sum_i X^L_{\kappa i} C^L_{n\kappa i} \tag{6a}$$

and

$$Q_{n\kappa}(r) = \sum_i X^S_{\kappa i} C^S_{n\kappa i} \ , \tag{6b}$$

where

$$X^L_{\kappa i} = \begin{cases} N_L r^{|\kappa|} \exp(-\zeta_{\kappa i} r^2) \text{ for } \kappa < 0 \ , \\ N_L r^{\kappa+1} \exp(-\zeta_{\kappa i} r^2) \text{ for } \kappa > 0 \ , \end{cases}$$

and

$$X^S_{\kappa i} = N_S \Pi^+_\kappa X^L_{\kappa i} \ .$$

Here the $\{C^L_{n\kappa i}\}$ and $\{C^S_{n\kappa i}\}$ are linear variation parameters. N_L and N_S are the normalization factors.

Klahn and Morgan [33] have shown that the rate of convergence of a variational calculation is determined by how quickly the basis functions replicate the analytic structure of the unknown function that one is trying to approximate. Our G-spinor functions mimic exactly the behavior of the wave function near the origin of a uniformly charged spherical nucleus [32]. This is precisely the reason why our G-spinor expansions exhibit fast and smooth convergence when the nucleus is modeled as a finite body of uniform proton-charge distribution [32]. Unlike the S-spinor basis functions [4,13,20,22–25], the exponent of r in the Gaussian functions does not depend on the speed of light. Therefore, our G spinors that satisfy the boundary conditions associated with the finite nucleus automatically satisfy the so-called kinetic balance for a finite value of c [21,32].

With the basis-set expansion in Eqs. (6a) and (6b), the SCF equation in Eq. (2) is cast in a matrix form,

$$\mathbf{F}_\kappa \mathbf{C}_\kappa = \mathbf{S}_\kappa \mathbf{C}_\kappa \mathbf{E}_\kappa \ .$$

Detailed accounts of the matrix DFB SCF formalism have been given in previous publications [4,16,21] and are not repeated here.

C. Relativistic MBPT scheme

Relativistic MBPT based on the algebraic approximation provides a tractable scheme for the calculation of relativistic correlation effects in atoms and molecules. By invoking a G-spinor basis-set-expansion method, the present approach not only applies to molecules in a straightforward manner, but also a compact representation of the Dirac spectrum is obtained, allowing a many-body perturbation-theory treatment with all the computational advantages [7].

In q-number theory, the negative-energy states are taken to be filled in the true vacuum state, and relativistic MBPT is conveniently described within the particle-hole second-quantized formalism in which the occupied positive-energy state as well as the negative-energy continuum are taken to be below the Fermi level [1–8]. A formalism given by Grant and Pyper [34] was used to evaluate the necessary Breit-interaction integrals for the MBPT calculations. Goldstone diagrams have been summed to compute relativistic correlation corrections up to second order. We evaluate only the positive-energy intermediate contribution of the second-order energy correction. In the no-virtual-pair approximation of Sucher [27,28], our relativistic MBPT thus yields a many-body perturbation expansion that contains the same diagrams as that from the nonrelativistic Schrödinger Hamiltonian in expansions based on Hartree-Fock wave functions [4,7]. Virtual spinors used in the study were calculated in the field of the nucleus and all the electrons (V^N potential).

Negative-energy states, as part of the complete set of states, play a role in many-body calculations. Contributions from the negative-energy states, however, are of the order of α^3, and are neglected here. In a recent study [2], Johnson, Blundell, and Sapirstein discussed in detail a pitfall when negative-energy states are also considered. In our DFB SCF calculations, the Coulomb one-photon and Breit one-photon diagrams are summed through all orders since the single-particle basis is determined self-consistently. Thus, the most important consequence of treating the low-frequency Breit interaction self-consistently is the substantial simplification in the relativistic many-body perturbation theory that results from the cancellation of these classes of diagram through all orders of perturbation theory [4,7,13]. The use of the two-body interaction operator that includes both the instantaneous Coulomb and low-frequency Breit interactions in both the self-consistent-field and MBPT calculations leads to a theory that accounts for all corrections to order α^2 [28].

D. Computation

Matrix DFB SCF and MBPT calculations on He and He-like ions up to $Z=50$ are performed by using moderately large, even-tempered basis sets of $14s\,10p\,8d\,7f\,6g\,5h\,4i$ G spinors. Thus, the order of the partial-wave expansion ($L_{\max}$), the highest angular momentum of the spinors included in the virtual space, is $L_{\max}=6$ throughout this study. In basis sets of even-tempered Gaussian functions, the exponents, $\{\zeta_{\kappa i}\}$ are given in terms of two parameters, α and β. In the present study, these parameters were taken from the previous study on the He atom and He-like ions [7]. For the He-like neon ion we have also employed larger G-spinor basis sets, $14s\,10p\,8d\,7f\,7g\,7h\,7i$ and $14s\,12p\,10d\,10f\,10g\,10h\,10i$ to study the effects of basis-set truncation on the electron-correlation energy. The Dirac-Fock SCF and MBPT calculations were also performed by excluding the Breit interaction. These are the matrix Dirac-Fock-Coulomb (DFC) SCF and MBPT calculations based on the Dirac-Coulomb (DC) Hamiltonian. The speed of light was taken to be 137.035 989 5 a.u. The nonrelativistic limit was simulated by setting the speed of light to $c=10^4$. The nuclei are modeled as spheres of uniform proton charge in all the calculations. The use of the finite nuclear model of uniform proton-charge distribution in our study is crucial because the G spinors satisfy only the boundary condition associated with the finite nuclear model. The atomic masses, A, used for He, Ne^{8+}, Ca^{18+}, Zn^{28+}, Zr^{38+}, and Ca^{48+} are, respectively, 4.0, 20.18, 40.08, 65.37, 91.22, and 118.71.

III. RESULTS AND DISCUSSION

Table I displays the SCF energies (E_{SCF}) as well as the second-order correlation corrections (E_2) for the He atom and the He-like ions up to $Z=50$. These results were computed by employing moderately large, even-tempered basis sets of $14s\,10p\,8d\,7f\,6g\,5h\,4i$ G spinors. In each entry in Table I the SCF energy ($E_{\mathrm{SCF(nr)}}$) and the second-order correlation correction ($E_{2(\mathrm{nr})}$) obtained in the nonrelativistic (nr) limit are given in the first row. In the second row, the DFC SCF energy ($E_{\mathrm{SCF(DC)}}$) and the second-order Coulomb correlation correction ($E_{2(\mathrm{DC})}$) are given. The DFC and instantaneous Coulomb correlation energies were computed by employing the DC Hamiltonian, i.e., by deleting the low-frequency Breit-interaction terms from the DCB Hamiltonian. The DFB SCF energy ($E_{\mathrm{SCF(DCB)}}$) as well as the second-order correlation energy ($E_{2(\mathrm{DCB})}$) based on the DCB Hamiltonian are given in the third row. In the last column of the table the electron-correlation energies due to the low-frequency Breit interaction ($E_{2(B)}$) are tabulated.

TABLE I. SCF and second-order correlation energies for the ground-state He-like ions (in a.u.).

		E_{SCF}	E_2	$E_{2(B)}$
He	NR	−2.861 679	−0.037 135	
($Z=2$)	DC	−2.861 812	−0.037 132	
	DCB	−2.861 748	−0.037 169	−0.000 037
Ne^{8+}	NR	−93.861 057	−0.044 368	
($Z=10$)	DC	−93.982 695	−0.044 294	
	DCB	−93.970 587	−0.045 692	−0.001 398
Ca^{18+}	NR	−387.610 430	−0.045 374	
($Z=20$)	DC	−389.665 357	−0.045 180	
	DCB	−389.563 213	−0.050 875	−0.005 695
Zn^{28+}	NR	−881.356 852	−0.045 710	
($Z=30$)	DC	−892.065 286	−0.045 517	
	DCB	−891.712 209	−0.058 152	−0.012 635
Zr^{38+}	NR	−1575.094 145	−0.045 876	
($Z=40$)	DC	−1609.865 822	−0.045 936	
	DCB	−1609.012 466	−0.068 049	−0.022 113
Sn^{48+}	NR	−2468.811 391	−0.045 976	
($Z=50$)	DC	−2556.310 106	−0.046 661	
	DCB	−2554.609 459	−0.080 851	−0.034 190

These values were computed as the difference $E_{2(\mathrm{DCB})}-E_{2(\mathrm{DC})}$.

The DFC energy, −2.861 812 a.u., of He computed with our G spinors is in excellent agreement with the value, −2.861 813 a.u., obtained by Blundell *et al.* using the B-spline expansion method [8]. For highly ionized He-like ions, the nuclear potential dominates over the electron-electron interactions, and thus the Dirac-Fock independent-particle approximation becomes an increasingly accurate approximation as Z increases. In these instances, the MBPT series converges very rapidly, and the second-order MBPT energy, in general, accounts for the total correlation correction to well over 99% accuracy [7].

The instantaneous Coulomb correlation energy for He and ions of the helium isoelectronic sequence computed by using the DC Hamiltonian remains almost constant, with a slight increase in magnitude as nuclear charge, Z, increases. In contrast, the electron correlation due to the Breit interaction, $E_{2(B)}$, increases dramatically as Z increases. For the $s_{1/2}$ and $p_{1/2}$ shells, the contribution is most significant because the magnetic interaction, the dominant term in the low-frequency Breit interaction, is a short-range interaction, which, in the classical limit, behaves as $1/r^3$. Drake has recently reported the results of high-precision nonrelativistic variational calculations with relativistic and quantum-electrodynamic corrections on a number of heliumlike ions up to $Z=100$ [35]. For the heliumlike Ne^{8+} ion, the relativistic many-body shift through order α^2 derived from Drake's calculation is −1254 μhartrees [20]. In the present study, the relativistic many-body shift including the Breit interaction computed as the difference $E_{2(\mathrm{DCB})}-E_{2(\mathrm{nr})}$, is −1324 μhartrees. This value compares well with the relativistic many-body shift derived from Drake's results at this order of approximation.

Table II displays the results of three sets of calculations on the Ne^{8+} ion obtained by increasing the size of the basis set. DFB and second-order correlation energies computed with three G-spinor basis sets, $14s\,10p\,8d\,7f\,6g\,5h\,4i$, $14s\,10p\,8d\,7f\,7g\,7h\,7i$, and $14s\,12p\,10d\,10f\,10g\,10h\,10i$, respectively, are tabulated in rows A, B, and C. The basis set exponents used for these calculations are tabulated in Table III. In the previous study [7], we have found that the effect of using larger G-spinor basis sets in s-, p-, and d-symmetry species has negligible effect on the computed electron-correlation energy since the basis sets used for these symmetry species are saturated. The effect of employing larger basis sets in f-, g-, h-, and i-symmetry species is noticeable. The improvement in the correlation energies, $E_{2(\mathrm{DC})}$ and $E_{2(\mathrm{DCB})}$, is on the order of 10^{-5} a.u. going from the $14s\,10p\,8d\,7f\,6g\,5h\,4i$ to the $14s\,10p\,8d\,7f\,7g\,7h\,7i$ basis set. The $14s\,10p\,8d\,7f\,7g\,7h\,7i$ basis set is nearly saturated, however, and the effect of enlarging the basis set is reduced by an order of magnitude, i.e., on the order of 10^{-6} a.u.

In their multiconfigurational finite-difference DF calculations on the Ne^{8+}, Ca^{18+}, Zn^{28+} and Sn^{48+} ions, Gorceix, Indelicato, and Desclaux included the magnetic interaction in the self-consistent-field step, and computed the electron-correlation energies due to both the Coulomb and magnetic interactions [12]. In Table IV the Coulomb and magnetic correlation contributions reported by Gorceix *et al.* are compared with the second-order correlation energies due to the Coulomb and low-frequency Breit interactions. In each entry in Table IV the second-order correlation contributions due to the instantaneous Coulomb and low-frequency Breit interactions are given in the first row. In the second row the Coulomb and magnetic correlation energies obtained by Gorceix *et al.* [12] are given. The Coulomb correlation energy that Gorceix *et al.* obtained for Ne^{8+} using up to f orbitals, −0.044 22 a.u., is slightly smaller in magnitude than the second-order Coulomb correlation correction that we obtained, −0.044 294 a.u., using partial-wave expansion up to $L_{\max}=6$. The third-order Coulomb correlation correction for Ne^{8+} that we obtained in a previous study is −0.001 072 a.u. [7]. Gorceix *et al.* determined the magnetic correlation in Ne^{8+} to be −1632 μhartree, whereas the correlation energy due to the Breit interaction, $E_{2(B)}$, obtained in the present study is −1398 μhartree. When the retardation contribution, which counteracts the magnetic contribution, is taken into account in their calculations, we expect that their value will give a much closer agreement with ours.

Although the magnetic correlation energy exceeds in magnitude the Coulomb correlation energy in the region $Z\approx 50$ [12], the correlation energy due to the low-frequency Breit interaction, $E_{2(B)}$, has not exceeded in magnitude the Coulomb correlation energy even at $Z\approx 50$. This is due to the retardation term that counteracts the magnetic term in the low-frequency form of the Breit interaction. Johnson, Blundell, and Sapirstein have performed B-spline basis-expansion DF SCF and MBPT calculations on the Li atom and Li-like ions [2]. Their results indicate that the second-order contribution of the low-frequency Breit interaction for the Li-like ions exceeds in magnitude the Coulomb correlation energy, $E_{2(\mathrm{DC})}$, in the region $Z\approx 74$.

TABLE II. The effects of basis-set size on the second-order energy in the Ne^{8+} ion (a.u.).

Basis set	E_2 DC	E_2 DCB
A: $14s\,10p\,8d\,7f\,6g\,5h\,4i$	−0.044 294	−0.045 692
B: $14s\,10p\,8d\,7f\,7g\,7h\,7i$	−0.044 308	−0.045 715
C: $14s\,12p\,10d\,10f\,10g\,10h\,10i$	−0.044 310	−0.045 719

TABLE III. Basis-set composition for Ne^{8+}. *A*, *B*, and *C* specify the exponents of the basis sets $14s10p8d7f6g5h4i$, $14s10p8d7f7g7h7i$, and $14s12p10d10f10g10h10i$, respectively.

α	s	p	d	f	g	h	i
317 641.33	*A,B,C*						
136 515.53	*A,B,C*						
58 671.488	*A,B,C*	*C*					
25 215.765	*A,B,C*	*C*					
10 837.203	*A,B,C*	*A,B,C*	*C*	*C*	*C*	*C*	*C*
4657.6007	*A,B,C*	*A,B,C*	*A,B,C*	*C*	*C*	*C*	*C*
2001.7383	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*B,C*	*B,C*	*B,C*
860.304 83	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*B,C*	*B,C*
369.740 83	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*
158.906 79	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*
68.294 780	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*
29.351 650	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*
12.614 720	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*A,B,C*	*B,C*
5.421 540	*A,B,C*	*A,B,C*	*C*	*C*	*C*	*C*	*C*

Table V compares the partial-wave contributions of the second-order pair correlation energies of Ne^{8+}, computed by using the basis set of *G* spinors, with those computed in the point-nucleus approximation by employing the *S*-spinor basis set [20]. In each entry in Table V the partial-wave contributions computed by using basis sets of *G* and *S* spinors [20] are given respectively, in the first and second row. The partial-wave contributions were computed by employing the DCB Hamiltonian as well, as in the nonrelativistic limit, in order to evaluate the relativistic many-body shift for each pair correlation energy. The relativistic many-body shift is given in the last column of the table. Agreement between the two sets of results is seen to be excellent. However, the results show that the finite nucleus does have a small but detectable effect, particularly for the $s_{1/2}$-pair energy at the *s* limit. The low-frequency Breit interaction is rather sensitive to the electron-nuclear effective potential near the origin because of the subtle way that the interaction couples the large and small components.

Table VI shows the partial-wave analysis of the second-order correlation energy, $E_{2(\mathrm{DCB})}$, of the Sn^{48+} ion. For this system, the computed relativistic many-body shift including the Breit interaction, $E_{2(\mathrm{DCB})}-E_{2(\mathrm{nr})}$, amounts to 34 875 μhartrees, whereas the relativistic many-body shift excluding the Breit interaction, $E_{2(\mathrm{DC})}-E_{2(\mathrm{nr})}$, is only 685 μhartrees. The terms in the partial-wave expansion for the relativistic many-body shift vary approximately as $1/l^2$, where l is the orbital angular momentum of the intermediate states. The results of DFC, DFB, SCF, and MBPT calculations show that the Breit interaction results in a significant amount of modification in relativistic many-body effects. The DC Hamiltonian accounts for only a fraction of the total relativistic correction to the correlation energy for highly ionized high-*Z* species. The bulk of the relativistic correction to the correlation energy comes from Coulomb one-photon and Breit one-photon diagrams [2,13], and these diagrammatic terms are summed to all orders when the spinors are determined self-consistently by the DFB SCF method.

As one goes to higher *Z*, the low-frequency Breit interaction does not account for the retardation interaction accurately [2,36], because the low-frequency form is no

TABLE IV. Comparison of the Coulomb and Breit correlation energies obtained by using the second-order MBPT with the correlation energies obtained by Gorceix *et al.* using the finite-difference multiconfigurational Dirac-Fock scheme (in a.u.).

	Electrostatic $E_{2(\mathrm{DC})}$	Correlation energy Low-frequency Breit $E_{2(B)}$	Magnetic
Ne^{8+}	−0.044 294	−0.001 398	
	−0.044 216		−0.001 632
Ca^{18+}	−0.045 180	−0.005 695	
	−0.044 492		−0.007 012
Zn^{28+}	−0.045 517	−0.012 635	
	−0.044 455		−0.016 34
Sn^{48+}	−0.046 661	−0.034 190	
	−0.044 371		−0.046 77

TABLE V. Comparison of the partial-wave contributions of the second-order pair-correlation energies of Ne^{8+} computed by using the *G*-spinor basis with those obtained by using the *S*-spinor basis set [20] (in μhartrees).

k	k		Nonrelativistic	DCB	Difference[a]
$s_{1/2}$	$s_{1/2}$	*G-S*	−14 109.5	−14 496.4	−386.9
		S-S	−14 104.3	−14 472.1	−367.8
$p_{1/2}$	$p_{1/2}$	*G-S*	−8277.7	−8596.6	−318.9
		S-S	−8274.9	−8593.3	−320.4
$p_{3/2}$	$p_{3/2}$	*G-S*	−16 555.5	−16 913.5	−358.0
		S-S	−16 549.7	−16 908.9	−359.2
$d_{3/2}$	$d_{3/2}$	*G-S*	−1502.4	−1579.7	−77.3
		S-S	−1499.0	−1575.7	−76.7
$d_{5/2}$	$d_{5/2}$	*G-S*	−2253.5	−2319.3	−65.8
		S-S	−2248.6	−2313.4	−64.8
$f_{5/2}$	$f_{5/2}$	*G-S*	−445.5	−478.9	−33.4
		S-S	−442.7	−475.2	−32.5
$f_{7/2}$	$f_{7/2}$	*G-S*	−594.0	−621.4	−27.4
		S-S	−590.2	−616.7	−26.5
$g_{7/2}$	$g_{7/2}$	*G-S*	−172.3	−190.2	−17.9
		S-S	−170.1	−187.2	−17.1
$g_{9/2}$	$g_{9/2}$	*G-S*	−215.4	−230.2	−14.8
		S-S	−212.6	−226.5	−13.9
$h_{9/2}$	$h_{9/2}$	*G-S*	−78.7	−89.4	−10.7
		S-S	−76.9	−86.9	−10.0
$h_{11/2}$	$h_{11/2}$	*G-S*	−94.4	−103.4	−9.0
		S-S	−92.3	−100.5	−8.2
$i_{11/2}$	$i_{11/2}$	*G-S*	−40.2	−47.1	−6.9
		S-S	−38.8	−45.0	−6.1
$i_{13/2}$	$i_{13/2}$	*G-S*	−46.9	−52.8	−5.9
		S-S	−45.3	−50.4	−5.1

[a] Relativistic many-body shift.

TABLE VI. Partial-wave analysis of the second-order correlation energy of Sn^{48+} (in μhartrees).

k	k	Nonrelativistic	DCB	Difference[a]
$s_{1/2}$	$s_{1/2}$	−14 278.2	−24 992.4	−10 714.2
$p_{1/2}$	$p_{1/2}$	−8713.4	−17 104.7	−8391.3
$p_{3/2}$	$p_{3/2}$	−17 427.6	−27 847.0	−10 419.4
$d_{3/2}$	$d_{3/2}$	−1543.6	−3185.8	−1642.2
$d_{5/2}$	$d_{5/2}$	−2315.7	−3888.6	−1572.9
$f_{5/2}$	$f_{5/2}$	−452.0	−1045.7	−593.7
$f_{7/2}$	$f_{7/2}$	−602.7	−1170.2	−567.5
$g_{7/2}$	$g_{7/2}$	−172.9	−445.5	−272.6
$g_{9/2}$	$g_{9/2}$	−216.2	−485.6	−269.4
$h_{9/2}$	$h_{9/2}$	−77.0	−213.9	−136.9
$h_{11/2}$	$h_{11/2}$	−92.5	−229.9	−137.4
$i_{11/2}$	$i_{11/2}$	−38.6	−116.3	−77.7
$i_{13/2}$	$i_{13/2}$	−45.1	−125.7	−80.6

[a] Relativistic many-body shift.

longer appropriate for interactions in which orbital-energy differences are comparable to c^2. For high-Z systems, it is necessary to treat the Breit interaction more rigorously by taking into account the frequency-dependent part of the transverse photon exchange. This may be achieved by first-order perturbation theory in the manner described by Johnson, Blundell, and Sapirstein [2].

IV. CONCLUSIONS

The relativistic many-body perturbation theory based on the Dirac-Fock-Breit wave functions has successfully been implemented by employing expansion in basis sets of Gaussian spinors. As the present study has demonstrated, the G-spinor basis-set calculations can be regarded as a highly accurate and versatile approximation in relativistic many-body calculations. The low-frequency Breit interaction, which gives the leading correction to the instantaneous Coulomb interaction in quantum electrodynamics, may be easily incorporated into the SCF and many-body perturbation calculations. The low-frequency Breit interaction results in a significant degree of modification in relativistic many-body effects, whereas the Dirac-Coulomb Hamiltonian accounts for only a fraction of the total relativistic correction to the correlation energy.

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[1] J. Andriessen, K. Raghunathan, S. N. Ray, and T. P. Das, Phys. Rev. B **15**, 2533 (1977); M. Vjed-Samii, S. N. Ray, and T. P. Das, Phys. Rev. A **20**, 1787 (1979); J. Andriessen, H. Postma, A. M. van den Brink, and T. P. Das, *ibid.* **45**, 1389 (1992).

[2] W. R. Johnson and J. Sapirstein, Phys. Rev. Lett. **57**, 1126 (1986); W. R. Johnson, M. Idrees, and J. Sapirstein, Phys. Rev. A **35**, 3218 (1987); W. R. Johnson, S. A. Blundell, and J. Sapirstein, *ibid.* **37**, 307 (1988); **37**, 2764 (1988); **41**, 1689 (1990).

[3] D. R. Beck and Z. Cai, Phys. Rev. A **37**, 4481 (1988); D. R. Beck, *ibid.* **37**, 1847 (1988); **45**, 1399 (1992).

[4] H. M. Quiney, I. P. Grant, and S. Wilson, Phys. Scr. **36**, 460 (1987); H. M. Quiney, I. P. Grant, and S. Wilson, in *Many-Body Methods in Quantum Chemistry,* edited by U. Kaldor, Lecture Notes in Chemistry Vol. 52 (Springer-Verlag, Berlin, 1989).

[5] S. Salomonson and P. Oster, Phys. Rev. A **40**, 5548 (1989).

[6] E. Lindroth, Phys. Rev. A **37**, 316 (1988).

[7] Y. Ishikawa, Phys. Rev. A **42**, 1142 (1990).

[8] S. A. Blundell, W. R. Johnson, Z. W. Liu, and J. Sapirstein, Phys. Rev. A **39**, 3768 (1989).

[9] Z. W. Liu and H. P. Kelly, Phys. Rev. A **43**, 3305 (1991).

[10] T. Kagawa, Y. Honda, and S. Kiyokawa, Phys. Rev. A **44**, 7092 (1991).

[11] Y.-K. Kim, in *Relativistic, Quantum Electrodynamic, and Weak Interaction Effects in Atoms,* Proceedings of the Conference on Relativistic Quantum Electrodynamic, and Weak Interaction Effects in Atoms, edited by W. R. Johnson, P. Mohr, and J. Sucher, AIP Conf. Proc. No. 189 (AIP, New York, 1989), p. 272.

[12] O. Gorceix, P. Indelicato, and J. P. Desclaux, J. Phys. B **20**, 639 (1987); P. Indelicato, O. Gorceix, and J. P. Desclaux, *ibid.* **20**, 651 (1987); P. Indelicato and J. P. Desclaux, Phys. Rev. A **42**, 5139 (1990).

[13] H. M. Quiney, I. P. Grant, and S. Wilson, J. Phys. B **23**, L271 (1990).

[14] K. Koc and J. Migdalek, J. Phys. B **23**, L5 (1990).

[15] H. P. Kelly, Adv. Chem. Phys. **14**, 129 (1969).

[16] Y. Ishikawa, Chem. Phys. Lett. **166**, 321 (1990).

[17] K.-N. Huang, Y.-K. Kim, K. T. Cheng, and J. P. Desclaux, Phys. Rev. Lett. **48**, 1245 (1982); Y.-K. Kim and K.-N. Huang, Phys. Rev. A **26**, 1984 (1982).

[18] B. Crasemann, K. R. Karim, and M. H. Chen, At. Data Nucl. Data Tables **36**, 356 (1987); M. H. Chen, B. Crasemann, N. Mårtensson, and B. Johansson, Phys. Rev. A **31**, 556 (1985); M. H. Chen, B. Crasemann, and H. Mark, *ibid.* **24**, 1158 (1981).

[19] D. Frye, S. Lakdawala, and L. Armstrong, Jr., Phys. Rev. A **27**, 1709 (1983).

[20] H. M. Quiney, in *The Effects of Relativity in Atoms, Molecules, and the Solid State,* edited by S. Wilson, I. P. Grant, and B. L. Gyorffy (Plenum, New York, 1991).

[21] Y. Ishikawa, H. M. Quiney, and G. L. Malli, Phys. Rev. A **43**, 3270 (1991).

[22] G. W. F. Drake and S. P. Goldman, Adv. At. Mol. Phys. **25**, 393 (1988).

[23] S. P. Goldman and A. Dalgarno, Phys. Rev. Lett. **57**, 408 (1986); S. P. Goldman, Phys. Rev. A **37**, 16 (1988); **40**, 1185 (1989).

[24] Y.-K. Kim, Phys. Rev. **154**, 17 (1967).

[25] T. Kagawa, Phys. Rev. A **12**, 2245 (1975); **22**, 2340 (1980).

[26] M. Mittleman, Phys. Rev. A **4**, 893 (1971); **5**, 2395 (1972).

[27] J. Sucher, Phys. Rev. A **22**, 348 (1980).

[28] J. Sucher, Phys. Scr. **36**, 271 (1987); J. Phys. B **21**, L585 (1988).

[29] E. Lindroth, A.-M. Mårtensson-Pendrill, A. Ynnerman, and P. Oster, J. Phys. B **22**, 2447 (1989).

[30] S. Okada, M. Shinada, and O. Matsuoka, J. Chem. Phys. **93**, 5013 (1990).

[31] F. A. Parpia, A. K. Mohanty, and E. Clementi, J. Phys. B **25**, 1 (1992).

[32] Y. Ishikawa and H. M. Quiney, Int. J. Quantum Chem. Symp. **21**, 523 (1987); Y. Ishikawa, R. Baretty, and R. C. Binning, Jr., Chem. Phys. Lett. **121**, 130 (1985).

[33] Klahn and Morgan, J. Chem. Phys. **81**, 410 (1984).

[34] I. P. Grant and N. C. Pyper, J. Phys. B **9**, 761 (1976).

[35] G. W. F. Drake, Can. J. Phys. **66**, 586 (1988).

[36] Mann and W. R. Johnson, Phys. Rev. A **4**, 41 (1971).