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Dirac-Fock-Breit self-consistent-field method: Gaussian basis-set calculations on many-electron atoms

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The self-consistent-field treatment of the frequency-independent Breit interaction is reviewed with applications to many-electron atoms. The implementation of the matrix Dirac-Fock-Breit self-consistent-field procedure is presented for Gaussian-type basis sets that show no near-linear dependency problem. The matrix Dirac-Fock-Breit procedure has the advantage over the finite-difference approach that it does not complicate the self-consistent-field procedure in basis-set expansion calculations. Basis sets of even- and well-tempered Gaussian functions were used to expand the large and small components of Dirac four-spinors. Expressions are derived for evaluating the matrix elements of the Dirac-Fock-Breit equations. Calculations done on rare-gas atoms He, Ne, Ar, Kr, and Xe and alkaline-earth metals Be, Mg, Ca, and Sr are presented.

I. INTRODUCTION

For many-electron systems, there is no exact relativistic Hamiltonian. In c-number theory, an approximate many-electron Hamiltonian consistent with quantum electrodynamics (QED) is the so-called no-pair Dirac-Coulomb (DC) Hamiltonian that separates the positive-energy states from the negative-energy ones in terms of the projection operator onto the space spanned by the products of the positive-energy eigenstates of the effective one-electron Hamiltonian.[1,2]

The no-pair DC Hamiltonian is deficient in that it is both noncovariant and inaccurate for precision calculation of fine-structure separations and binding energies of the inner-shell electrons. Adding the low-frequency Breit interaction to the instantaneous Coulomb operator introduces the leading effects of the transverse photon exchange[1-3] and partially remedies the lack of covariance of the no-pair DC Hamiltonian.[1-4]

Relativistic atomic-structure calculations are most frequently performed by employing finite-difference methods.[5-8] In these calculations, the low-frequency Breit interaction has traditionally been treated as a first-order perturbation correction to calculations based on the no-pair DC Hamiltonian.[5-8] In fact, many successful calculations have been performed in which the Breit interaction has been treated as a perturbation on the zero-order DC Hamiltonian in order to predict fine-structure separations.[9-11]

In contrast to the perturbative approach, the leading effects of transverse photon exchange may be included in the zero-order Hamiltonian by adding the frequency-independent Breit interaction to the instantaneous Coulomb operator.[1,2] This approach has the advantage that all effects through order α^2 are included in the zero-order Hamiltonian.[3] The use of such a zero-order Hamiltonian in variational calculations naturally leads to the Dirac-Fock-Breit (DFB) self-consistent-field (SCF) equations. As Quiney, Grant, and Wilson[12] pointed out, incorporation of the Breit term in the SCF process has the advantage that both the electrostatic and Breit interactions are included to the same order in SCF potentials within the algebraic approximation. The inclusion of the low-frequency Breit interaction leads to changes in the orbitals and their energies, which in turn modify the Coulomb interaction among the electrons in the SCF process. This interference between the Coulomb and Breit interactions and the resulting orbital reorganization is naturally taken into account in the matrix DFB SCF procedure.

In the region $Z \approx 50$, Gorceix, Indelicato, and Desclaux found that the magnetic correlation between the inner-shell electrons becomes as important as the electrostatic correlation.[13] For such systems, the Breit interaction can have significant effects on the inner-shell orbitals and their energies. In order to study the electron correlation induced by the Breit interaction, the instantaneous Coulomb and frequency-independent Breit interactions may be treated as an integral part of the two-electron interaction in relativistic SCF and many-body perturbation calculations.[14-16] Treating the Breit interaction together with the instantaneous Coulomb interaction has the added advantage that multiple perturbation theory calculations may be avoided.[15,16]

Mann and Johnson[8] showed that the finite energy of the exchanged photon makes a non-negligible contribution to the inner-shell binding energies of heavier systems. In an earlier study, Smith and Johnson[17] showed how to treat the finite-frequency Breit interaction in the SCF procedure. The justification for using the frequency-independent Breit interaction in the present study instead of the finite-frequency form is the added complexity of the latter. This latter effect, which is of order α^4, may be treated by perturbation theory together with the self-energy because they are closely interrelated.[15]

The purpose of the present paper is to provide a detailed description of a recently introduced matrix DFB SCF method[12,18] that treats both the instantaneous Coulomb and the low-frequency Breit interactions in the SCF process within the algebraic approximation. There are distinct advantages in approaches based on the finite basis-set expansion if the Breit interaction is to be included in the SCF procedure. Once the integrals over the Breit operator for a given set of basis functions have been calculated, there is no difficulty in including this term in the SCF process. In an earlier work, the matrix DFB SCF treatment of the low-frequency Breit interaction was outlined and prototype calculations were performed on He, He-like ions, Be, Be-like ions, and Ar.[12,14,18]

This is a successful implementation of the analytic DFB SCF procedure on truly many-electron, multiple-shell systems. The implementation of the matrix DFB SCF procedure, using Gaussian-type function (GTF) basis sets for the calculation of variational Breit energies is reviewed in Sec. II. In Sec. III, orbital and total energies as well as variational Breit energies are given for rare-gas atoms He, Ne, Ar, Kr, and Xe and alkaline-earth metals Be, Mg, Ca, and Sr. The variational Breit energies are compared with the perturbative Breit energies computed by using finite-difference DF wave functions. Our variational Breit energy of the Ar atom is also compared with the benchmark variational Breit energy computed by using the Slater-spinor (*S*-spinor) basis set.[14]

II. MATRIX DIRAC-FOCK-BREIT SCF PROCEDURE

An approximate relativistic many-electron Hamiltonian, most commonly used for relativistic many-body calculations, is the so-called Dirac-Coulomb Hamiltonian. The DC Hamiltonian is one in which one-electron effects are treated relativistically while two-electron effects are "nonrelativistic." This approximation has been scrutinized as being inconsistent with the foundation of atomic structure theory, QED.[1-3]

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

The DC Hamiltonian $H_{\rm DC}$, which is the usual starting point for relativistic atomic-structure calculations, is (in a.u.)

$$H_{\rm DC}=\sum_i h_D(i)+\sum_{\substack{i,j\\ i>j}} V_{ij} \ , \tag{1}$$

which is the sum of the one-electron Dirac Hamiltonians

$$h_D=c\boldsymbol{\alpha}\cdot\mathbf{p}+\beta c^2+V_{\rm nuc} \tag{2}$$

and the instantaneous Coulomb interactions between electrons

$$V_{ij}=1/r_{ij} \ . \tag{3}$$

$H_{\rm DC}$ has been accepted in the relativistic treatment of atomic structure, but it has been scrutinized as being inconsistent with QED. The DC Hamiltonian is deficient in that it does not contain the field-theoretic condition that the negative-energy states are filled.[1,2] In *c*-number theory, a more appropriate many-electron Hamiltonian is the so-called no-pair Hamiltonian[1,2]

$$H_+=\sum_i h_D(i)+\mathcal{L}_+\left[\sum_{\substack{i,j\\ i>j}} V_{ij}\right]\mathcal{L}_+ \ , \tag{4}$$

where $\mathcal{L}_+=L_+(1)L_+(2)\cdots L_+(n)$, with $L_+(i)$ the projection operator onto the space spanned by the positive-energy eigenfunctions of the DF operator.[2] In this form, the no-pair Hamiltonian is restricted to contributions from the positive-energy branch of the DF spectrum. The no-pair Hamiltonian H_+, however, is deficient in that it is not covariant. Use of the covariant electron-electron interaction leads, in Coulomb gauge, to the sum of the instantaneous Coulomb interaction plus the transverse photon interaction T_{12},

$$V_{12}=1/r_{12}+T_{12} \ . \tag{5}$$

In the limit as $\omega\rightarrow 0$, the frequency-independent Breit interaction is obtained from T_{12}:

$$B_{12}=-(1/2r_{12})\{\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2+[(\boldsymbol{\alpha}_1\cdot\mathbf{r}_{12})(\boldsymbol{\alpha}_2\cdot\mathbf{r}_{12})/r_{12}^2]\} \ . \tag{6}$$

There is justification for including the frequency-independent Breit interaction in the H_+ Hamiltonian. Addition of the Breit interaction to the electrostatic potential partially remedies the noncovariance of the H_+ Hamiltonian.[1,2] Inclusion of the Breit interaction results in a Hamiltonian that contains all effects through order α^2, and, in the no-pair approximation of Sucher,[1,3] yields a many-body perturbation expansion[4,15,16] which contains the same diagrams as that from the nonrelativistic Schrödinger Hamiltonian in expansions based on Hartree-Fock wave functions.

Sucher[3] argues that the no-pair Dirac-Coulomb-Breit (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 Coulomb and Breit interactions on the same footing in relativistic DFB SCF and many-body perturbation-theory calculations. Its presence does not complicate the SCF process in basis-set expansion calculations, although it does in finite-difference numerical calculations.[15] If we follow the procedure given by Mittleman,[19] the use of the no-pair DCB Hamiltonian as a starting point for variational calculations leads to the DFB SCF equations.

B. The matrix Dirac-Fock-Breit SCF method

In the DFB SCF scheme, the behavior of an electron in a central field potential V is described by a radial equation of the form

$$F_\kappa \phi_{n\kappa} = \epsilon_{n\kappa} \phi_{n\kappa} \ , \tag{7}$$

where

$$F_\kappa = \begin{bmatrix} V & c\Pi_\kappa \\ c\Pi_\kappa^+ & V - 2c^2 \end{bmatrix} , \tag{8}$$

with

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

and

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

Here

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

In the Dirac-Fock basis-set expansion method[20] pioneered by Kim, the radial large and small components $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$, respectively, are expanded in terms of a set of basis functions $\{X_{\kappa i}^L\}$ and $\{X_{\kappa i}^S\}$,

$$P_{n\kappa}(r) = \sum_i X_{\kappa i}^L C_{n\kappa i}^L \ , \tag{9}$$

$$Q_{n\kappa}(r) = \sum_i X_{\kappa i}^S C_{n\kappa i}^S \ , \tag{10}$$

where $\{C_{n\kappa i}^L\}$ and $\{C_{n\kappa i}^S\}$ are linear variational parameters.

In recent studies,[18,21] we have performed DF Gaussian basis-set expansion calculations on one- and many-electron systems with a finite nucleus model. In these studies, we have emphasized alteration of the boundary conditions such that the GTF's become the best form for basis functions. Representing the nucleus as a finite body of uniform proton charge accomplishes that feat. With this representation of the potential, for example, the exact $s_{1/2}$ solutions of the Dirac equation near the origin are

$$P(r)/r = 1 + g_2 r^2 + g_4 r^4 + \cdots \ , \tag{11}$$

$$Q(r)/r = f_1 r + f_3 r^3 + \cdots \ , \tag{12}$$

so that, for α arbitrary parameters

$$P(r) = r + g_2 r^3 + \cdots \approx r\exp(-\alpha r^2) \ , \tag{13}$$

$$Q(r) = f_1 r^2 + f_3 r^4 + \cdots \approx r^2 \exp(-\alpha r^2) \ . \tag{14}$$

Thus, in the finite nuclear model, the GTF's of integer power of r are appropriate basis functions because imposition of the finite nuclear boundary results in a solution which is Gaussian at the origin. In the previous study,[21] we have shown that the failure to satisfy proper boundary conditions near the origin may lead to a spurious solution.

The GTF basis functions that satisfy the boundary conditions associated with the finite nucleus automatically satisfy the condition of the so-called "kinetic balance"[22-24] for a finite value of c. If we choose for our large-component radial basis set $\{X_{\kappa i}^L\}$ Gaussian-type functions of the form

$$X_{\kappa i}^L = N_L r \exp(-\alpha_i r^2) \ . \tag{15}$$

Then the condition of kinetic balance imposes the small-component radial basis set $\{X_{\kappa i}^S\}$ to be[22-24]

$$X_{\kappa i}^S = \left[\frac{d}{dr} + \frac{\kappa}{r}\right] X_{\kappa i}^L = N_S r^2 \exp(-\alpha_i r^2) \ . \tag{16}$$

Here N_L and N_S are the normalization constants.

These kinetically balanced GTF basis functions are precisely the form given in Eqs. (13) and (14). This is a consequence of the fact that the exponent of r in the GTF basis functions does not depend on the speed of light. In contrast, the S-spinor basis functions,[14] in which the exponent of r explicitly depends on the speed of light, do not satisfy the kinetic balance for a finite value of c.[23] The kinetic balance simply guarantees that the solution of matrix DF equations approaches the correct nonrelativistic limit when c is taken to infinity.[21]

In matrix DFB calculations on closed-shell systems, the SCF equation in the algebraic approximation for symmetry-type κ takes the form

$$\mathbf{F}_\kappa \mathbf{C}_\kappa = \mathbf{S}_\kappa \mathbf{C}_\kappa \mathbf{E}_\kappa \ , \tag{17}$$

where, following the notation used by Quiney, Grant, and Wilson,[12] the overlap matrix is given in a block-diagonal form

$$\mathbf{S}_\kappa = \begin{bmatrix} \mathbf{S}_\kappa^{LL} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}_\kappa^{SS} \end{bmatrix} . \tag{18}$$

The superscripts LL and SS indicate which of the large- or small-component bases have been employed. The Fock matrix may be written

$$\mathbf{F}_\kappa = \mathbf{f}_\kappa + \mathbf{g}_\kappa + \mathbf{b}_\kappa \ , \tag{19}$$

where the one-electron part $\mathbf{f}_\kappa$ is

$$\mathbf{f}_\kappa = \begin{bmatrix} \mathbf{V}_\kappa^{LL} & c\Pi_\kappa^{LS} \\ c\Pi_\kappa^{SL} & \mathbf{V}_\kappa^{SS} - 2c^2 \mathbf{S}_\kappa^{SS} \end{bmatrix} . \tag{20}$$

The two-electron part $\mathbf{g}_\kappa$, which consists of the matrices of two-electron Coulomb and exchange interactions, is given by[12,20]

$$\mathbf{g}_\kappa = \begin{bmatrix} \mathbf{J}_\kappa^{LL} - \mathbf{K}_\kappa^{LL} & -\mathbf{K}_\kappa^{LS} \\ -\mathbf{K}_\kappa^{SL} & \mathbf{J}_\kappa^{SS} - \mathbf{K}_\kappa^{SS} \end{bmatrix} . \tag{21}$$

The matrices $\mathbf{J}_\kappa^{TT}$ and $\mathbf{K}_\kappa^{TT'}$, where the subscripts T and T' are either L or S, have matrix elements of the form[12,20]

$$J_{\kappa ij}^{TT} = \sum_{\kappa',k,l} (2j'+1)(D_{\kappa' kl}^{TT} J_{\kappa ij,\kappa' kl}^{0,TT,TT} + D_{\kappa' kl}^{\overline{TT}} J_{\kappa ij,\kappa' kl}^{0,TT,\overline{TT}}) \ , \tag{22}$$

$$K_{\kappa ij}^{T\bar{T}}=\sum_{\nu}\sum_{\kappa' kl}(2j'+1)b_\nu(jj')D_{\kappa' kl}^{T\bar{T}}K_{\kappa ij,\kappa' kl}^{\nu,T\bar{T},T\bar{T}} \ . \tag{23}$$

Here the superscripts $T\bar{T}$ represent a pair LS or SL. The Coulomb and exchange integrals in Eqs. (22) and (23) are given in terms of the GTF basis functions, $\{X_{\kappa i}^L\}$ and $\{X_{\kappa i}^S\}$ as

$$J_{\kappa ij,\kappa' kl}^{\nu,TT,T'T'}=\int_0^\infty\int_0^\infty X_{\kappa i}^T(r)X_{\kappa j}^T(r)U_\nu(r,s)X_{\kappa' k}^{T'}(s)X_{\kappa' l}^{T'}(s)\times ds\,dr \ , \tag{24}$$

$$K_{\kappa ij,\kappa' kl}^{\nu,TT',TT'}=\int_0^\infty\int_0^\infty X_{\kappa i}^T(r)X_{\kappa' k}^T(r)U_\nu(r,s)X_{\kappa j}^{T'}(s)X_{\kappa' l}^{T'}(s)\times ds\,dr \ , \tag{25}$$

where

$$U_\nu(r,s)=\begin{matrix} r^\nu/s^{\nu+1} \ , & r<s \\ s^\nu/r^{\nu+1} \ , & s<r \end{matrix}$$

and

$$D_{\kappa ij}^{TT}=C_{\kappa i}^T C_{\kappa j}^T \ .$$

The frequency-independent Breit interaction in Eq. (6) leads to the term $\mathbf{b}_\kappa$ in the matrix SCF equation,

$$\mathbf{b}_\kappa=\begin{bmatrix}\mathbf{B}_\kappa^{LL} & \mathbf{B}_\kappa^{LS}\\ \mathbf{B}_\kappa^{SL} & \mathbf{B}_\kappa^{SS}\end{bmatrix} \ . \tag{26}$$

The Breit-interaction matrices are given as

$$B_{\kappa ij}^{LL}=\sum_\nu\sum_{\kappa' kl}(2j'+1)e_\nu^{LL}(\boldsymbol{\kappa},\boldsymbol{\kappa}')D_{\kappa' kl}^{SS}K_{\kappa ij,\kappa' kl}^{\nu,LL,SS} \ , \tag{27a}$$

$$B_{\kappa ij}^{SL}=\sum_\nu\sum_{\kappa' kl}(2j'+1)[f_\nu(\boldsymbol{\kappa},\boldsymbol{\kappa}')D_{\kappa' kl}^{LS}K_{\kappa ij,\kappa' kl}^{\nu,SL,LS}+g_\nu(\boldsymbol{\kappa},\boldsymbol{\kappa}')D_{\kappa' kl}^{LS}W_{\kappa ij,\kappa' kl}^{\nu,SL,LS}] \ , \tag{27b}$$

$$B_{\kappa ij}^{SS}=\sum_\nu\sum_{\kappa' k,l}(2j'+1)e_\nu^{SS}(\boldsymbol{\kappa},\boldsymbol{\kappa}')D_{\kappa' kl}^{LL}K_{\kappa ij,\kappa' kl}^{\nu,SS,LL} \ , \tag{27c}$$

where

$$W_{\kappa ij,\kappa' kl}^{\nu,T\bar{T},\bar{T}T}=\int_0^\infty\int_0^r X_{\kappa i}^T(r)X_{\kappa' k}^{\bar{T}}(r)U_\nu(r,s)X_{\kappa j}^{\bar{T}}(s)X_{\kappa' l}^T(s)ds\,dr-\int_0^\infty\int_r^\infty X_{\kappa i}^T(r)X_{\kappa' k}^{\bar{T}}(r)U_\nu(r,s)X_{\kappa j}^{\bar{T}}(s)X_{\kappa' l}^T(s)ds\,dr \ .$$

The relativistic angular coefficients $e_\nu^{LL}(\boldsymbol{\kappa},\boldsymbol{\kappa}')$, $e_\nu^{SS}(\boldsymbol{\kappa},\boldsymbol{\kappa}')$, $f_\nu(\boldsymbol{\kappa},\boldsymbol{\kappa}')$, and $g_\nu(\boldsymbol{\kappa},\boldsymbol{\kappa}')$ were evaluated by using the technique described by Grant and Pyper.[25] These coefficients are tabulated up to $p_{3/2}$ symmetry (see Table I).

C. Computation

Using the expansion scheme outlined above, the DFB SCF calculations were performed on rare-gas atoms He, Ne, Ar, Kr, and Xe and alkali-earth metals Be, Mg, Ca, and Sr. For all these species, the SCF calculations were repeated without the Breit term, $\mathbf{b}_\kappa$ in the Fock matrix. This is the conventional Dirac-Fock-Coulomb (DFC) SCF scheme. Basis sets of nonrelativistically optimized even-tempered[26] and well-tempered[27] GTF's were used in all the calculations except for Ne and Ar, in which calculations were also performed using small- and medium-size GTF basis sets given by Van Duijneveldt.[28] For Be, Ne, and Ar, we have performed a number of calculations by systematically enlarging the basis set in order to study the convergence pattern of DFB, DFC, and Breit-interaction energies.

The finite nulceus model discussed in Ref. 21 was used in all the calculations. The atomic masses used for He, Ne, Ar, Kr, and Xe are, respectively, 4.00, 20.179, 39.948, 83.80, and 131.30. The atomic masses used for Be, Mg, Ca, and Sr are, respectively, 9.00, 24.305, 40.080, and 87.62.

TABLE I. Table of the angular Breit-interaction coefficients.

κ	κ'	ν	$e_\nu^{LL}(\kappa,\kappa')$	$e_\nu^{SS}(\kappa,\kappa')$	$f_\nu(\kappa,\kappa')$	$g_\nu(\kappa,\kappa')$
$s_{1/2}$	$s_{1/2}$	1	0.333 333	0.333 333	0.333 333	0.0
$p_{1/2}$	$s_{1/2}$	0	0.0	1.0	0.166 666	0.166 666
		2	0.2	0.0	0.166 666	−0.166 666
$p_{1/2}$	$p_{1/2}$	1	0.333 333	0.333 333	0.333 333	0.0
$p_{3/2}$	$s_{1/2}$	0	0.5	0.0	−0.083 333 3	−0.083 333 3
		2	0.1	0.2	0.216 666	0.083 333 3
$p_{3/2}$	$p_{1/2}$	1	0.333 333	0.033 333 3	−0.016 666 6	−0.15
		3	0.0	0.128 571	0.15	0.15
$p_{3/2}$	$p_{3/2}$	1	0.183 333	0.183 333	0.083 333 3	0.0
		3	0.064 285 7	0.064 285 7	0.107 143	0.0

TABLE II. The effects of the basis-set size on the DFB SCF, DFC SCF, and variational Breit-interaction energies of the Be atom.

N	E_{DFB}	E_{DFC}	$E_{\mathrm{B}}(\mathcal{S})$
6	−14.537 218 70	−14.537 916 07	0.000 697 37
8	−14.568 630 14	−14.569 332 13	0.000 701 99
10	−14.573 886 44	−14.574 588 74	0.000 702 30
12	−14.574 867 06	−14.575 569 48	0.000 702 42
14	−14.575 117 42	−14.575 819 85	0.000 702 43
16	−14.575 169 42	−14.575 871 86	0.000 702 44
20	−14.575 189 13	−14.575 891 57	0.000 702 44
Numerical limit[a]		−14.575 891 9	

[a]Computed by using the finite-difference DF program (Ref. 29).

III. RESULTS AND DISCUSSION

A number of DFB and DFC SCF calculations on ground-state Be were performed in which the even-tempered GTF basis sets[26] were systematically enlarged. The speed of light used in these calculations was 137.0370 a.u. Table II contains the seven representative sets of total DFB and DFC energies, E_{DFB} and E_{DFC}, respectively, of Be along with the DFC energy obtained by using the finite-difference DF program.[29] $E_B(\mathcal{S})$ denotes the variational Breit interaction energies computed as the difference $E_{\mathrm{DFB}}-E_{\mathrm{DFC}}$. The variational Breit energy is the level shift in the total SCF energy due to the inclusion of the Breit term in the SCF process.

The results clearly demonstrate the convergence pattern of the total energies as well as the variational Breit-interaction energy in Be. While the total energies computed with the smaller basis sets have not converged to the numerical limit as well as with the larger, the variational Breit-interaction energy computed with a set of 12 even-tempered GTF's has already converged to four figures and agrees well with that obtained with the largest basis set. A basis set of 16 GTF's is necessary to obtain convergence to five figures in $E_B(\mathcal{S})$. The E_{DFC} calculated with 20 GTF expansion agrees well with that obtained in the finite-difference calculation. Basis-set truncation error is on the order of 0.1 μhartrees.

A series of DFB and DFC SCF calculations on ground-state Ne and Ar were performed in which the GTF basis sets were systematically enlarged. The speed of light was taken to be 137.0370 a.u. Table III contains seven representative sets of results for Ne along with the DFC energy obtained with the finite-difference numerical DF program.[29] The variational Breit-interaction energy computed with the smallest basis set, $10s5p$ GTF of Van Duijneveldt,[28] has already converged to three figures, i.e., to 0.1 mhartrees, although the total energy is only accurate to 0.1 hartree in this basis set. The variational Breit energy computed with the medium-size $14s10p$ well-tempered GTF basis set of Huzinaga[27] has converged to five figures, i.e., to microhartrees, although the total energy has converged only to millihartrees. Fourteen well-tempered GTF basis functions used for $s_{1/2}$ symmetry are nearly saturated. The use of ten well-tempered GTF basis functions, however, does not saturate the $p_{1/2}$ and $p_{3/2}$ symmetries, and enlarging the basis set in p symmetry improves the convergence of the variational Breit energy by another digit to six figures. The variational Breit-interaction energy of 0.016 640 76 a.u. obtained by using $14s12p$ well-tempered GTF basis set[27] is in excellent agreement with the value 0.016 640 80 a.u. computed with the largest $23s17p$ basis set. The total DFC energy of Ne calculated with the even-tempered $23s17p$ GTF basis set is in excellent agreement with the numerical lim-

TABLE III. The effects of the basis-set size on the DFB SCF, DFC SCF, and variational Breit-interaction energies of the Ne atom (in a.u.).

	E_{DFB}	E_{DFC}	$E_B(\mathcal{S})$
Ne $10s5p$	−128.659 456 10	−128.676 079 53	+0.016 623 43
$12s7p$	−128.673 792 33	−128.690 430 98	+0.016 638 65
$13s8p$	−128.674 698 20	−128.691 338 09	+0.016 639 89
$14s10p$	−128.675 066 94	−128.691 707 52	+0.016 640 58
$14s11p$	−128.675 129 12	−128.691 769 87	+0.016 640 75
$14s12p$	−128.675 135 77	−128.691 776 53	+0.016 640 76
$23s17p$	−128.675 290 24	−128.691 931 04	+0.016 640 80
Numerical limit[a]		−128.691 94	

[a]Computed by using the finite-difference DF program (Ref. 29).

TABLE IV. The effects of the basis-set size on the DFB SCF, DFC SCF, and variational Breit-interaction energies of the Ar atom (in a.u.).

	E_{DFB}	E_{DFC}	$E_B(\mathcal{S})$
Ar 10s7p	−527.988 940 0	−528.120 319 3	+0.131 379 3
14s10p	−528.534 308 4	−528.666 604 0	+0.132 295 6
16s11p	−528.549 164 3	−528.681 481 6	+0.132 317 3
17s13p	−528.550 723 2	−528.683 044 8	+0.132 321 6
17s14p	−528.550 998 6	−528.683 321 3	+0.132 322 7
17s15p	−528.551 037 8	−528.683 360 6	+0.132 322 8
27s22p	−528.551 446 4	−528.683 769 4	+0.132 323 0
28s23p	−528.551 476 0	−528.683 799 0	+0.132 323 0
Numerical limit[a]		−528.683 84	

[a]Computed by using the finite-difference DF program (Ref. 29).

it obtained in the finite-difference calculation. Basis-set truncation error is on the order of 10 μhartrees.

Table IV contains eight representative sets of results for Ar. The variational Breit-interaction energy computed with the smallest $10s7p$ basis set of Van Duijneveldt[28] has converged to two figures. Use of the moderately large $17s15p$ well-tempered basis set[27] is enough to obtain convergence to six figures in $E_B(\mathcal{S})$. The variational Breit-interaction energy of 0.132 322 8 a.u. obtained with the $17s15p$ basis set is in excellent agreement with the value, 0.132 323 0 a.u. computed with the largest $28s23p$ even-tempered GTF basis set. The results shown in Tables III and IV demonstrate that, with the use of medium to moderately large GTF basis sets, the variational Breit-interaction energies have converged very rapidly to at least five figures, although the total DFB and DFC energies have not converged as well.

For the Ar atom, both the perturbative and variational Breit-interaction energies were reported in recent studies.[8,14] In those studies, however, the value of the speed of light used was different from the one we used to obtain the results in Table IV. The previous calculations were performed by using either $c=137.035\,989\,5$ a.u. or $c=137.0390$ a.u. In order to directly compare our results with those of the recent studies,[8,14] we have repeated our matrix DFB and DFC SCF calculations by using both these values of c.

In Table V, the total energies as well as the perturbative and variational Breit-interaction energies of Ar reported in previous studies are compared with our results computed with a $27s22p$ even-tempered basis set. Quiney, Grant, and Wilson[14] have performed matrix DFB SCF calculations on Ar using a $17s17p$ S-spinor basis set. The S-spinor basis-set calculations employed the point representation of the nucleus and $c=137.035\,989\,5$ a.u. In Table V, their results are given in the second row (the entry denoted by STF). The total DFC energy they obtained by employing the point nucleus representation is approximately 0.6 mhartrees below our DFC energy computed in finite-nucleus representation. However, their variational Breit-interaction energy $E_B(\mathcal{S})(=0.132\,325\,5$ a.u.) computed in the point nucleus approximation is in excellent agreement with our GTF results of 0.132 325 0 a.u. obtained in the finite nucleus representation. The

TABLE V. Comparison of the energies of Ar computed by GTF expansion with those computed by S-spinor expansion and finite-difference methods (in a.u.).

			$c=137.035\,989\,5$	$c=137.0390$
GTF[a]	27s22p	E_{DFC}	−528.683 797 2	−528.683 714 5
		$E_B(\mathcal{S})$	+0.132 325 0	+0.132 319 1
STF[b]	17s17p	E_{DFC}	−528.684 450 5	
		$E_B(\mathcal{S})$	+0.132 325 5	
		$E_B(P)$	+0.132 365 3	
MCDF[a]		E_{DFC}	−528.683 86	
		$E_B(P)$	+0.132 364 6	
Mann-Johnson[c,d]		E_{DFC}		−528.683 7
		$E_B(P)$		+0.132 36

[a]Finite nucleus of uniform proton charge distribution.
[b]S-spinor basis-set expansion calculations employing the point nucleus approximation.
[c]Finite-difference DF calculations employing the finite nucleus of Fermi-charge distribution.
[d]Reference 8.

TABLE VI. Total DFC SCF, DFB SCF, and variational Breit-interaction energies of the rare-gas atoms (in a.u.). Speed of light used is 137.0370 a.u.

		GTF	Finite difference
He	E_{DFC}	−2.861 812 846 6	−2.861 813 3
	E_{DFB}	−2.861 749 071 9	
	$E_B(\mathcal{S})$	+0.000 063 774 7	
Ne	E_{DFC}	−128.691 776 53	−128.691 94
	E_{DFB}	−128.675 135 77	
	$E_B(\mathcal{S})$	+0.016 640 76	
Ar	E_{DFC}	−528.683 360 6	−528.683 84
	E_{DFB}	−528.551 037 8	
	$E_B(\mathcal{S})$	+0.132 322 8	
Kr	E_{DFC}	−2788.856 297	−2788.861 81
	E_{DFB}	−2787.430 423	
	$E_B(\mathcal{S})$	+1.425 874	
Xe	E_{DFC}	−7446.894 950	−7446.9010
	E_{DFB}	−7441.125 194	
	$E_B(\mathcal{S})$	+5.769 756	

effect on $E_B(\mathcal{S})$ of the different representation of the nucleus is approximately 0.5 μhartrees and thus is negligible in this system.

Quiney, Grant, and Wilson[14] have also computed the first-order Breit-interaction energy $E_B(P)$ using their DFC wave function as an unperturbed wave function. The perturbative Breit-interaction energy of 0.132 365 3 a.u. is slightly larger by approximately 40 μhartrees than the variational Breit-interaction energy of 0.132 325 5 a.u. The perturbative Breit energy computed by using the finite-difference DF program[5] is given in the third row of Table V. This value is in excellent agreement with the perturbative Breit energy obtained in the S-spinor basis expansion calculations, although the former used the finite nucleus representation, the difference being approximately 0.7 μhartrees.

Mann and Johnson[8] calculated the perturbative Breit-interaction energy on a number of neutral atoms using $c=137.0390$ a.u. Their results on Ar are given in the last row of Table V for comparison. Our DFC energy computed in GTF basis-set expansion is in excellent agreement with the numerical limit given by Mann and Johnson. The perturbative Breit-interaction energy, 0.132 36 a.u., is slightly larger by approximately 40 μhartrees than our variational Breit-interaction energy, 0.132 319 1 a.u.

Table VI shows the total DFC and DFB SCF energies of the rare-gas atoms He, Ne, Ar, Kr, and Xe. Also shown are the variational Breit-interaction energies $E_B(\mathcal{S})$. In the fourth column, the DFC energies obtained by using the finite-difference Dirac-Fock program[29] are tabulated for comparison. DFC and DFB SCF calculations were performed on He in 16 even-tempered GTF's.[26] For Ne, Ar, Kr, and Xe, respectively, basis sets

TABLE VII. Total DFC SCF, DFB SCF, and variational Breit-interaction energies of the alkali-metal atoms (in a.u.). Speed of light used is 137.0370 a.u.

		GTF	Finite difference
Be	E_{DFC}	−14.575 871 86	−14.575 891 9
	E_{DFB}	−14.575 169 42	
	$E_B(\mathcal{S})$	+0.000 702 44	
Mg	E_{DFC}	−199.934 788 6	−199.935 08
	E_{DFB}	−199.902 961 7	
	$E_B(\mathcal{S})$	+0.031 826 9	
Ca	E_{DFC}	−679.709 594 1	−679.710 28
	E_{DFB}	−679.518 600 1	
	$E_B(\mathcal{S})$	+0.190 994 0	
Sr	E_{DFC}	−3178.074 209	−3178.081 5
	E_{DFB}	−3176.355 672	
	$E_B(\mathcal{S})$	+1.718 537	

TABLE VIII. DFC and DFB orbital energies of Xe (in a.u.).

Orbital	Orbital energies[a] DFC SCF	DFB SCF
$1s_{1/2}$	−1277.258	−1274.292
$2s_{1/2}$	−202.4650	−202.1845
$2p_{1/2}$	−189.6782	−189.1988
$2p_{3/2}$	−177.7045	−177.3806
$3s_{1/2}$	−43.010 36	−42.969 91
$3p_{1/2}$	−37.659 54	−37.584 81
$3p_{3/2}$	−35.325 18	−35.280 06
$3d_{3/2}$	−26.023 29	−26.000 13
$3d_{5/2}$	−25.537 03	−25.526 86
$4s_{1/2}$	−8.429 814	−8.424 185
$4p_{1/2}$	−6.452 325	−6.440 767
$4p_{3/2}$	−5.982 693	−5.977 144
$4d_{3/2}$	−2.711 237	−2.711 006
$4d_{5/2}$	−2.633 670	−2.635 577
$5s_{1/2}$	−1.010 069	−1.009 779
$5p_{1/2}$	−0.492 489 3	−0.491 736 3
$5p_{3/2}$	−0.439 730 7	−0.439 636 7

[a]Computed by using the $23s21p14d$ GTF basis set.

of $14s12p$, $17s15p$, $20s15p10d$, and $23s21p14d$ well-tempered GTF's of Huzinaga[27] were used. The speed of light used in these calculations was 137.0370 a.u.

Table VII shows the total DFC and DFB SCF energies of the alkali-metal atoms Be, Mg, Ca, and Sr. The variational Breit-interaction energies are tabulated in the third column. In the fourth column, the DFC energies obtained by using the finite-difference Dirac-Fock program are tabulated for comparison. For Be, the results are those obtained by using a moderately large basis set of 16 even-tempered GTF's taken from Table II. For Mg, Ca, and Sr, basis sets of $17s11p$, $20s14p$, and $22s15p10d$ well-tempered GTF's (Ref. 27) were used. The speed of light used in these calculations was 137.0370 a.u. The variational Breit-interaction energies obtained in all these calculations are accurate to at least five figures.

Table VIII contains two sets of orbital energies of Xe obtained in the DFC and DFB SCF calculations. One can see that the $1s_{1/2}$ orbital energy obtained by DFB SCF is higher by 3 hartrees than that computed by DFC SCF. The level-shift decreases to approximately 0.3 hartrees for $2s_{1/2}$ and approximately 0.45 hartrees for the $2p_{1/2}$ orbital. These level shifts due to the inclusion of the Breit-interaction term in the SCF procedure are much smaller in magnitude for outer-shell orbitals. In higher-Z systems, the major effects of the inclusion of the Breit interaction in the SCF process are the reorganization of the orbitals and a large shift in the inner-shell orbital energies.[8]

Table IX contains our variational Breit-interaction energies for He, Ar, and Xe evaluated by using two different values of the speed of light. Also shown are the first-order Breit-interaction energies evaluated perturbatively by using finite-difference numerical methods.[5,8] The results show that the variational Breit-interaction energies computed with the GTF basis-set expansion agree well with the perturbative Breit-interaction energies. For all the species considered, however, the perturbative Breit energies are seen to be slightly larger in magnitude than the variationally determined Breit-interaction energies. This small difference may be attributed to the inclusion of higher-order ($\alpha^4, \ldots$) contributions in the self-consistent treatment of the Breit interaction that are absent in the first-order perturbation treatment.

IV. CONCLUSION

Theoretical methods developed to describe the structure of many-electron atoms must be able to yield wave functions that can be refined to account for relativistic, electron-correlation, and QED effects to high accuracy. They must be computationally efficient because they will have to eventually describe electronic effects in very-high-Z neutral atoms. Finally they should be capable of being extended in a straightforward way to the study of molecules. The present study has employed one such approach, i.e., the solution of the Dirac-Fock-Breit SCF equations by expansion in basis sets of Gaussian functions.

It is usually assumed that Breit-energy contributions are small, but even for moderate nuclear charge, the transverse interaction is now known to contribute a substantial part of the correction to mean-field approximations and must be included in any approach that aims to treat relativistic effects to an accuracy of order α^2.

The frequency-independent Breit interaction, which gives the leading correction to the instantaneous

TABLE IX. Variational Breit energy $E_B(\mathcal{S})$ and perturbative Breit energy $E_B(P)$ computed with two different values of the speed of light, $c=137.036\,989\,5$ and $c=137.0390$. Square brackets denote powers of ten.

	$c=137.035\,989\,5$ $E_B(\mathcal{S})$[a]	$E_B(P)$[b]	$c=137.0390$ $E_B(\mathcal{S})$[a]	$E_B(P)$[c]
He	0.637 756[−4]	0.637 774[−4]	0.637 728[−4]	0.65[−4]
Ar	0.132 325 0	0.132 364 6	0.132 319 1	0.132 36
Xe	5.769 845	5.775 315	5.769 580	5.775 09

[a]Present study.
[b]First-order Breit energy evaluated by using GRASP (Ref. 5).
[c]First-order Breit energy (Ref. 8).

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 SCF procedure of basis-set expansion Dirac-Fock calculations. The interference between the Coulomb and Breit terms, which causes the large orbital reorganization and one-electron energy shift for large Z, can easily be taken into account in the matrix Dirac-Fock-Breit SCF procedure.

As the present study has demonstrated, the Gaussian basis expansion method has the advantage that large GTF basis sets can achieve high accuracy without encountering the numerical near-linear dependency problem reported with Slater basis sets.[12,30,31] The GTF basis-set calculations can be regarded as a highly accurate and versatile approximation in relativistic atomic- and molecular-structure calculations. The finite basis-set methods, using both local[16,32,33] and global basis functions,[14,34–36] are being developed for relativistic many-body calculations, which gives us hope that the radiative QED corrections may be evaluated as a routine part of atomic-structure calculations.

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