PHYSICAL REVIEW A VOLUME 37, NUMBER 1 JANUARY 1, 1988

Variational Dirac-Hartree-Fock method: Results for the He, Be, C, and Ne isoelectronic sequences

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(Received 29 July 1987)

A detailed presentation of an analytic variational Dirac-Hartree-Fock (VDHF) procedure that avoids the problems of spurious roots and collapse is given. The conditions for the avoidance of spurious roots are discussed, as well as the behavior of the one-electron and total energies as upper bounds under variations of the nonlinear parameters or the dimension of the basis sets. The implementation of the VDHF procedure and the Breit-interaction corrections is presented for Slater-type basis sets, with emphasis on the computational efficiency of the calculations. The Breit-interaction corrections in particular are reviewed in detail. Optimized results are presented for the He, Be, C, and Ne isoelectronic sequences.

I. INTRODUCTION

The aim of this paper is to provide a detailed presentation of a recently introduced analytic variational Dirac-Hartree-Fock method[1] (VDHF) that avoids the problems of spurious roots and variational collapse. This is a successful implementation of an analytic Dirac-Hartree-Fock (DHF) procedure proposed in the pioneering work of Kim in 1967.[2] Since then several attempts have been made which were unsuccessful due to either the incompleteness of the basis set used (because of the elimination of negative-energy states from the basis set)[2,3] or the lack of appropriate conditions to avoid spurious roots.[4,5]

A short review of the DHF equations and the VDHF procedure is presented in Sec. II, together with a discussion of the basis set used. Examples of the behavior of the energy eigenvalues as the nonlinear parameters of the basis set are changed are persented, as well as examples of the convergence of the results as the dimension of the basis set is increased. In Sec. III a review of the Breit interaction and its implementation in VDHF calculations is presented, together with a comparison of the results obtained when different forms of the Breit interaction are used. The implementation of the procedure, using Slater-type basis sets for the calculation of VDHF energies and Breit-interaction corrections, is reviewed in Secs. IV and V, respectively. Emphasis is given to the computational efficiency of the calculations. Finally, in Sec. VI optimized values of the nonlinear parameters, one-electron and total energies, and Breit-interaction corrections are given for the He, Be, C, and Ne isoelectronic sequences.

II. THE VDHF METHOD

In the one-electron case, the relativistic Dirac equation for the case of a Coulomb potential can be written as[6]

$$H_D\psi = E_D\psi \,, \tag{2.1}$$

with

$$H_D = c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2 - \frac{Z}{r} \,, \tag{2.2}$$

where $\boldsymbol{\alpha}$ and β are the usual 4×4 Dirac matrices. Atomic units are used throughout, with $c = 1/\alpha$ used sometimes to avoid confusion between the Dirac matrices α_i and the fine-structure constant $\alpha = 1/137.036\,04$.

The solutions to (2.2) can be written in the form

$$\psi = \begin{bmatrix} i\dfrac{g(r)}{r} & \Omega_{jlM}(\hat{\mathbf{r}}) \\ -\dfrac{f(r)}{r} & \Omega_{j\bar{l}M}(\hat{\mathbf{r}}) \end{bmatrix}, \quad \bar{l} = 2j - l \tag{2.3}$$

where Ω_{jlm} is a two-component spherical spinor. The functions $g(r)$ and $f(r)$ are the large and small radial components, respectively; these names derive from the fact that for bound states they satisfy the identities[7]

$$\begin{aligned} \int_0^\infty g^2 dr &= \tfrac{1}{2}(1+\alpha^2 E) \approx 1 - \frac{(\alpha Z)^2}{4n^2} \,, \\ \int_0^\infty f^2 dr &= \tfrac{1}{2}(1-\alpha^2 E) \approx \frac{(\alpha Z)^2}{4n^2} \,, \end{aligned} \tag{2.4}$$

where Z is the nuclear charge and n is the nonrelativistic principal quantum number. Using (2.4) we can write the virial theorem in the form

$$\int_0^\infty (g^2 - f^2) dr = \langle \psi \,|\, \beta \,|\, \psi \rangle = \alpha^2 E \,. \tag{2.5}$$

A similar identity is satisfied by the variational solutions to the DHF equations.[2,8] We shall come back later on to Eq. (2.5) in the context of the VDHF calculations.

With a solution of the form (2.3), the radial part of the equations for the case of a central potential uncouples. It is then advantageous to define a two-component radial spinor

$$\Phi=\begin{bmatrix} g(r) \\ f(r) \end{bmatrix} . \tag{2.6}$$

This spinor satisfies the radial equation

$$H_{D,r}\Phi=E_D\Phi , \tag{2.7}$$

where the radial Dirac Hamiltonian is given by

$$H_{D,r}=\begin{bmatrix} \dfrac{1}{\alpha}-\dfrac{\alpha Z}{r} & \dfrac{\kappa}{r}-\dfrac{d}{dr} \\ \dfrac{d}{dr}+\dfrac{\kappa}{r} & -\dfrac{1}{\alpha}-\dfrac{\alpha Z}{r} \end{bmatrix} , \tag{2.8}$$

where κ is the Dirac quantum number $\kappa=\pm(j+\frac{1}{2})$ for $l=j\pm\frac{1}{2}$.

The exact bound-state solutions to (2.7) are of the form

$$\Phi_{n,\kappa}=r^{\gamma}e^{-\lambda_{n,\kappa}r}\sum_{i=0}^{N_{n,\kappa}}\begin{bmatrix} a_i \\ b_i \end{bmatrix} r^{i} , \tag{2.9}$$

where

$$\gamma=[\kappa^2-(\alpha Z)^2]^{1/2} . \tag{2.10}$$

In order to provide a finite-basis-set representation of the solutions to (2.7), following the nonrelativistic model, one could attempt to use a set of radial basis functions that decay exponentially at infinity and close to the origin behave as r^{γ}. Such a general representation can be achieved with a basis set of the form[9]

$$\begin{aligned} \phi_i&=r^{\gamma+i}e^{-\lambda r}\begin{bmatrix} 1 \\ 0 \end{bmatrix} , \\ \phi_{N+i}&=r^{\gamma+i}e^{-\lambda r}\begin{bmatrix} 0 \\ 1 \end{bmatrix} , \quad i=0,1,\ldots,N-1 . \end{aligned} \tag{2.11}$$

It has been shown[9] that upon diagonalization of the Hamiltonian (2.8) in the basis set $\{\phi\}$ one gets N positive-energy eigenvalues that are upper bounds to the exact values for the bound states and N negative eigenvalues that are lower bounds to $-mc^2$. There is, however, a spurious root appearing for the states with positive κ that is degenerate with the lowest positive-energy variational solution with a negative κ of the same magnitude [e.g., for $\kappa=1$, a spurious "$1p_{1/2}$" state appears that is degenerate with the $1s_{1/2}$ state ($\kappa=-1$) obtained variationally with the same nonlinear parameters]. This spurious root does not affect atomic-physics calculations involving hydrogenic ions,[10–12] allowing the use of basis set (2.11) to perform accurate relativistic calculations involving sums over the complete energy spectrum. The same is not true, however, if one applies this basis set to VDHF calculations. Due to the presence of the spurious roots, this approach fails to provide energy bounds when shells with $\kappa>0$ are present in the electronic configuration to which the VDHF procedure is applied.[5] An approach to eliminate these spurious roots from the positive-energy spectrum is therefore necessary.

In the one-electron Coulomb case, it has been shown that the spurious roots in the positive-energy spectrum can be avoided by imposing on the basis set differential conditions at the origin.[10,13]

Consider the expansion at the origin:

$$\begin{aligned} g&=r^{\gamma}(g_0+g_1r+\cdots) , \\ f&=r^{\gamma}(f_0+f_1r+\cdots) . \end{aligned} \tag{2.12}$$

In the nonrelativistic limit ($\alpha\to 0$), at the origin,

$$g\approx r^{l+1} . \tag{2.13}$$

For states with $\kappa>0$ this means that $g_0\to 0$ in the nonrelativistic limit, with g_1 remaining as the lowest-order coefficient in the expansion (2.12) of g. The necessary constraint on the basis functions that will force them to satisfy (2.13) can be obtained by replacing (2.12) to first order in the radial Dirac equation to obtain[10,13]

$$\begin{aligned} &\frac{g_0}{\alpha}-\alpha Zg_1+(\kappa-\gamma-1)f_1=\alpha Eg_0 , \\ &(\kappa+\gamma+1)g_1-\frac{f_0}{\alpha}+\alpha Zf_1=\alpha Ef_0 . \end{aligned} \tag{2.14}$$

From these equations we obtain

$$(q+2\alpha Z)g_1+(1-2\alpha Zq)f_1=\frac{2q}{\alpha}f_0 . \tag{2.15}$$

Condition (2.15) is level independent, and can then easily be implemented in the basis set. The question is if this condition can also be applied to the VDHF scheme.

Consider the radial DHF equations[8] for an electron in shell a (the indices a and b denote closed electronic shells):

$$-\frac{f_a'}{\alpha}+\frac{\kappa_a}{\alpha r}f_a-\frac{Z}{r}g_a+\frac{1}{r}\sum_b[\mu_{bb}(r)g_a+\nu_{ab}(r)g_b]=e_ag_a , \tag{2.16}$$

$$\frac{g_a'}{\alpha}+\frac{\kappa_a}{\alpha r}g_a-\left[\frac{2}{\alpha^2}+\frac{Z}{r}\right]f_a+\frac{1}{r}\sum_b[\mu_{bb}(r)f_a+\nu_{ab}(r)f_b]=e_af_a , \tag{2.17}$$

where

$$e_a=\varepsilon_a-mc^2 \tag{2.18}$$

and ε_a is the energy of an electron in shell a. The screening due to all other electrons is contained in the terms under the summations (without these summations we recover the Dirac equation). In these terms, the following definitions were used:

$$\mu_{bb}(r)=\sum_k C_{bk}r\int\frac{r_<^k}{r_>^{k+1}}P_{bb}(r_1)dr_1 , \tag{2.19}$$

$$\nu_{ab}(r)=\sum_k D_{abk}r\int\frac{r_<^k}{r_>^{k+1}}P_{ab}(r_1)dr_1 , \tag{2.20}$$

$$P_{ab}(r)=g_a(r)g_b(r)+f_a(r)f_b(r) , \tag{2.21}$$

$$C_{bk}=\delta_{k0}(2j_b+1) , \tag{2.22}$$

$$D_{abk}=\begin{cases}\begin{pmatrix} j_a & k & j_b \\ \frac{1}{2} & 0 & -\frac{1}{2}\end{pmatrix}^2 & \text{if } l_a+l_b+k \text{ is even ,} \\ 0 \text{ otherwise .} \end{cases} \tag{2.23}$$

To find a first-order condition similar to (2.15) for the VDHF case, we expand $\mu_{bb}(r)$ and $v_{ab}(r)$ at the origin. With this purpose in mind, we expand $g(r)$ and $f(r)$ at the origin as in Eq. (2.12) but treat the lowest power of r as an unknown:

$$\begin{aligned} g &= r^{\sigma}(g_0+g_1 r+\cdots) , \\ f &= r^{\sigma}(f_0+f_1 r+\cdots) . \end{aligned} \tag{2.24}$$

Calling

$$Q_{abk}(r) \equiv r\int_0^\infty \frac{r_<^k}{r_>^{k+1}} P_{ab}(r_1)dr_1 , \tag{2.25}$$

this can be rewritten as

$$\begin{aligned} Q_{abk}(r) &= \frac{1}{r^k}\int_0^r x^k P_{ab}(x)dx + r^{k+1}\int_r^\infty \frac{P_{ab}(x)dx}{x^{k+1}} \\ &= \frac{1}{r^k}\int_0^r x^k P_{ab}(x)dx - r^{k+1}\int_0^r \frac{P_{ab}(x)dx}{x^{k+1}} \\ &\quad + A_{abk} r^{k+1} , \end{aligned} \tag{2.26}$$

where A_{abk} is the constant

$$A_{abk}=\int_0^\infty \frac{P_{ab}(x)dx}{x^{k+1}} . \tag{2.27}$$

Using now the expansion (2.24) in (2.26) we obtain

$$Q_{abk}(r) \underset{(r\to 0)}{\sim} P_{0ab}(r^{\sigma_a+\sigma_b+1}-r^{\sigma_a+\sigma_b+1})+A_{abk}r^{k+1} , \tag{2.28}$$

with

$$P_{0ab}=g_{0a}g_{0b}+f_{0a}f_{0b} . \tag{2.29}$$

Then close to the origin

$$\frac{1}{r}\sum_b \mu_{bb}(r)g_a(r) \approx \left[\sum_b C_{b0}A_{ab0}\right] g_{0a} r^{\sigma_a} , \tag{2.30a}$$

and

$$\frac{1}{r}\sum_b v_{ab}(r)g_b(r) \approx \sum_{b,k} D_{abk}A_{abk}g_{0b}r^{\sigma_b+k} . \tag{2.30b}$$

Collecting terms of order r^{σ_a-1} in Eqs. (2.17) we obtain

$$\sigma_a=\gamma_a . \tag{2.31}$$

Therefore, the lowest power of r in the radial large and small components of the VDHF one-electron wave functions is the same as the one for the pure Coulomb case. As in the Coulomb case, in order to avoid the appearance of spurious roots, this term has to vanish in the nonrelativistic limit in the case of shells with $\kappa>0$.

Consider first the case in which the index a denotes a $p_{1/2}$ shell. Due to the constraints (2.23) imposed on the index k in Eq. (2.31), the lowest-order contribution at the origin in (2.30b) is

$$A_{aa0}g_{0a}r^{\gamma_a} . \tag{2.32}$$

Therefore, for $p_{1/2}$ shells we recover Eqs. (2.14) and conditions (2.15), if in the right-hand side of Eq. (2.14) we substitute

$$\alpha E \to \alpha E^* \equiv \alpha E - \sum_b C_{b0}A_{ab0} - A_{aa0}D_{aa0} . \tag{2.33}$$

In other words, the differential constraints to impose on $p_{1/2}$ states in the VDHF case are the same as those for the one-electron Coulomb case.

In the case of shells with $\kappa \geq 2$ the analysis becomes more complicated. As an illustration consider the $d_{3/2}$ states. In this case, if $a=2$ in Eq. (2.30b) denotes a $\kappa=2$ shell and $b=1$ a $\kappa=1$ ($p_{1/2}$) shell, then the lowest-order contributions in (2.30b) come from the terms

$$D_{220}A_{220}r^{\gamma_2}g_{02}+D_{211}A_{211}r^{\gamma_1+1}g_{01} , \tag{2.34}$$

where

$$\gamma_1+1=1+[1-(\alpha Z)^2]^{1/2}<\gamma_2=[4-(\alpha Z)^2]^{1/2} . \tag{2.35}$$

A straightforward analysis of the DHF equations (2.17) at the origin shows that the lowest power in an expansion of the $d_{3/2}$ large and small components must be γ_2 and that a term in r^{γ_1+1} is absent in the expansion at the origin. Therefore, an expansion of the radial components of the $d_{3/2}$ states at the origin can be written as the sum of two series in powers of r: one starting at r^{γ_2}, and a second one starting at r^{γ_1+2}. Of these, only the term in γ_2 will have the wrong nonrelativistic limit and then yield a spurious root. It is then sufficient to require the $d_{3/2}$ basis set to satisfy conditions (2.15) to eliminate the spurious roots from the positive-energy spectrum. A similar argument holds for states with higher values of $\kappa>0$.

It is interesting to note that the mixing of different powers of r occurring in Eq. (2.30b), will occur in general whenever shells with different values of $|\kappa|$ are involved in the calculation. This implies that convergence of the results could be improved by adding terms with these different real powers of r in the basis representing each shell. However, the numerical feasibility and advantages of this procedure should be studied at low Z, where γ is "almost" an integer and degeneracy in the basis set may occur, and at high Z, where the correlation effects are very small.

In this work, a single value of γ has been used for each of the basis sets representing each shell. As a consequence of the previous argument, for the states with $\kappa>0$ we use the same type of basis sets that satisfy conditions (2.15), as proposed in Ref. 10, with the added flexibility of multiple exponential parameters.

The variational solution of Eqs. (2.17) will be written as the linear combination

$$\Phi = \sum_{i,j} a_{ij}\phi_{i,j} \ . \tag{2.36}$$

In the case $\kappa < 0$, the bispinors $\phi_{i,j}$ are given by

$$\begin{aligned} \phi_{i,j} &= r^{\gamma+1} e^{-\lambda_j r} \begin{bmatrix} 1 \\ 0 \end{bmatrix} , \\ \phi_{N+i,j} &= r^{\gamma+i} e^{-\lambda_j r} \begin{bmatrix} 0 \\ 1 \end{bmatrix} , \end{aligned} \tag{2.37a}$$

with

$$j = 1,2, \dots, M, \quad i = 0,1, \dots, N-1 \ . \tag{2.37b}$$

In the case $\kappa > 0$, for $i = 1$, $\phi_{1,j}$ and $\phi_{N+1,j}$ are given by[10]

$$\phi_{1,j} = r^{\gamma} e^{-\lambda_j r} \begin{bmatrix} q + \dfrac{2(Z+\kappa\lambda_j)}{\alpha Z(1+2\kappa+2\gamma)} r \\ 1 \end{bmatrix} , \tag{2.38a}$$

$$\phi_{N+1,j} = r^{\gamma} e^{-\lambda_j r} \begin{bmatrix} q \\ 1 + \dfrac{2q(Z+\kappa\lambda_j)}{\alpha Z(1-2\kappa+2\gamma)} r \end{bmatrix} ; \tag{2.38b}$$

for all other values of i the bispinors $\phi_{i,j}$ are given by

$$\phi_{i,j} = r^{\gamma+i} e^{-\lambda_j r} \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad i = 2,3, \dots, N-1 \ , \tag{2.38c}$$

$$\phi_{N+i,j} = r^{\gamma+i} e^{-\lambda_j r} \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \quad i = 0,2,3, \dots, N-1 \tag{2.38d}$$

with $i = 0$ only if $j = 1$, and

$$j = 1,2, \dots, M \ . \tag{2.38e}$$

Let the bispinor $\theta_{a,m}$ denote in general the mth orthonormal basis vector of the set used to represent the shell a, built with basis vectors of the form (2.37) and (2.38). The radial DHF Hamiltonian matrix for shell a constructed with this orthonormal basis set, will be given by

$$\begin{aligned} H_{a,mn} = {} & \int dr\, \theta^{\dagger}_{a,m} H_{D,r} \theta_{a,n} + \int dr\, \theta^{\dagger}_{a,m} \frac{1}{r} \sum_b \mu_{bb} \theta_{a,n} \\ & + \int dr\, \theta^{\dagger}_{a,m} \frac{1}{r} \sum_b \nu_{ab,n} \Phi_b \ , \end{aligned} \tag{2.39}$$

where $H_{D,r}$ is the radial Dirac Hamiltonian (2.8), Φ_b is the radial one-electron eigenvector of shell b, μ_{bb} is defined in Eq. (2.19), and $\nu_{ab,n}$ is given by Eq. (2.20) with the replacement

$$P_{ab} \rightarrow P_{ab,n} = \Phi^{\dagger}_b \theta_{a,n} \ .$$

The diagonalization of the DHF Hamiltonian matrix (2.39) yields a set of linear coefficients in the expansion of the wave function for shell a in terms of the $\theta_{a,n}$. This linear combination minimizes the total energy for a given set of nonlinear parameters.

The calculation of the direct and exchange terms assumes knowledge of the wave functions for the shells labeled by the index b. The initial guesses for the large and small components g_b and f_b used in the direct and exchange integrals are, in this work, the variational solutions of the one-electron Dirac Hamiltonian with the basis functions (2.37) and (2.38). This starts the usual iteration process to obtain self-consistency, i.e., the eigenfunctions obtained for each shell as solutions of the VDHF equations do not differ from those assumed for each shell (obtained from the previous iteration). Each step in the iteration process yields for the one-electron orbitals NM positive-energy and NM negative-energy eigenstates for shells with $\kappa < 0$ and NM positive-energy and $NM+1$ negative-energy eigenstates for states with $\kappa > 0$. There are no spurious roots in the positive-energy spectrum.

The total energy E of the system under consideration is given by[8]

$$E = \sum_i I_i + \tfrac{1}{2} \sum_{i,j} (J_{ij} - K_{ij}) \ , \tag{2.40}$$

where the sum is taken over all electrons, J_{ij} and K_{ij} are the direct and exchange integrals, respectively, and I_a is the expectation value of the Dirac Hamiltonian for an electron in shell a: $I_a = \langle \Phi_a \mid (H_d - mc^2) \mid \Phi_a \rangle$.

It is found that once self-consistency is achieved for a certain set of nonlinear parameters, the total energy E is *always* an upper bound to the exact (numerical) DHF values. One can then obtain the best representation for a given basis set (i.e., best set of nonlinear parameters) by minimizing the total energy with respect to the nonlinear parameters in the basis set. In previous attempts,[2,3] a minimization was not possible because the total energy could collapse below the exact value. For this reason Kim[2] introduced the idea of using a relativistic virial theorem to find the best value of the total energy, with no guarantee that the result would provide an upper bound to the exact value. In our case, in which the variational result does provide bounds, the virial theorem is used to construct an efficient optimization technique for the variational calculation of DHF energies. Moreover, this technique provides a natural criterion for the maximum accuracy to pursue in the minimization process.[14]

In Fig. 1, we display the way in which the total energy typically behaves as the nonlinear parameters are varied. In this example the calculations are done for carbon, with a simple basis set for each of the s and p orbitals. This basis set consists of one exponential parameter and seven powers [$M = 1$ and $N = 7$ in Eqs. (2.37) and (2.38)]. In Fig. 1, the open circles describe the total energy as the nonlinear parameter for the s shell is varied with the parameter for the p shell fixed at its optimal value. The closed circles describe the variation of E as the p parameter is varied with the s parameter fixed at its optimal value. In each case, λ_0 in the abscissa denotes the optimal value of the parameter being varied. In both cases, the total energy is always an upper bound to the exact value E_0. A similar behavior has been observed in all He-, Be-, C-, and Ne-like systems investigated.

In Figs. 2–4 we present similar graphs for the $1s$, $2s$, and $2p$ one-electron energies. These are not upper bounds to the exact values (e_0), in general, although they are *always* upper bounds for the values of the non-

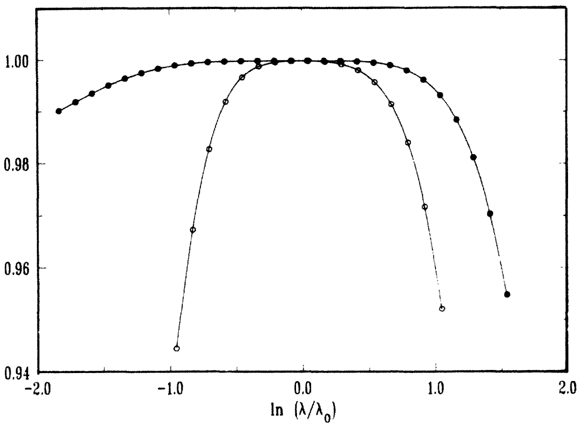

FIG. 1. Values of the total energy E of carbon relative to the optimized value E_0, as a function of the nonlinear parameter λ for the s shell (open circles) and the p shell (solid circles). A basis set with one exponential parameter and seven powers has been used for each shell. λ_0 is the optimal value of the parameter being varied.

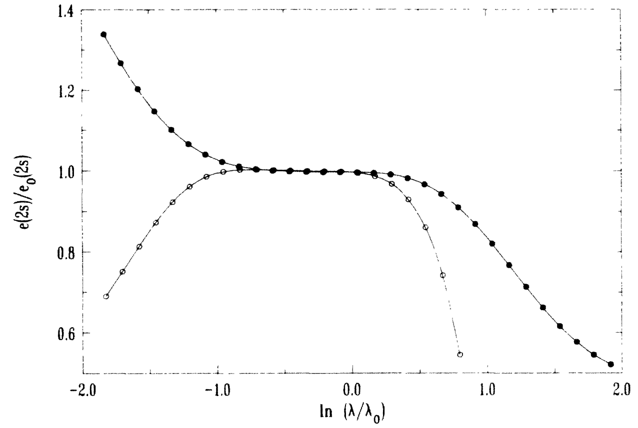

FIG. 3. Values of the one-electron energy $e(2s)$ of the $2s$ shell of carbon relative to the optimized value $e_0(2s)$, as a function of the nonlinear parameter λ for the s shell (open circles) and the p shell (solid circles). A basis set with one exponential parameter and seven powers has been used for each shell. λ_0 is the optimal value of the parameter being varied.

linear parameters that optimize the total energy. The lack of bounds on the one-electron energies is a consequence of the inadequate screening provided by the nonoptimized wave functions describing the other electronic shells. This is apparent in Figs. 2–4, where the one-electron energy has a minimum when the parameter of the basis set representing its own shell is varied, but goes through a saddle point when the parameter representing another shell is varied, i.e., when the screening due to that shell is changed.

In Table I we show the convergence of the results for C as the dimension of the basis set is increased. The optimal values of the one-electron energies for the $1s$, $2s$, and $2p$ shells, and of the total energy are shown for different numbers of powers in basis sets with two exponential parameters, i.e., $M=2$ and $N=2$, 3, 4, 5, and 6 in Eqs. (2.37) and (2.38). As in all systems investigated, the total energy and the one-electron energies converge uniformly from above to the exact numerical value.

The computational details of the calculations discussed in this section are presented in Sec. IV. Results for energies and wave functions for He-, Be-, C-, and Ne-like ions are presented in Sec. VI.

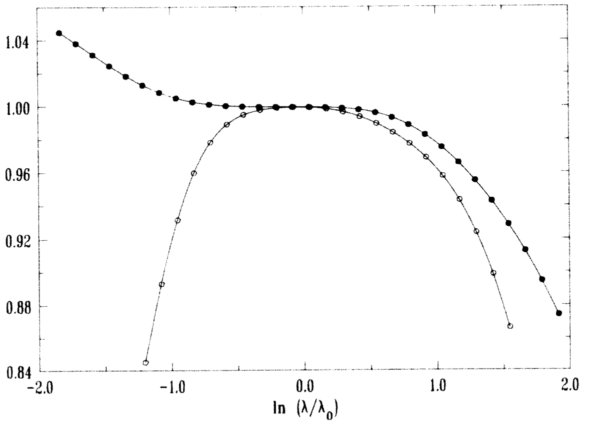

FIG. 2. Values of the one-electron energy $e(1s)$ of the $1s$ shell of carbon relative to the optimized value $e_0(1s)$, as a function of the nonlinear parameter λ for the s shell (open circles) and the p shell (solid circles). A basis set with one exponential parameter and seven powers has been used for each shell. λ_0 is the optical value of the parameter being varied.

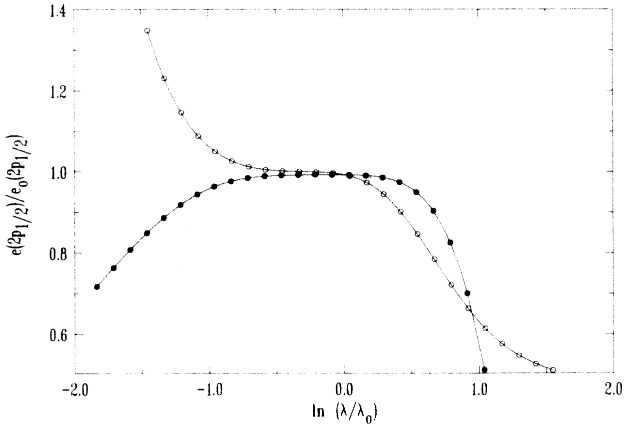

FIG. 4. Values of the one-electron energy $e(2p_{1/2})$ of the $2p_{1/2}$ shell of carbon relative to the optimized value $e_0(2p_{1/2})$, as a function of the nonlinear parameter λ for the s shell (open circles) and the p shell (solid circles). A basis set with one exponential parameter and seven powers has been used for each shell. λ_0 is the optimal value of the parameter being varied.

TABLE I. Optimal values of the one-electron energies and total energy for carbon. N and M are the number of nonlinear parameters and of powers used in the basis set, respectively. The numbers between parentheses are the errors in the last digit of the total energy as given by the virial-theorem optimization method.

M	N	$\varepsilon(1s)$	$\varepsilon(2s)$	$\varepsilon(2p^*)$	E
2	2	−11.318	−0.702	−0.378	−37.675(50)
2	3	−11.344	−0.711	−0.385	−37.654(17)
2	4	−11.351 838 0	−0.716 846 0	−0.389 718 1	−37.657 413 2(93)
2	5	−11.351 855 4	−0.716 855 0	−0.389 724 6	−37.657 417 2(72)
2	6	−11.351 866 6	−0.716 862 82	−0.389 730 2	−37.657 421 7(23)
Exact		−11.351 866 8	−0.716 862 83	−0.389 730 2	−37.657 421 8

III. THE BREIT INTERACTION

For the calculation of the Breit-interaction corrections, we follow the analysis of Mann and Johnson.[15] In their work it is emphasized that it is incorrect to use the Breit interaction to determine the self-consistent field[15–17] because the Breit interaction follows from quantum electrodynamics *in first-order perturbation theory*. Therefore, in this work the Breit-interaction correction is not obtained by adding the Breit operator to the Hamiltonian to be diagonalized. The correction will be obtained as a perturbation correction to the total energy.

The Breit interaction is usually written as the sum of two terms:

$$H_{\mathrm{Br}}=H_G+H_{\mathrm{ret}} \tag{3.1}$$

where H_G is the Gaunt interaction and H_{ret} is the retardation interaction. In their work, Mann and Johnson present three alternative versions of the Breit interaction. The first version is that proposed by Breit:[18]

$$H_G=-\left(\frac{\alpha}{R}\right)\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2 , \tag{3.2a}$$

$$H_{\mathrm{ret}}=\left(\frac{\alpha}{2R}\right)(\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2-\boldsymbol{\alpha}_1\cdot\hat{\mathbf{n}}\,\boldsymbol{\alpha}_2\cdot\hat{\mathbf{n}}) , \tag{3.2b}$$

where α is the fine-structure constant, R is the interelectron separation, the components of $\boldsymbol{\alpha}$ are Dirac matrices, and $\hat{\mathbf{n}}=\mathbf{R}/R$. This is the approximation used by Kim[2] and Grant[19] in their self-consistent calculations.

The second form of the Breit interaction is the nonlocal generalization of (3.2), obtained by treating in lowest-order perturbation theory the exchange of a single transverse photon between two atomic electrons. This interaction is given by

$$H'_G=-\frac{\alpha}{R}\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2\cos(\omega R) , \tag{3.3a}$$

$$H'_{\mathrm{ret}}=-\alpha\alpha_{1i}\alpha_{2j}\frac{\partial^2}{\partial R_i\partial R_j}\frac{\cos(\omega R)-1}{\omega^2 R} , \tag{3.3b}$$

where ω is the energy transferred by the virtual photon. H_{Br} approximates H'_{Br} to order ω^2, thus providing an approximation suitable for the study of light atoms $[(\alpha Z)^2\ll 1]$.[15]

The third version of the Breit interaction is a simpler form of Eq. (3.3) that can be used in the case in which the electrons are described by eigenfunctions of a local Dirac Hamiltonian:[20,21]

$$H''_G=H'_G=-\frac{\alpha}{R}\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2\cos(\omega R) , \tag{3.4a}$$

$$H''_{\mathrm{ret}}=-\frac{\alpha}{R}[1-\cos(\omega R)] . \tag{3.4b}$$

As pointed out by Mann and Johnson, it is the matrix elements of H' that should be used within the DHF method.

We summarize now the results obtained in Ref. 15 for the matrix elements of the Breit interaction. The two-electron matrix element of H'_{Br}, after averaging over the projection quantum number in each shell, is written as

$$E'^{\mathrm{Br}}_{ab}=E'^{G}_{ab}+E'^{\mathrm{ret}}_{ab} , \tag{3.5}$$

where a and b are a shorthand for the quantum numbers describing electrons a and b, and

$$E'^{G}_{ab}=-\alpha\sum_J\left[\frac{D_{abJ}}{2j_b+1}\left(\frac{J}{2J-1}T^{J-1}_{abJ}+\frac{J+1}{2J+3}T^{J+1}_{abJ}\right)\right.$$
$$\left.+\frac{D_{a'bJ}}{2j_b+1}\frac{(\kappa_a+\kappa_b)^2}{J(J+1)}T^{J}_{abJ}\right] , \tag{3.6}$$

$$E'^{\mathrm{ret}}_{ab}=\alpha\sum_J\frac{D_{abJ}}{2j_b+1}\left[\frac{J^2}{(2J+1)(2J-1)}T^{J-1}_{abJ}\right.$$
$$+\frac{(J+1)^2}{(2J+1)(2J+3)}T^{J+1}_{abJ}$$
$$\left.+\frac{J(J+1)}{2J+1}X_{abJ}\right] , \tag{3.7}$$

where D_{abJ} is defined in Eq. (2.23), $\kappa_{a'}=-\kappa_a$, and

$$T^{J\pm1}_{abJ}=\int_0^\infty dr_1\int_0^\infty dr_2\, j_{J\pm1}(\omega r_<)y_{J\pm1}(\omega r_>)P^{+}_{ab}(r_1)P^{+}_{ab}(r_2) , \tag{3.8}$$

$$T^{J}_{abJ}=\int_0^\infty dr_1\int_0^\infty dr_2\, j_J(\omega r_<)y_J(\omega r_>)U^{+}_{ab}(r_1)U^{+}_{ab}(r_2) , \tag{3.9}$$

$$\begin{aligned} X_{abJ}=\int_0^\infty dr_1 \int_0^{r_1} dr_2 \Bigg[&-2 \left[\omega j_{J-1}(\omega r_<) y_{J+1}(\omega r_>) + \frac{2J+1}{\omega^2} \frac{r_<^{J-1}}{r_>^{J+2}} \right] P_{ab}^-(r_1) P_{ab}^-(r_2) \\ &-2\omega j_{J+1}(\omega r_<) y_{J-1}(\omega r_>) P_{ab}^+(r_1) P_{ab}^-(r_2) \Bigg] , \end{aligned} \tag{3.10}$$

where j_J and y_J are spherical Bessel functions, $\omega = |e_b - e_a|$ is the energy carried by the virtual photon, and

$$P_{ab}^{\pm}(r) = \pm U_{ab}^-(r) + \left[\frac{(\kappa_b - \kappa_a)}{J + (1 \mp 1)/2} \right] U_{ab}^+(r) , \tag{3.11}$$

$$U_{ab}^{\pm}(r) = g_a(r) f_b(r) \pm f_a(r) g_b(r) . \tag{3.12}$$

The relevant value to calculate, to be added to the total DHF energy, is the averaged Breit-interaction energy for the atomic system. In terms of the two-electron matrix elements, this quantity is given by

$$E_{\mathrm{Br}} = \sum_{\substack{a,b \\ a \neq b}} q_a q_b (E_{ab}^{\prime G} + E_{ab}^{\prime \mathrm{ret}}) + \tfrac{1}{2} q_a (q_a - 1) \frac{(2j_a+1)}{2j_a} E_{aa}^{\prime G} , \tag{3.13}$$

where q_i represents the number of electrons in shell i.

In all the calculations performed in this work, the transverse form of the Breit interaction E'_{Br} has been used. The strategies followed to calculate the integrals (3.8)–(3.10) in a Slater-type basis set will be reviewed in Sec. V.

It is interesting to compare the differences between E_G and E'_G and between E_{ret}, E'_{ret}, and E''_{ret} for a certain isoelectronic sequence. Relativistic effects increase as $(\alpha Z)^2$; therefore, one expects the values of E_G and E'_G, and E_{ret} and E'_{ret} to differ more and more as the nuclear charge is increased with the total number of electrons fixed. In other words, calculations that include only unretarded terms will have an appreciable loss of accuracy for large values of Z. On the other hand, one expects the local potential calculation E''_{ret} to converge towards E'_{ret} for large values of Z, as correlation effects become smaller (by $1/Z$) relative to the nuclear Coulomb potential.

As an example, results for the carbon isoelectronic sequence are presented in Table II and in Figs. 5 and 6. The points marked in Figs. 5 and 6 correspond to the values presented in Table II. The closed circles in Fig. 5 show the magnitude of the Gaunt-interaction energy E'_G relative to the VDHF energy: E'_G/E_{VDHF}. This relative contribution increases almost linearly with Z ($E'_G/E_{\mathrm{VDHF}} \sim Z^{1.1}$). The open circles show the relative contribution to the total energy of the retardation term E'_{ret}. E'_{ret} affects the sixth or seventh digit of E_{VDHF} for low values of the nuclear charge, but changes the fourth digit of E_{VDHF} for large values of Z. This limits the accuracy of any DHF calculation that does not include the retardation term. In Fig. 6 we show the differences $E'_G - E_G$ (closed circles), $E'_{\mathrm{ret}} - E_{\mathrm{ret}}$ (open circles), and $E'_{\mathrm{ret}} - E''_{\mathrm{ret}}$ (squares) relative to the VDHF total energy for different values of Z in the carbon isoelectronic sequence. For low values of Z only the eighth or ninth significant digit in the calculation of the total energy will be affected if E_{Br} is used instead of E'_{Br}. For large values of Z, however, the $\omega = 0$ approximation is incorrect to the fifth significant digit of the total energy. The relative difference between E'_{ret} and E''_{ret} decreases with Z, as expected, from 19% for $Z=6$ to 9% for $Z=75$. This decrease is, however, not sufficient to decrease the error introduced in E_{VDHF} by using E'' instead of E'. This error affects the sixth digit of E_{VDHF} over the whole range of values of Z, and in fact E''_{ret} is more accurate than E_{ret} for $Z > 34$.

IV. MATRIX ELEMENTS OF THE RADIAL HAMILTONIAN

In the VDHF method, in order to calculate the expectation value of the DHF Hamiltonian, it is necessary to calculate its matrix elements within a basis set; in our case the set defined by Eqs. (2.37) and (2.38). In this section we discuss the actual implementation of the method presented in Sec. II. Emphasis is given to the aspects of speed and efficiency in the computation of the large number of matrix elements to be calculated during the self-consistent iterative calculations.

Let κ denote the Dirac quantum number that identifies the one-electron eigenstates, and use the notation

$$\phi_{ij}^{\kappa}(r) = \begin{bmatrix} \phi_{ij}^{\kappa u}(r) \\ \phi_{ij}^{\kappa d}(r) \end{bmatrix} \tag{4.1}$$

to denote the upper and lower radial components of a basis vector with indices i,j [Eqs. (2.37) and (2.38)] belonging to the set used to represent the electron states with quantum number κ. With this notation, a typical matrix element of the radial DHF Hamiltonian can be separated into four contributions:

$$\langle \phi_{i'j'}^{\kappa} | H_{\mathrm{DHF}}^{\mathrm{radial}} | \phi_{ij}^{\kappa} \rangle = H^{uu} + H^{ud} + H^{du} + H^{dd} , \tag{4.2}$$

with

$$\begin{aligned} H^{uu} = &\int dr \phi_{i'j'}^{\kappa u} \frac{Z}{r} \phi_{ij}^{\kappa u} + \sum_b \int dr \phi_{i'j'}^{\kappa u} \frac{\mu_{bb}(r)}{r} \phi_{ij}^{\kappa u} \\ &+ \sum_b D_{\kappa b L} \int dr \phi_{i'j'}^{\kappa u}(r) g_b(r) \int dr' \frac{r_<^{\prime L}}{r_>^{\prime L+1}} [\phi_{ij}^{\kappa u}(r') g_b(r') + \phi_{ij}^{\kappa u}(r') g_b(r')] , \end{aligned} \tag{4.3a}$$

TABLE II. Values of the Breit-interaction corrections to the VDHF total energy for different ions in the carbon isoelectronic sequence. E denotes calculations without retardation effects ($\omega=0$), E' is the transverse form of the Breit interaction, and E'' denotes the values in the local-potential approximation.

Z	E_{VDHF}	E'_G	E_G	E'_{ret}	E_{ret}	E''_{ret}
6	−37.657 421 7	0.002 903 1	0.002 903 1	−0.000 058 5	−0.000 058 6	−0.000 069 7
7	−53.853 523 1	0.004 971 5	0.004 971 6	−0.000 128 5	−0.000 128 6	−0.000 147 9
8	−73.073 086 9	0.007 875 6	0.007 876 0	−0.000 237 4	−0.000 237 7	−0.000 266 9
9	−95.313 509 1	0.011 760 0	0.011 760 7	−0.000 393 3	−0.000 393 9	−0.000 435 2
10	−120.575 921	0.016 769 4	0.016 770 6	−0.000 604 5	−0.000 605 6	−0.000 660 6
11	−148.863 269	0.023 048 9	0.023 051 1	−0.000 878 9	−0.000 881 0	−0.000 951 4
12	−180.179 661	0.030 744 3	0.030 747 9	−0.001 224 8	−0.001 228 3	−0.001 315 5
13	−214.530 086	0.040 001 8	0.040 007 6	−0.001 650 2	−0.001 655 7	−0.001 761 2
14	−251.920 274	0.050 968 3	0.050 977 1	−0.002 163 2	−0.002 171 6	−0.002 296 4
15	−292.356 631	0.063 791 3	0.063 804 1	−0.002 772 0	−0.002 784 1	−0.002 929 3
16	−335.846 199	0.078 619 0	0.078 637 4	−0.003 484 2	−0.003 501 7	−0.003 667 8
17	−382.396 637	0.095 600 6	0.095 626 1	−0.004 308 1	−0.004 332 7	−0.004 519 9
18	−432.016 210	0.114 885 9	0.114 920 7	−0.005 251 8	−0.005 285 4	−0.005 493 6
20	−540.498 839	0.160 971 9	0.161 033 0	−0.007 529 8	−0.007 589 4	−0.007 837 7
25	−866.110 668	0.327 192 1	0.327 390 4	−0.015 873 1	−0.016 069 6	−0.016 379 8
30	−1270.688 22	0.582 044 4	0.582 553 5	−0.028 778 8	−0.029 291 6	−0.029 531 9
35	−1756.141 86	0.946 075 8	0.947 191 5	−0.047 204 1	−0.048 346 7	−0.048 249 9
40	−2324.839 52	1.441 073 7	1.443 252 2	−0.072 084 1	−0.074 356 5	−0.073 467 9
45	−2979.664 89	2.090 410 1	2.094 303 5	−0.104 332 5	−0.108 478 8	−0.106 098 2
50	−3724.093 24	2.919 469 7	2.925 952 9	−0.144 844 2	−0.151 915 2	−0.147 033 9
55	−4562.289 72	3.956 170 1	3.966 351 4	−0.194 499 2	−0.205 915 9	−0.197 154 6
60	−5499.237 45	5.231 682 7	5.246 888 0	−0.254 175 6	−0.271 793 2	−0.257 334 8
65	−6540.904 95	6.781 294 0	6.803 013 5	−0.324 759 3	−0.350 926 2	−0.328 458 3
70	−7694.469 12	8.645 559 1	8.675 337 0	−0.407 159 5	−0.444 766 6	−0.411 440 5
75	−8968.615 42	10.872 076	10.911 322	−0.502 354 9	−0.554 870 1	−0.507 252 6
80	−10 373.9500	13.517 621	13.567 312	−0.611 418 6	−0.682 897 1	−0.616 966 9
85	−11 923.5787	16.651 393	16.711 614	−0.735 575 2	−0.830 632 0	−0.741 815 3
90	−13 633.9433	20.360 080	20.429 353	−0.876 314 1	−1.000 045 4	−0.883 267 3

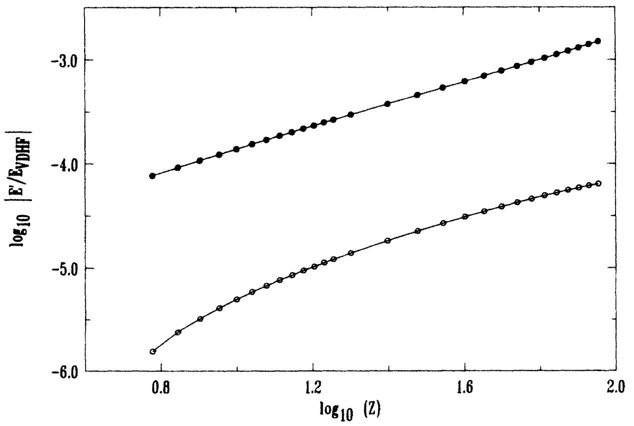

FIG. 5. Values relative to the total energy E_{VDHF} of the Gaunt interaction E'_G (solid circles) and the retardation term E'_{ret} (open circles) for different values of the nuclear charge Z in the carbon isoelectronic sequence.

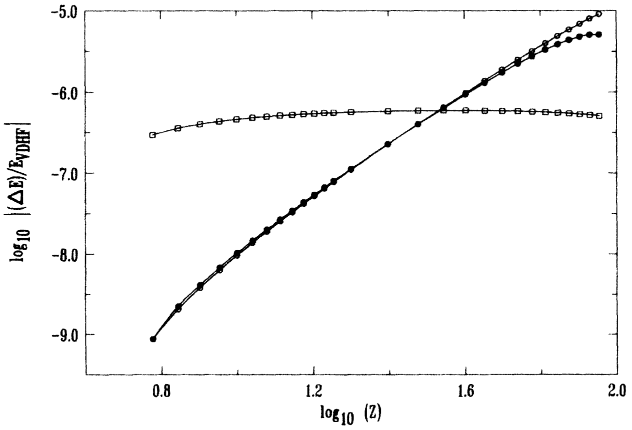

FIG. 6. Values of the difference $E'_G - E_G$ (solid circles), $E'_{\text{ret}} - E_{\text{ret}}$ (open circles), and $E'_{\text{ret}} - E''_{\text{ret}}$ (squares) relative to the total energy E_{VDHF} for different values of the nuclear charge Z in the carbon isoelectronic sequence.

$$H^{ud}=\frac{1}{\alpha}\int dr\,\phi^{\kappa u}_{i'j'}\left[\frac{\kappa}{r}-\frac{d}{dr}\right]\phi^{\kappa d}_{ij} \tag{4.3b}$$

$$H^{du}=\frac{1}{\alpha}\int dr\,\phi^{\kappa d}_{i'j'}\left[\frac{\kappa}{r}+\frac{d}{dr}\right]\phi^{\kappa u}_{ij}\ , \tag{4.3c}$$

$$\begin{aligned}H^{dd}=&\int dr\,\phi^{\kappa d}_{i'j'}\left[\frac{2}{\alpha^2}+\frac{Z}{r}\right]\phi^{\kappa d}_{ij}+\sum_b\int dr\,\phi^{\kappa d}_{i'j'}\frac{\mu_{bb}(r)}{r}\phi^{\kappa d}_{ij}\\&+\sum_b D_{\kappa bL}\int dr\,\phi^{\kappa d}_{i'j'}(r)g_b(r)\int dr'\frac{r'^{L}_{<}}{r'^{L+1}_{>}}[\phi^{\kappa d}_{ij}(r')g_b(r')+\phi^{\kappa d}_{ij}(r')g_b(r')]\ ,\end{aligned} \tag{4.3d}$$

where $\mu_{bb}(r)$ and $D_{\kappa bL}$ are defined in Eqs. (2.19) and (2.23). The functions $g_b(r)$ and $f_b(r)$ stand for the large and small radial components of the eigenstates of each of the shells in the electronic configuration; g_b and f_b are of course not known *a priori*.

In this work, variational hydrogenic Coulomb eigenstates were chosen as initial guesses to start the calculation. With this initial guess, all the matrix elements in Eq. (4.3) can be calculated, and the expectation value of the total VDHF energy can be minimized with respect to the linear (variational) parameters in the expansion of Eq. (2.36). This is achieved by the diagonalization of the DHF Hamiltonian matrix. This diagonalization yields a new set of functions g_b and f_b that are in general different from the initial guess. The new functions are now used in Eq. (4.3), and the DHF equations are solved again to obtain a new set of eigenvalues and eigenfunctions. This process is continued until self-consistency is achieved, i.e., until the change in all the eigenstates is smaller than a certain convergence criterion.

The whole process is then repeated for different sets of the nonlinear parameters λ_j in Eqs. (2.37) and (2.38), until the total energy (2.40) is minimized. There are standard strategies for nonlinear minimization.[22] In this work, a new and very efficient minimization method based on the relativistic virial theorem (2.5) (Ref. 14) has been used. This method is based on the fact that the virial theorem (2.5) is satisfied in the VDHF case at the variational minimum. Its strategy is to follow the directions defined by the gradients with respect to the nonlinear parameters, of the expectation value of β and of the total energy, to find the minimum of E_{VDHF}. For a finite (incomplete) basis set, the values of the nonlinear parameters for which E and $\langle\beta\rangle$ are stationary do not coincide. Therefore, at a precision better than the difference between these stationary points, the method fails to continue to minimize. This method has then the added advantage that it provides a natural end to the nonlinear optimization procedure, i.e., it decides at which point it is worthless to continue minimizing the total energy.[14]

In this work, the radial basis vectors are expressed in terms of the normalized basis functions

$$\xi_p=\left[\frac{(\lambda_{j_p})^{\sigma_p}}{\Gamma(\sigma_p)}\right]^{1/2} r^{\eta_p}\exp(-\lambda_{j_p}r)\ , \tag{4.4a}$$

where

$$\eta_p=\gamma_p+i_p=[\kappa_p^2-(\alpha Z)^2]^{1/2}+i_p\ , \tag{4.4b}$$

$$\sigma_p=2\eta_p+1\ , \tag{4.4c}$$

and

$$i_p=0,1,\ldots,N-1;\ j_p=1,2,\ldots,M\ . \tag{4.4d}$$

The matrix elements of H^{ud} and H^{du}, the first term in H^{uu}, and the first two terms of H^{dd} can all be written as linear combinations of the integral

$$\int dr\,\xi_1\frac{1}{r^m}\xi_2=\frac{\Gamma(\eta_1+\eta_2+m+1)}{[\Gamma(\sigma_1)\Gamma(\sigma_2)]^{1/2}}\frac{[(\lambda_{j_1})^{\sigma_1}(\lambda_{j_2})^{\sigma_2}]^{1/2}}{(\lambda_{j_1}+\lambda_{j_2})^{\eta_1+\eta_2+m+1}}\ . \tag{4.5}$$

The calculation of the direct and exchange terms in (4.3a) and (4.3b) is more involved. These terms can be written as linear combinations of the integrals $V_L(1,2,3,4;0,0)$ that are special cases of the general integral

$$\begin{aligned}V_L(1,2,3,4;m',m)&\equiv\int_0^\infty dr_1\int_0^\infty dr_2\,\xi_1(r_1)\xi_2(r_1)\xi_3(r_2)\\&\quad\times\xi_4(r_2)\frac{r_<^{L+2m'}}{r_>^{L+1+2(m'-m)}}\ .\end{aligned} \tag{4.6}$$

The case $m'\neq 0$, $m\neq 0$ will be used below to calculate the Breit interaction.

The integral (4.6) can be expressed in closed form in terms of hypergeometric functions.[23] Writing

$$\begin{aligned}V_L(1,2,3,4;m',m)=&\,W_L^{>}(1,2,3,4;m',m)\\&+W_L^{<}(1,2,3,4;m',m)\ ,\end{aligned} \tag{4.7}$$

where $W^>$ is the contribution to V_L from the domain $r_2>r_1$ and $W^<$ is the contribution from the domain $r_2<r_1$, we obtain

$$W_L^{>}(1,2,3,4;m',m)=\frac{N(1,2,3,4;m)}{\eta_1+\eta_2+L+2m'+1}\,{}_2F_1[1,\eta+2m+1,\eta_1+\eta_2+L+2m'+2;(\lambda_{j_1}+\lambda_{j_2})/\lambda] \tag{4.8a}$$

(the equation for $W^{<}$ is the same with η_3,η_4,j_3,j_4 substituted for η_1,η_2,j_2,j_2), where

$$\eta=\eta_1+\eta_2+\eta_3+\eta_4,\quad \lambda=\lambda_{j_1}+\lambda_{j_2}+\lambda_{j_3}+\lambda_{j_4}\ , \tag{4.8b}$$

and

$$N(1,2,3,4;m)=\frac{[(\lambda_{j_1})^{\sigma_1}(\lambda_{j_2})^{\sigma_2}(\lambda_{j_3})^{\sigma_3}(\lambda_{j_4})^{\sigma_4}]^{1/2}}{\lambda^{(\sigma_1+\sigma_2+\sigma_3+\sigma_4+2m+1)}}\times\frac{\Gamma(\eta+2m+1)}{[\Gamma(\sigma_1)\Gamma(\sigma_2)\Gamma(\sigma_3)\Gamma(\sigma_4)]^{1/2}}\ . \tag{4.8c}$$

The number of integrals of the form (4.6) to be calculated is, in principle, very large for the size of basis sets used in the present work. A straight calculation of all these terms in each of the iterations would make use of a prohibitive amount of computer memory and CPU time. There are, however, several shortcuts to make the calculations more efficient.

(i) The integral (4.6) is invariant under several permutations of the functions in the integrand, like 1↔2; 3↔4; 1,2↔3,4; etc. It is necessary therefore, to calculate only a subset of the possible combinations occurring in (4.6).

(ii) The basis set used is not changed during the iteration process leading to self-consistency. Therefore, the integrals (4.5) and (4.6) need to be calculated only once for a given set of nonlinear parameters. They can then be stored and reused in each of the iterations.

(iii) For a given set of nonlinear parameters, the exchange of powers $i_1 \leftrightarrow i_2$ or $i_3 \leftrightarrow i_4$ in (4.6) is irrelevant. Only terms involving different values of the *sums* i_1+i_2 or i_3+i_4 need to be calculated.

(iv) For each set of nonlinear parameters, only a few of the hypergeometric functions in (4.8) need to be calculated. The rest can be obtained using the recursion relations[24]

$$F(1,b;c+1;z)=[-c(1-z)F(1,b;c;z)+cF(1,b-1;c;z)]/[(c-1)z]\ , \tag{4.9a}$$

$$F(1,b+1;c;z)=\{(c-b)F(1,b-1;c;z)-[c-2b+(b-1)z]F(1,b;c;z)\}/[b(1-z)]\ . \tag{4.9b}$$

V. MATRIX ELEMENTS OF THE BREIT INTERACTION

In Sec. III the Breit interaction was written in terms of the expressions (3.8)–(3.10) that consist of integrals involving products of two spherical Bessel functions and four basis functions of the form (4.4). In order to calculate these terms in closed form, we perform a power expansion of each of the products of Bessel functions needed. The standard expansions of $j_J(x)$ and $y_J(x)$ are[24]

$$j_J(x)=\sum_{k=0}^{\infty}\frac{(-1)^k}{k!2^k(2J+2k+1)!!}x^{2k+J} \tag{5.1}$$

and

TABLE III. Values of the optimized nonlinear parameters for basis functions of the form (2.37) for the $\kappa=-1$ states ($s_{1/2}$ states) in He-, Be-, C-, and Ne-like ions. The parameters are scaled by the nuclear charge Z.

	$\kappa=-1$							
	He		Be		C		Ne	
Z	λ_1/Z	λ_2/Z	λ_1/Z	λ_2/Z	λ_1/Z	λ_2/Z	λ_1/Z	λ_2/Z
2	0.594 921	2.380 86						
3	0.609 794	2.440 38						
4	0.631 289	2.440 38	0.273 470	1.425 60				
5	0.647 071	2.440 38	0.292 915	1.439 86				
6	0.686 056	2.488 55	0.307 561	1.439 86	0.276 535	1.306 66		
7	0.829 059	2.567 04	0.329 430	1.484 83	0.292 037	1.366 25		
8	0.849 786	2.567 04	0.345 902	1.480 53	0.308 409	1.428 55		
9	0.833 691	2.544 82	0.363 197	1.515 21	0.322 473	1.442 84		
10	0.854 533	2.544 82	0.385 170	1.516 86	0.337 178	1.457 26	0.286 624	1.409 77
11	0.854 533	2.544 56	0.400 385	1.555 39	0.352 555	1.471 84	0.311 307	1.456 02
12	0.854 533	2.544 56	0.420 404	1.567 68	0.368 632	1.518 29	0.339 977	1.485 70
13	0.875 063	2.554 83	0.441 424	1.565 52	0.385 442	1.508 89	0.358 504	1.484 90
14	0.896 941	2.590 46	0.468 130	1.565 52	0.403 020	1.523 98	0.371 141	1.499 75
15	0.892 798	2.707 96	0.486 621	1.640 21	0.421 398	1.541 41	0.384 224	1.499 75
16	0.892 798	2.707 96	0.476 799	1.625 49	0.440 615	1.556 83	0.393 829	1.499 75
17	0.915 117	2.707 96	0.500 638	1.624 10	0.465 315	1.572 43	0.403 675	1.499 75
18	0.919 297	2.718 15	0.494 764	1.625 74	0.465 315	1.572 43	0.417 905	1.537 24

$$y_J(x) = -\sum_{k=0}^{\infty} \frac{(2J+1)!!}{k!2^k(2J+1)\cdots(2J-2k+1)} x^{2k-J-1} . \tag{5.2}$$

Using these expansions for each of the products $j_J(\omega r_<) y_{J'}(\omega r_>)$ and regrouping the terms with the same power of ω, we obtain the following general expression:

$$\begin{aligned} j_{J+q}(\omega r_<) y_{J-q}(\omega r_>) &= \frac{(2J-2q-1)!!}{(2J+2q+1)!!} \frac{r_<^{J+q}}{r_>^{J-q+1}} \omega^{2q-1} \\ &\quad \times \sum_{m=0}^{\infty} \omega^{2m} \sum_{m'=0}^{m} A^q_{J,m',m-m'} \frac{r_<^{2m'}}{r_>^{2(m'-m)}} , \end{aligned} \tag{5.3}$$

where

$$q = 1, 0, -1$$

and

$$\begin{aligned} A^q_{j,k,k'} &= \frac{(-1)^{k+1}}{k!k'!2^{k+k'}} \frac{(2J+2q+1)}{\prod_{m=0}^{k} (2J+2q+2m+1)} \\ &\quad \times \frac{(2J-2q+1)}{\prod_{m'=0}^{k} (2J-2q-2m'+1)} . \end{aligned} \tag{5.4}$$

The terms in the basis-set expansion of the integrals (3.8)–(3.10) are of the form

$$\begin{aligned} Q_n(1,2,3,4) &= \int_0^{\infty} dr_1 \int_0^{\infty} dr_2 \xi_1(r_1) \xi_2(r_1) \xi_3(r_2) \\ &\quad \times \xi_4(r_2) j_n(\omega r_<) y_n(\omega r_>) . \end{aligned} \tag{5.5}$$

Using the definitions (4.6), (5.3), and (5.4) this can be expanded as a series in powers of ω:

$$\begin{aligned} Q_n&(1,2,3,4) \\ &= \frac{1}{\omega(2n+1)} \sum_{m=0}^{\infty} \omega^{2m} \sum_{m'=0}^{m} A^0_{n,m',m-m'} \\ &\quad \times V_n(1,2,3,4;m',m). \end{aligned} \tag{5.6}$$

Let R_n^q be a typical term in the basis-set expansion of the retardation term (3.10). R_n^q differs from (5.5) in the relative order of the Bessel functions involved, and in the limits of integration,

$$\begin{aligned} R_n^q(1,2,3,4) &= \int_0^{\infty} dr_1 \int_0^{r_1} dr_2 \xi_1(r_1) \xi_2(r_1) \xi_3(r_2) \xi_4(r_2) \\ &\quad \times j_{n-q}(\omega r_<) y_{n+q}(\omega r_>) . \end{aligned} \tag{5.7}$$

Using the definitions (4.7), (4.8), (5.3), and (5.4) we obtain in this case

$$R_n^q(1,2,3,4) = \frac{(2n-2q-1)!!}{(2n+2q+1)!!} \omega^{2q-1} \sum_{m=0}^{\infty} \omega^{2m} \sum_{m'=0}^{m} A^q_{n,m',m-m'} W^<_{n+q}(1,2,3,4;m',m-q) . \tag{5.8}$$

The Breit interaction can therefore be written as an expansion in powers of $\omega = \Delta e$, where Δe is the energy difference between the two electron states involved in the calculation of Eqs. (3.6) and (3.7). Each term in the expansion in ω involves a linear combination of hypergeometric functions. The same computational shortcuts described in Sec. IV also apply here.

With the method described above, one avoids the need

TABLE IV. Values of the optimized nonlinear parameters for basis functions of the form (2.37) and (2.38) for the $\kappa=1$ states ($p_{1/2}$ states) in C- and Ne-like ions; and for the $\kappa=-2$ states ($p_{3/2}$) states in Ne-like ions. The parameters are scaled by the nuclear charge Z.

	$\kappa=1$				$\kappa=-2$	
	C		Ne		Ne	
Z	λ_1/Z	λ_2/Z	λ_1/Z	λ_2/Z	λ_1/Z	λ_2/Z
6	0.179 441	0.673 266				
7	0.187 624	0.679 999				
8	0.196 180	0.686 799				
9	0.205 127	0.693 667				
10	0.214 481	0.700 603	0.217 705	0.750 533	0.216 995	0.769 620
11	0.224 262	0.700 603	0.227 633	0.735 094	0.220 196	0.785 089
12	0.229 868	0.700 558	0.223 103	0.716 521	0.309 064	0.823 970
13	0.233 259	0.703 072	0.220 872	0.713 228	0.326 857	0.914 800
14	0.236 699	0.696 041	0.220 872	0.713 228	0.341 763	0.995 356
15	0.236 699	0.696 041	0.221 889	0.706 096	0.357 348	1.083 005
16	0.236 699	0.696 041	0.225 162	0.706 096	0.369 945	1.178 373
17	0.242 617	0.699 729	0.226 198	0.699 035	0.369 945	1.219 910
18	0.246 195	0.699 729	0.229 534	0.699 035	0.382 985	1.237 904

TABLE V. VDHF values (in a.u.) of the 1*s*-subshell energy and the total energy for several ions of the helium isoelectronic sequence. These values are obtained using a basis set with two exponential parameters and six powers per exponential, for each of the large and small components. The numbers between parentheses are the errors in the last digit of the total energy as given by the virial-theorem optimization method.

Z	$e(1s)$	E	$E+E'_{\mathrm{Br}}$
2	−0.917 990 688 2	−2.861 813 342 1(4)	−2.861 749 564 7(4)
3	−2.792 635 394 6	−7.237 205 520 7(3)	−7.236 947 773 9(3)
4	−5.668 149 524 6	−13.614 001 410(3)	−13.613 335 212(3)
5	−9.544 788 733 4	−21.993 149 188(4)	−21.991 780 042(4)
6	−14.423 138 486	−32.375 989 218(1)	−32.373 542 520(1)
7	−20.303 983 463	−44.764 201 119(4)	−44.760 222 033(4)
8	−27.188 282 671	−59.159 794 044(1)	−59.153 747 357(1)
9	−35.077 162 827	−75.565 105 006(1)	−75.556 374 959(1)
10	−43.971 916 565	−93.982 799 546(1)	−93.970 689 631(1)
11	−53.874 002 344	−114.415 873 36	−114.399 606 10
12	−64.785 045 089	−136.867 654 51	−136.846 371 20
13	−76.706 837 241	−161.341 805 96	−161.314 566 41
14	−89.641 340 072	−187.842 328 57	−187.808 110 77
15	−103.590 685 22	−216.373 564 30	−216.331 264 10
16	−118.557 176 38	−246.940 199 80	−246.888 630 54
17	−134.543 291 21	−279.547 270 23	−279.485 162 41
18	−151.551 683 37	−314.200 163 58	−314.126 164 33

for numerical integrations and is able to achieve high accuracy in the calculation of the Breit interaction. The expansion in powers of ω converges very fast even for large values of the nuclear charge. The number of even powers of ω needed to obtain the total energy accurate to ten significant digits, varies from a few for small Z to about 30 powers for large Z.

There is another advantage in the use of the expansion (5.3): The term $-\alpha/R$ in H''_{ret} [Eq. (3.4b)] and the term $[(2J+1)/\omega^2](r_<^{J-1}/r_>^{J+2})$ in E'^{ret} [Eqs. (3.7) and (3.10)] are exactly canceled by the lowest-order term ($m=0$) in the expansion of

$$(2J+1)j_J(\omega r_<)y_J(\omega r_>)$$

and

$$\omega j_{J-1}(\omega r_<)y_{J+1}(\omega r_>)\ ,$$

respectively. In other words the lowest-order cancellation occurring in (3.4b) and (3.11) can be extracted *a priori*, avoiding in this way the loss of numerical accuracy.

TABLE VI. VDHF values (in a.u.) of the 1*s* and 2*s*-subshell energies and the total energy for several ions of the beryllium isoelectronic sequence. These values were obtained using a basis set with two exponential parameters and six powers per exponential, for each of the large and small components. The numbers between parentheses are the errors in the last digit of the total energy as given by the virial-theorem optimization method

Z	$e(1s)$	$e(2s)$	E	$E+E'_{\mathrm{Br}}$
4	−4.733 498 0	−0.309 322 07	−14.575 892 2(1)	−14.575 189 7(1)
5	−8.188 200 9	−0.874 080 27	−24.245 166 3(2)	−24.243 685 3(2)
6	−12.655 791 4	−1.694 814 51	−36.425 154 7(3)	−36.422 459 2(3)
7	−18.130 367 1	−2.768 517 26	−51.114 501 69(3)	−51.110 058 07(3)
8	−24.610 519 0	−4.094 272 97	−68.314 413 16(20)	−68.307 590 00(20)
9	−32.096 294 5	−5.671 854 52	−88.027 228 46(1)	−88.017 296 27(1)
10	−40.588 405 9	−7.501 339 80	−110.256 007 7(1)	−110.242 138 6(1)
11	−50.087 958 34	−9.582 975 77	−135.004 381 78(5)	−134.985 649 29(5)
12	−60.596 338 84	−11.917 121 8	−162.276 489 86(1)	−162.251 868 48(1)
13	−72.115 165 80	−14.504 223 5	−192.076 951 43(5)	−192.045 316 28(5)
14	−84.646 263 97	−17.344 798 9	−224.410 853 69(9)	−224.370 980 12(9)
15	−98.191 651 54	−20.439 432 02	−259.283 746 70(3)	−259.234 309 82(3)
16	−112.753 533 6	−23.788 768 24	−296.701 642 65(3)	−296.641 216 84(3)
17	−128.334 298 8	−27.393 512 86	−336.671 017 69(1)	−336.598 076 05(1)
18	−144.936 518 5	−31.254 429 73	−379.198 815 22(2)	−379.111 729 02(2)

TABLE VII. VDHF values (in a.u.) of the 1*s*, 2*s*, and $2p^*$ subshell energies and the total energy for several ions of the carbon isoelectronic sequence. These values were obtained using a basis set with two exponential parameters and six powers per exponential, for each of the large and small components for each shell. The numbers between parentheses are the errors in the last digit of the total energy as given by the virial-theorem optimization method.

Z	$e(1s)$	$e(2s)$	$e(2p^*)$	E	$E+E'_{\mathrm{Br}}$
6	−11.351 866 6	−0.716 862 8	−0.389 730 2	−37.657 421 7(23)	−37.654 577 2(23)
7	−16.313 131 7	−1.472 291 5	−1.047 011 7	−53.853 523 1(20)	−53.848 680 1(20)
8	−22.296 027 8	−2.489 749 0	−1.962 681 0	−73.073 086 9(13)	−73.065 448 7(13)
9	−29.292 361 4	−3.763 208 5	−3.133 227 9	−95.313 509 1(11)	−95.302 142 4(11)
10	−37.299 436 8	−5.290 706 1	−4.557 283 8	−120.575 920 8(7)	−120.559 755 8(7)
11	−46.316 554 1	−7.071 517 7	−6.234 292 8	−148.863 268 9(6)	−148.841 098 9(6)
12	−56.344 016 0	−9.105 460 3	−8.164 108 9	−180.179 661 3(1)	−180.150 141 9(1)
13	−67.382 729 6	−11.392 641	−10.346 830	−214.530 085 7(6)	−214.491 734 1(6)
14	−79.434 021 0	−13.933 349	−12.782 716	−251.920 273 7(1)	−251.871 468 6(1)
15	−92.499 537 9	−16.728 001	−15.472 148	−292.356 630 9(4)	−292.295 611 5(4)
16	−106.581 196	−19.777 114	−18.415 605	−335.846 199 3(10)	−335.771 064 4(10)
17	−121.681 149	−23.081 290	−21.613 646	−382.396 637 3(22)	−382.305 344 8(22)
18	−137.801 769	−26.641 204	−25.066 906	−432.016 210 3(27)	−431.906 576 1(27)

VI. RESULTS

In this section, results of the VDHF calculations are presented for members of the He, Be, C, and Ne isoelectronic sequences with values of the nuclear charge up to $Z=18$.

In all cases, Slater-type basis functions of the form (4.4) were used, with two exponential parameters and six powers for each of the configurations:

$$\xi_{i,j}=Nr^{\gamma+i}e^{-\lambda_j r},\quad i=0,1,\ldots,5,\quad j=1,2\ , \tag{6.1}$$

where N is a normalization constant.

The nonlinear parameter γ in (6.1) has been chosen to reproduce the exact behavior of the one-electron wave function at the origin, i.e.,

$$\gamma=[\kappa^2-(\alpha Z)^2]^{1/2}\ , \tag{6.2}$$

where κ is the Dirac quantum number identifying the electronic shell.

In all cases, the total energy has been optimized with respect to (i) the linear coefficients in the expansion (2.36), by diagonalizing the radial VDHF Hamiltonian matrix; and (ii) all the nonlinear coefficients λ_j in (6.1), using the virial-theorem optimization method.[14]

The values of the optimized nonlinear parameters scaled by the nuclear charge Z are presented in Table III for the $\kappa=-1$ shells ($s_{1/2}$ states), and in Table IV for the $\kappa=1$ shells ($p_{1/2}$ states) and the $\kappa=-2$ shell ($p_{3/2}$ states). Tables of the optimized linear coefficients have not been included because of the large amount of space required. These can be obtained from the author.

In Tables V–VIII we display the optimized VDHF values for the one-electron energies and the total energies for He-, Be-, C-, and Ne-like ions, respectively. In all cases these values are upper bounds to the numerical DHF solutions and, in general, differ from those solutions in the last digit quoted. The numbers between parentheses in the columns for the total energy are the errors in the last digit of the total energy provided by the virial-theorem optimization method. This error is given by the difference $|E-\langle\beta\rangle|$ at the point in which the minimization process came to an end. The values

TABLE VIII. VDHF values (in a.u.) of the 1*s*, 2*s*, $2p^*$, and 2*p*-subshell energies and the total energy for several ions of the neon isoelectronic sequence. These values were obtained using a basis set with two exponential parameters and six powers per exponential, for each of the large and small components for each shell. The numbers between parentheses are the errors in the last digit of the total energy as given by the virial-theorem optimization method.

Z	$e(1s)$	$e(2s)$	$e(2p^*)$	$e(2p)$	E	$E+E'_{\mathrm{Br}}$
10	−32.817 470 3	−1.935 845 3	−0.852 829 0	−0.848 265 9	−128.691 969 2(20)	−128.675 329 3(20)
11	−40.826 574 0	−3.082 402 3	−1.801 417 4	−1.794 008 8	−161.895 968 0(1)	−161.872 609 5(2)
12	−49.864 792 7	−4.496 468 8	−3.013 354 0	−3.001 745 4	−199.150 137 2(4)	−199.118 376 7(4)
13	−59.925 489 3	−6.171 319 0	−4.483 865 3	−4.466 379 1	−240.451 870 7(2)	−240.409 830 9(3)
14	−71.006 252 3	−8.104 131 4	−6.210 924 0	−6.185 500 2	−285.802 800 3(7)	−285.748 409 3(7)
15	−83.106 533 2	−10.293 639	−8.193 623 2	−8.157 772 6	−335.206 897 9(9)	−335.137 889 0(9)
16	−96.226 821 0	−12.739 342	−10.431 628	−10.382 388	−388.669 697 7(18)	−388.583 608 6(18)
17	−110.368 280	−15.441 174	−12.924 944	−12.858 834	−446.197 918 5(23)	−446.092 091 0(23)
18	−125.532 561	−18.399 346	−15.673 800	−15.586 780	−507.799 261 9(39)	−507.670 841 2(39)

TABLE IX. Values of the Gaunt and retardation contributions to the transverse form of the Breit interaction [Eq. (3.3)] for He-, Be-, C-, and Ne-like ions.

	He	Be		C		Ne	
	E'_G	E'_G	E'_{ret}	E'_G	E'_{ret}	E'_G	E'_{ret}
Z	10^{-2} a.u.	10^{-2} a.u.	10^{-2} a.u.	10^{-1} a.u.	10^{-1} a.u.	10^{-1} a.u.	10^{-1} a.u.
2	0.006 377 74						
3	0.025 774 70						
4	0.066 619 82	0.070 634 0	−0.000 384 9				
5	0.136 914 53	0.149 319 1	−0.001 217 1				
6	0.244 669 80	0.272 303 8	−0.002 751 2	0.029 030 9	−0.000 585 43		
7	0.397 908 62	0.449 556 2	−0.005 193 6	0.049 715 0	−0.001 285 06		
8	0.604 668 65	0.691 068 5	−0.008 752 8	0.078 756 4	−0.002 373 70		
9	0.873 004 71	1.006 858 3	−0.013 688 3	0.117 600 1	−0.003 933 07		
10	1.210 991 5	1.406 972 1	−0.020 063 5	0.167 693 5	−0.006 044 52	0.175 354 2	−0.008 955 27
11	1.626 726 0	1.901 489 4	−0.028 241 0	0.230 488 9	−0.008 789 21	0.247 493 5	−0.013 908 58
12	2.128 330 6	2.500 525 9	−0.038 387 8	0.307 442 9	−0.012 248 18	0.338 001 3	−0.020 396 66
13	2.723 955 2	3.214 237 7	−0.050 723 2	0.400 018 1	−0.016 502 29	0.449 018 3	−0.028 620 24
14	3.421 780 5	4.052 825 8	−0.065 469 4	0.509 683 0	−0.021 632 25	0.582 688 2	−0.038 778 42
15	4.230 020 2	5.026 539 7	−0.082 852 0	0.637 912 8	−0.027 718 55	0.741 158 1	−0.051 068 91
16	5.156 924 5	6.145 681 8	−0.003 100 2	0.786 190 3	−0.034 841 51	0.926 578 7	−0.065 688 09
17	6.210 782 5	7.420 611 4	−0.026 446 8	0.956 005 9	−0.043 081 22	1.141 105 4	−0.082 830 95
18	7.399 925 0	8.861 749 5	−0.053 129 0	1.148 858 9	−0.052 517 54	1.386 898 2	−0.102 690 98

obtained for the Gaunt and retardation contributions of the Breit-interaction corrections are given in Table IX.

The one-electron energies can be interpolated by a polynomial expansion in powers of Z^{-1}. However, an intuitive understanding can be gained if instead we express the one-electron results in terms of screening parameters. This can be achieved if for each value Z_i of the nuclear charge we express the DHF one-electron energies e_i as one-electron Dirac-Coulomb energies with a screened value of the nuclear charge $Z_i-\sigma_i(Z)$:

$$\alpha e_i=\left[1+\frac{\alpha^2(Z_i-\sigma_i)^2}{\{n-|\kappa|+[\kappa^2-\alpha^2(Z_i-\sigma_i)^2]^{1/2}\}^2}\right]^{-1/2}, \tag{6.3}$$

where n is the (nonrelativistic) principal quantum number.

A least-squares fit has been made for each of the one-electron states in each of the isoelectronic sequences. The screening function $\sigma(z)$ is approximated by either the polynomial ratio

$$\sigma(Z)\approx\sigma_0\frac{1+\sigma_1\zeta+\sigma_2\zeta^2}{1+\sigma_3\zeta+\sigma_4\zeta^2}, \tag{6.4a}$$

or the polynomial

$$\sigma(z)\approx\sum_{i=0}^{4}\sigma_i\zeta^i, \tag{6.4b}$$

with the one giving the better fit having been chosen. In (6.4), for each value Z_i of the nuclear charge,

$$\zeta_i=1-\frac{Z_0}{Z_i}, \tag{6.5}$$

TABLE X. Coefficients for the expansion of the nuclear-charge screening $\sigma(Z)$ defined by Eq. (6.3). The coefficients refer to Eq. (6.4a) or (6.4b), as indicated in the third column of the table.

			σ_0	σ_1	σ_2	σ_3	σ_4
He	1*s*	(a)	0.645 033 274	−0.682 865 651	−0.394 319 895	−0.639 217 963	−0.440 167 370
Be	1*s*	(a)	0.923 345 676	−0.153 751 657	−1.022 858 592	−0.342 686 559	−0.815 948 331
	2*s*	(a)	2.426 946 974	−0.358 618 997	−0.653 357 202	−0.188 822 026	−0.821 575 571
C	1*s*	(b)	1.235 876 949	0.405 192 024	−0.236 959 677	0.136 323 520	−0.060 271 545
	2*s*	(b)	3.605 359 950	−0.227 503 438	−0.310 210 991	0.675 587 641	−0.450 958 476
	$2p^*$	(a)	4.234 277 519	1.224 416 342	−0.759 972 283	1.488 879 172	−0.876 083 852
Ne	1*s*	(b)	1.902 001 343	0.766 005 760	−0.375 019 811	0.226 292 679	−0.173 514 510
	2*s*	(b)	6.065 198 029	−0.264 059 853	−0.904 295 779	2.054 064 262	−1.720 005 847
	$2p^*$	(a)	7.388 121 020	2.081 115 133	−0.674 522 347	2.411 440 175	−0.653 397 069
	2*p*	(a)	7.395 011 823	5.253 331 366	4.342 137 591	5.586 937 210	5.328 347 281

with Z_0 being the nuclear charge of the neutral atom of the isoelectronic sequence under consideration. The variable ζ in (6.5) is zero for the neutral atom and is always smaller than 1: $0 \leq \zeta < 1$. Therefore, σ_0 is the screening of the lowest member of the sequence and the coefficients in the expansion (6.4) will be of similar orders of magnitude.

The values of the coefficients σ_i are given in Table X, where in the third column it is indicated if Eq. (6.4a) or (6.4b) was used. The interpolated one-electron energy values obtained using Eqs. (6.3)–(6.5) with the coefficients of Table X agree in general to the fifth significant figure with the exact values. The use of (6.4) to extrapolate the values of the one-electron energies has been tested for carbon, yielding values accurate to better than 1% up to $Z = 90$.

ACKNOWLEDGMENTS

The author would like to thank Dr. A. Dalgarno for his encouragement during the initial stages of this work, Dr. W. R. Johnson for discussions regarding the Breit interaction, and Dr. R. A. Holt and Dr. S. D. Rosner for many useful discussions during the development of this work. Research support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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