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# Relativistic many-body perturbation theory based on the no-pair Dirac-Coulomb-Breit Hamiltonian: Relativistic correlation energies for the noble-gas sequence through Rn ($Z = 86$), the group-II*B* atoms through Hg, and the ions of Ne isoelectronic sequence

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Relativistic correlation energies have been computed for the neutral rare-gas atoms Ne, Ar, Kr, Xe, and Rn, the group-II*B* atoms Zn, Cd, and Hg, and the ions of the Ne isoelectronic sequence with up to $Z = 100$ by means of a recently developed relativistic many-body perturbation theory based on the no-pair Dirac-Coulomb-Breit Hamiltonian. Analytic basis sets of Gaussian-type functions are employed to expand the upper and lower components of the Dirac four-spinors in the matrix Dirac-Fock self-consistent-field and relativistic many-body perturbation procedures. The effects of the low-frequency Breit interaction on relativistic many-body effects for high-$Z$ neutral atoms and Ne-like highly ionized ions are examined.

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## I. INTRODUCTION

Construction of an effective many-body theory that accurately accounts for both relativistic and electron correlation effects in many-electron systems is a challenging problem. A great deal of effort has been directed toward developing a relativistic many-body theory formulated in particular with discrete basis expansion methods [1–9]. As Johnson *et al.* argue [1], one needs a many-body method that accounts for relativistic and correlation effects at a level of accuracy adequate to examine the residual quantum electrodynamics (QED) effects. The accurate determination of relativistic and correlation energies is also becoming important for calibrating density-functional theory because of the growing interest in testing the performance of a variety of functionals for correlation energy [10].

Electron correlation effects are corrections to the independent-electron approximation and their importance depends on the choice of the model on which they are based. In nonrelativistic many-body theory, the most widely used definition of the correlation energy is that due to Lowdin [11]: "The correlation energy for a certain state with respect to a specified Hamiltonian is the difference between the exact eigenvalue of the Hamiltonian and its expectation value in the Hartree-Fock (HF) approximation for the state under consideration." Kim has recently argued [12] that this definition of electron correlation energy is inadequate in the framework of relativistic many-body theory. In relativistic many-body theory for atoms and molecules, it is appropriate to replace the HF approximation by the well-defined relativistic independent-electron model, the Dirac-Fock (DF) approximation [12]. Unlike the nonrelativistic Schrödinger Hamiltonian, the relativistic many-body Hamiltonian for atomic and molecular systems cannot be expressed in closed potential form. In order to construct relativistic many-body theories, e.g., relativistic many-body perturbation theory (MBPT) and coupled-cluster (CC) theory, it is convenient to express the problem to a desired degree of accuracy in the form of a Schrödinger-like equation with an effective Hamiltonian [13,14]. The effective many-body Hamiltonian approach is attractive because it conveys the idea that atoms and molecules are weakly bound inhomogeneous many-electron systems in which pair production processes are suppressed and particle number is conserved. With such a relativistic many-body Hamiltonian, one can employ the techniques developed in nonrelativistic many-body theories to calculate correlation effects. Relativistic many-body Hamiltonians may be derived from first principles, i.e., from QED. Depending on the order of QED effects included, effective Hamiltonians may be derived in varying degrees of approximation. The most commonly used effective many-body Hamiltonians for relativistic calculations on atoms and molecules are the no-pair Dirac-Coulomb (DC) [13,14] and Dirac-Coulomb-Breit (DCB) Hamiltonians [13,14]. The relativistic independent-electron models derived from the no-pair DC and DCB Hamiltonians are the Dirac-Fock-Coulomb (DFC) [15–20] and Dirac-Fock-Breit (DFB) self-consistent-field (SCF) methods [20–22].

A number of highly ionized ions have been studied

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using relativistic MBPT [1,3,6,23], CC theory [3,24,25], configuration-interaction theory [2,26], and multiconfigurational SCF methods [12,27] to examine relativistic, QED, and electron correlation effects. For highly ionized ions, a description of the system in terms of the DFB SCF wave function plus the second-order MBPT is sufficient for the study of QED effects [1,6]. On the other hand, there are only a few published relativistic MBPT and CC calculations [9,28–31] on neutral heavy atoms that account for both relativistic and correlation effects because of the difficulty in evaluating relativistic and correlation effects for truly many-electron high-$Z$ systems. Applications of relativistic many-body calculations have been mainly limited to lighter elements and highly ionized high-$Z$ few-electron ions because application to larger systems requires large integral storage space and computation time. For neutral atoms with a low nuclear charge $Z$, the effects of electron correlation are far more important than relativistic and QED corrections. As the nuclear charge increases, electron correlation is expected to be relatively large and relativistic and electron correlation effects become intertwined. Except for the study of Johnson *et al.* on alkali metal atoms [1,3,28], for heavy atoms that contain large number of bound electrons, few many-body calculations have been performed to systematically examine the magnitude of electron correlation and the $Z$ dependence of relativistic correlation energy. In the present study, we examine the effects of relativity and electron correlation for heavy-atom systems by means of a recently developed relativistic MBPT theory [6]. Our relativistic MBPT calculations are based on DFC SCF and DFB SCF wave functions [20] derived, respectively, from the no-pair DC and no-pair DCB Hamiltonians.

In a previous study on highly ionized He-like ions [6], the low-frequency Breit interaction was shown to cause significant modification of relativistic many-body effects, the DC Hamiltonian accounting for only a fraction of the total relativistic correction to the correlation energy. In the present study, the effects of the low-frequency Breit interaction on relativistic many-body effects are examined for high-$Z$ neutral atoms as large as Rn ($Z = 86$) and for Ne-like highly ionized ions. These calculations were undertaken to develop the computational techniques necessary to carry out large-scale relativistic many-body perturbation theory calculations including relativity and electron correlation for atoms with a large number of bound electrons by discrete basis expansion in Gaussian-spinors ($G$ spinors) [6,20]. A relativistic description of heavy-atom systems has awaited development of a reliable procedure for expansion of single-particle spinors in discrete basis sets [1–6,18–20,22]. We show that a relativistic MBPT procedure on truly many-electron, multishell systems by a $G$-spinor expansion method can be successfully implemented.

## II. RELATIVISTIC MANY-BODY PERTURBATION THEORY

The relativistic many-body Hamiltonian cannot be expressed in closed potential form. This difficulty has to do with the requirement of relativistic covariance in many-body systems and with separation of electrons from positrons, which are not considered in low-energy atomic and molecular electronic structure calculations. However, relativistic many-body theory may be developed by employing an effective many-body Hamiltonian expressed in terms of an effective electron-electron interaction derived with arbitrary accuracy from QED [13,14,32]. With such an effective Hamiltonian, one can apply the many-body formalisms developed in nonrelativistic many-body theory to relativistic many-body systems where relativity and electron correlation are strongly intertwined.

### A. The effective many-body Hamiltonian

An effective many-body Hamiltonian most commonly used for relativistic atomic structure calculations is the time-honored "no-pair" Dirac-Coulomb Hamiltonian [13,14]

$$H_{+}^{DC} = \sum_{i} h_D(i) + \mathcal{L}_{+} \left( \sum_{i>j} V_{ij}^{C} \right) \mathcal{L}_{+}, \qquad (1)$$

where (in a.u.) $h_D$ is the one-electron Dirac Hamiltonian

$$h_D(i) = c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2(\beta_i - 1) + V_N(i). \qquad (2)$$

Here $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are the Dirac matrices. The effective electron-electron interaction $V_{ij}^{C}$ is given by the classical instantaneous Coulomb interactions between electrons

$$V_{ij}^{C} = r_{ij}^{-1}. \qquad (3)$$

Here $\mathcal{L}_{+} = L_{+}(1)L_{+}(2)\cdots L_{+}(n)$ with $L_{+}(i)$ the projection operator onto the space spanned by the positive-energy eigenfunctions of the DF operator [14]. In this form, the no-pair Hamiltonian is restricted to contributions from the positive-energy branch of the DF spectrum. In $c$-number theory, the projection operator takes into account the field-theoretic condition that the negative energy states are filled.

Because the electron-electron interaction is approximated by the classical instantaneous Coulomb interactions, 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 [33,34]. A higher approximation involves modification of the instantaneous Coulomb interaction $V_{ij}^{C}$. The modification is derived from field theory and leads to a well-defined QED perturbation series with $\alpha$, the fine-structure constant, as an order parameter. Adding the low-frequency Breit interaction

$$B_{12} = -\frac{1}{2r_{12}} \left[ \boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 + (\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})\, (\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})/r_{12}^2 \right] \qquad (4)$$

to the instantaneous Coulomb operator introduces the leading effects of the transverse photon exchange in QED and remedies the lack of covariance of the no-pair DC

Hamiltonian [13,14]. Inclusion of the Breit interaction in the effective electron-electron interaction results in an effective Hamiltonian that contains all effects through order $\alpha^2$ [13]. Sucher argued that the no-pair Dirac-Coulomb-Breit Hamiltonian [13]

$$H_+^{DCB} = \sum_i h_D(i) + \mathcal{L}_+ \left( \sum_{i>j} V_{ij}^{CB} \right) \mathcal{L}_+, \tag{5}$$

where

$$V_{ij}^{CB} = r_{ij}^{-1} + B_{ij} \tag{6}$$

provides a satisfactory starting point for calculations on many-electron systems 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 DFB SCF and MBPT calculations [5,6]. In the present study, the instantaneous Coulomb and frequency-independent Breit interactions are treated as an integral part of the two-electron interaction in both the DFB SCF and MBPT calculations [5,6] in order to study the electron correlation induced by the Breit interaction.

The effective electron-electron interaction in the many-body Hamiltonian depends on the gauge employed and many-body corrections evaluated numerically in terms of the low-frequency forms of the Coulomb- and Feynman-gauge interactions may be different in no-pair theory. There is justification for choosing the Coulomb-gauge Breit operator in Eq. (4) in the no-pair $N$-electron Hamiltonian rather than the simpler Gaunt interaction in the present study. In a recent study, Sucher [13] analyzed the apparent gauge dependence of the effective potentials between electrons derived in the Coulomb and Feynman gauges and indicated that the Feynman-gauge form of the interaction should not be used in no-virtual-pair calculations because the leading-order relativistic effects are incompletely determined. The addition of the low-frequency Breit interaction to the instantaneous Coulomb interaction provides covariance of the effective many-body Hamiltonian to first order and increases the accuracy in fine-structure splittings and inner-shell binding energies [33,34].

### B. Relativistic correlation

Electron correlation effects are corrections to the independent electron approximation and their importance depends on the choice of the approximation in which they are calculated. In nonrelativistic many-body calculations, the correlation energy $E_{corr}^{NR}$ is defined as the difference between the exact eigenvalue of the $N$-electron Schrödinger Hamiltonian $E_{exact}^{NR}$ and the nonrelativistic single-configuration HF energy $E_{HF}$:

$$E_{corr}^{NR} = E_{exact}^{NR} - E_{HF}. \tag{7}$$

As Kim recently argued [12], this definition of electron correlation energy is inadequate in the framework of relativistic many-body theory. In relativistic quantum theory for atoms and molecules, it is most convenient to replace the HF approximation by the well-defined relativistic independent-electron model, the Dirac-Fock SCF method. This choice has the advantage that, as the speed of light tends to infinity, the DF method smoothly approaches the HF method. Since relativistic $N$-electron Hamiltonians are approximate and take a variety of forms depending on the degree of approximation with which they are derived from QED, relativistic correlation energy must be defined in terms of the effective Hamiltonian used to construct the relativistic many-body theory.

In the present study, we employ in our MBPT calculations two different effective $N$-electron Hamiltonians, the no-pair DCB Hamiltonian and the no-pair DC Hamiltonian. With respect to the two effective many-body Hamiltonians, we can define the DCB correlation energy ($E_{corr}^{DCB}$) as the difference between the exact eigenvalue of the DCB Hamiltonian ($E_{exact}^{DCB}$) and the DFB SCF energy ($E_{SCF(DCB)}$) and the DC correlation energy ($E_{corr}^{DC}$) as the difference between the exact eigenvalue of the DC Hamiltonian ($E_{exact}^{DC}$) and the DFC SCF energy ($E_{SCF(DC)}$),

$$E_{corr}^{DCB} = E_{exact}^{DCB} - E_{SCF(DCB)}, \tag{8}$$

$$E_{corr}^{DC} = E_{exact}^{DC} - E_{SCF(DC)}. \tag{9}$$

The difference between the DCB correlation and the DC correlation, i.e., $E_{BR} = E_{corr}^{DCB} - E_{corr}^{DC}$, is the relativistic many-body shift due to the low-frequency Breit interaction.

### C. Matrix Dirac-Fock-Breit SCF method

The relativistic independent-electron models derived from the no-pair DC and DCB Hamiltonians are the DFC and DFB SCF methods. Variation of the energy in terms of the DC and DCB Hamiltonians leads to pseudoeigenvalue equations of the form [15]:

$$F_\kappa \phi_{n\kappa} = \varepsilon_{n\kappa} \phi_{n\kappa}, \tag{10}$$

where $F$ is the effective one-electron Hamiltonian for the DFC or DFB SCF equation, solved self-consistently. The effective one-electron Hamiltonian for the $\kappa$th symmetry takes the form [15–20]

$$F_\kappa = \begin{pmatrix} V_N + U^{LL} & c\Pi_\kappa + U^{LS} \\ c\Pi_\kappa^+ + U^{SL} & V_N + U^{SS} - 2c^2 \end{pmatrix} \tag{11}$$

with $\Pi_\kappa = -d/dr + \kappa/r$ and $\Pi_\kappa^+ = d/dr + \kappa/r$. Here

$$\phi_{n\kappa} = \begin{pmatrix} P_{n\kappa}(r) \\ Q_{n\kappa}(r) \end{pmatrix}, \tag{12}$$

where $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are referred to as the large and small component radial functions, respectively. $V_N(r)$ is the nuclear attraction term

$$\begin{aligned} V_N(r) &= -Z/r && \text{for } r > R \\ &= -(Z/2R)(3 - r^2/R^2) && \text{for } r \leq R. \end{aligned} \tag{13}$$

The nucleus is modeled as a sphere of uniform proton charge distribution. $Z$ is the nuclear charge. $R$ is the radius of the nucleus and is related to the atomic mass $A$ by the relationship $R = 2.2677 \times 10^{-5} A^{1/3}$. $U^{AB}$ ($A, B = L$ or $S$) is the one-body mean-field potential and accounts approximately for electron-electron interaction in the SCF scheme.

The no-pair DCB Hamiltonian in Eq. (5) may be used for variational calculations in place of the no-pair Dirac-Coulomb Hamiltonian. The low-frequency Breit interaction, which gives the leading correction to the instantaneous Coulomb interaction in quantum electrodynamics, is a two-body potential of the same general form as the instantaneous Coulomb interaction and is easily incorporated in the matrix DFB self-consistent field procedure [5,6,20].

In our matrix DFB SCF calculations, both $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are expanded in terms of a set of Gaussian-type functions $\{X^L_{\kappa i}\}$ and $\{X^S_{\kappa i}\}$ [19–22]:

$$P_{n\kappa}(r) = \sum_i X^L_{\kappa i} C^L_{n\kappa i} \tag{14}$$

and

$$Q_{n\kappa}(r) = \sum_i X^S_{\kappa i} C^S_{n\kappa i}, \tag{15}$$

where

$$\begin{aligned} X^L_{\kappa i} &= N_L r^{|\kappa|} \exp(-\xi_{\kappa i} r^2) && \text{for } \kappa < 0 \\ &= N_L r^{\kappa+1} \exp(-\xi_{\kappa i} r^2) && \text{for } \kappa > 0 \end{aligned} \tag{16}$$

and

$$X^S_{\kappa i} = N_S \Pi^+_\kappa X^L_{\kappa i}. \tag{17}$$

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

Klahn and Morgan [35] have shown that the rate of convergence of a variational calculation is determined by how quickly the basis functions replicate the analytic structure of the unknown function one is trying to approximate. In matrix Dirac-Fock calculations, it is necessary to use spinor basis functions which correctly relate the spinor components in a given potential [5,6,20]. This is vital to ensure that the solution converges to the physical result from above as the basis set is enlarged. Our $G$-spinor functions mimic exactly the behavior of the wave function in the high-field region near the origin of a uniformly charged spherical nucleus [20], precisely the reason why $G$-spinor expansions exhibit fast and smooth convergence when the nucleus is so modeled [20]. Unlike the $S$-spinor basis functions [5], the exponent of $r$ in the $G$-spinor basis functions does not depend on the speed of light. Therefore, our $G$ spinors that satisfy the boundary conditions associated with the finite nucleus automatically satisfy the so-called kinetic balance condition for finite $c$ [20]. For an unbounded Hamiltonian, it is essential that the basis sets for upper and lower components are chosen to satisfy the boundary conditions near the origin to ensure that the basis functions behave properly in the high-field region and that the computed energy converges to the physical solution from above as the basis set is enlarged. With the basis-set expansion in Eqs. (14) and (15), the SCF equation is cast in matrix form

$$\mathbf{F}_\kappa \mathbf{C}_\kappa = \mathbf{S}_\kappa \mathbf{C}_\kappa \mathbf{E}_\kappa. \tag{18}$$

Detailed accounts of the matrix DFC and DFB SCF formalisms have been given in previous publications [6,20] and are not repeated here.

### D. Relativistic MBPT scheme

Relativistic MBPT based on the algebraic approximation provides a tractable scheme for calculating relativistic correlation effects in atoms and molecules. Our $G$-spinor basis set expansion method not only applies to molecules in a straightforward manner, but also provides a compact representation of the Dirac spectrum. It therefore lends itself to comutationally efficient application of relativistic MBPT [6]. The "no-pair" DC and DCB Hamiltonians may be expressed as normally ordered products of the spinor operators $[r^+s]$ and $[r^+s^+ut]$,

$$H_N = \sum_{r,s} f_{rs}[r^+s] + \frac{1}{4} \sum_{r,s,t,u} \langle rs \parallel tu \rangle [r^+s^+ut], \tag{19}$$

where

$$\langle rs \parallel tu \rangle = \langle rs \mid tu \rangle - \langle rs \mid ut \rangle$$

and

$$\langle rs \mid tu \rangle = \int dx_1 dx_2 \phi_r(x_1) \phi_s(x_2) V^{CB}_{12} \phi_t(x_1) \phi_u(x_2).$$

Here $f_{rs}$ and $\langle rs||tu \rangle$ are, respectively, one-electron DF and antisymmetrized two-electron interaction matrices over the DF four-component spinors $r$, $s$, $t$, and $u$. Normal ordering implies that, in the vacuum state, annihilation operators are moved to the right of creation operators as if all anticommutators vanish. The Fermi level is shifted to the highest occupied positive energy state. The creation operator then appears to the right of a normally ordered set when it refers to an occupied positive-energy state, while the annihilation operator remains on the right for a positive-energy virtual state. In this form the no-pair Hamiltonian is restricted to contributions from the positive-energy branch of the spectrum.

In $q$-number theory, negative-energy states are taken to be filled in the true vacuum state and relativistic MBPT is conveniently described within the particle-hole second-quantized formalism in which the occupied positive-energy state as well as the negative-energy continuum are taken to be below the Fermi level [5,6]. A formalism given by Grant and Pyper [36] was used to evaluate the necessary Breit interaction integrals for the MBPT calculations. Goldstone diagrams have been summed to compute relativistic correlation corrections up to second order. We evaluate only the positive-energy intermediate contribution of the second order-energy correction. In the no-pair approximation of Sucher [13], our relativistic MBPT thus yields a many-body perturbation expansion which contains the same diagrams as those from the nonrelativistic Schrödinger Hamiltonian in expansions based on Hartree-Fock wave functions [5]. Virtual spinors used in the study were calculated in the field of nucleus and all electrons ($V^N$ potential).

Contributions from the negative-energy states are of the order of $\alpha^3$ and are neglected here. In our DFB SCF calculations, the one-Coulomb and one-Breit photon diagrams are summed through all orders since the single-particle basis is determined self-consistently. Thus the most important consequence of treating the low-frequency Breit interaction self-consistently is the simplification of relativistic many-body perturbation theory, which results from the cancellation of these classes of diagram through all orders of perturbation theory [5,6]. The use of the two-body interaction operator that includes both the instantaneous Coulomb and low-frequency Breit interactions in the self-consistent field and MBPT calculations leads to a theory which accounts for all corrections to order $\alpha^2$ [5,6,13].

In a recent study [9], Eliav, Kaldor, and Ishikawa have developed a relativistic coupled-cluster algorithm based on the $G$-spinor expansion method and applied it in calculations of ionization and transition energies of Au. Because such all-order calculations become increasingly difficult for atoms with many bound electrons, we used a partial-wave expansion with $L_{max}=3$ and correlated only the $4s4p4d4f5s5p5d$ electrons in Au, keeping the inner-shell electrons frozen in the relativistic CC scheme, accounting only for valence-electron correlation. The relativistic CC method involves summation of certain classes of diagrammatic terms through infinite order and becomes computationally prohibitive for all-electron correlated calculations on heavy atoms. On the other hand, the finite-order MBPT provides a powerful approach to the all-electron correlation problem, recovering the bulk of correlation energy in finite order. It remains useful even if the number of electrons in the system becomes very large. For heavy-atom systems, therefore, relativistic MBPT appears to be one of the most promising approaches to accounting for electron correlation.

### E. Computation

Matrix DFB SCF and MBPT calculations on the noble-gas atoms Ne, Ar, Kr, Xe, and Rn and the group-II$B$ atoms Zn, Cd, and Hg are performed by using large well-tempered basis sets of $G$ spinors. For the Ne-like ions with $Z$ up to 100, large even-tempered basis sets of $G$ spinors are employed. The order of the partial-wave expansion ($L_{max}$), the highest angular momentum of the spinors included in the virtual space, is $L_{max} = 6$ throughout this study. The well-tempered basis-set exponents were taken from the works of Huzinaga and Klobukowski [37]. Parameters of the even-tempered basis sets [38] were optimized in the present study. Table I shows the well-tempered basis set employed in the SCF and MBPT calculations on Hg.

TABLE I. Basis set for Hg. Exponents of the basis functions are specified by ×.

| Exponent | Symmetry | | | | |
|---|---|---|---|---|---|
| | $s_{1/2}$ | $p_{1/2,3/2}$ | $d_{3/2,5/2}$ | $f_{5/2,7/2}$ | $g, h, i$ |
| 33723176.0 | × | ×[a] | ×[a] | ×[a] | |
| 5516822.4 | × | ×[a] | ×[a] | ×[a] | |
| 1355483.5 | × | × | ×[a] | ×[a] | |
| 383787.47 | × | × | ×[a] | ×[a] | |
| 115889.46 | × | × | ×[a] | ×[a] | |
| 37855.841 | × | × | ×[a] | ×[a] | |
| 13685.687 | × | × | ×[a] | ×[a] | |
| 5472.5852 | × | × | × | × | × |
| 2377.9943 | × | × | × | × | × |
| 1094.6624 | × | × | × | × | × |
| 520.42181 | × | × | × | × | × |
| 251.24947 | × | × | × | × | × |
| 122.12994 | × | × | × | × | × |
| 59.531589 | × | × | × | × | × |
| 29.506942 | × | × | × | × | × |
| 14.412245 | × | × | × | × | × |
| 6.9610937 | × | × | × | × | × |
| 3.4002906 | × | × | × | × | × |
| 1.6986682 | × | × | × | × | × |
| 0.80853674 | × | × | × | × | × |
| 0.36385964 | × | × | × | × | × |
| 0.14602676 | × | × | × | × | × |
| 0.06935530 | × | × | × | × | × |
| 0.03689019 | × | × | × | × | × |
| 0.01962140 | × | × | ×[a] | ×[a] | |

[a] Included in DF calculations, but excluded in MBPT calculations.

The Dirac-Fock SCF and MBPT calculations were also performed by excluding the Breit interaction. These are the matrix DFC SCF and MBPT calculations based on the DC Hamiltonian. The speed of light was taken to be 137.0370 a.u. The nonrelativistic limit was simulated by setting the speed of light $c = 10^4$. The nuclei are modeled as spheres of uniform proton charge in all the calculations. The use of the finite nuclear model of uniform proton charge distribution in our study is crucial because the $G$ spinors satisfy the boundary conditions associated with the finite nuclear model [20].

## III. RESULTS AND DISCUSSION

Table II displays the SCF energies ($E_{SCF}$) as well as the second-order correlation energies ($E_2$) for the noble-gas atoms Ne, Ar, Kr, Xe, and Rn and the group II$B$ atoms Zn, Cd, and Hg. In each entry in Table II, the SCF energy ($E_{SCF(NR)}$) and the second-order correlation energy ($E_{2(NR)}$) obtained in the nonrelativistic (NR) limit are given in the first row. In the second row, the DFC SCF energy ($E_{SCF(DC)}$) and the second-order Coulomb correlation correction ($E_{2(DC)}$) are given. The DFC and instantaneous Coulomb correlation energies were computed with the DC Hamiltonian. The DFB SCF energy ($E_{SCF(DCB)}$) as well as the second-order correlation en-

TABLE II. SCF and second-order correlation energies.

| Z | Atom | Atomic mass | Method | $E_{SCF}$ | $E_2$ |
|---|---|---|---|---|---|
| 10 | Ne | 20.18 | NR | -128.5470878 | -0.3831882 |
| | | | DC | -128.6919254 | -0.3833856 |
| | | | DCB | -128.6752847 | -0.3852591 |
| 18 | Ar | 39.95 | NR | -526.8173311 | -0.6972791 |
| | | | DC | -528.6838208 | -0.6981223 |
| | | | DCB | -528.5514977 | -0.7060424 |
| 30 | Zn | 65.39 | NR | -1777.844400 | -1.6506117 |
| | | | DC | -1794.610963 | -1.6611270 |
| | | | DCB | -1793.849916 | -1.6875521 |
| 36 | Kr | 83.80 | NR | -2752.047329 | -1.8354321 |
| | | | DC | -2788.861465 | -1.8468226 |
| | | | DCB | -2787.435574 | -1.8878912 |
| 48 | Cd | 112.41 | NR | -5465.098845 | -2.6181147 |
| | | | DC | -5593.319974 | -2.6539737 |
| | | | DCB | -5589.481095 | -2.7362939 |
| 54 | Xe | 131.29 | NR | -7232.069451 | -2.9211312 |
| | | | DC | -7446.887980 | -2.9587009 |
| | | | DCB | -7441.118205 | -3.0674532 |
| 80 | Hg | 200.59 | NR | -18408.53586 | -5.0862400 |
| | | | DC | -19648.84818 | -5.2894722 |
| | | | DCB | -19626.21565 | -5.5722140 |
| 86 | Rn | 222 | NR | -21866.11626 | -5.3920715 |
| | | | DC | -23601.96583 | -5.5874268 |
| | | | DCB | -23572.61431 | -5.9400218 |

ergy ($E_{2(DCB)}$) based on the DCB Hamiltonian are given in the third row.

The DFC SCF energy $-128.691925$ a.u. of Ne computed with our $G$ spinors is in excellent agreement with the value $-128.69194$ a.u., obtained with Desclaux's numerical finite difference method [39]. For Rn ($Z = 86$), the heaviest atom considered in the present study, the DFC SCF energy $-23601.9658$ a.u. computed with our $G$-spinor basis set compares well with the numerical finite-difference result $-23601.974$ a.u., with a difference of only 0.008 a.u. While the difference between the nonrelativistic HF and relativistic DFC energies (i.e., the relativistic energy lowering) in Ne is small, on the order of 0.1 hartree, the difference rises to 1736 a.u. for Rn. The variational Breit-interaction energy, which is the difference between the DFB and DFC SCF energies, also is very small for Ne ($\approx 0.017$ a.u.). For Rn, however, the variational Breit-interaction energy increases to 29.35 a.u.

The DCB second-order correlation energies $E_{2(DCB)}$ range from $-0.38319$ a.u. for Ne ($Z = 10$) to $-5.5722$ a.u. for Rn ($Z = 86$). Because large $G$-spinor basis sets were employed to saturate the occupied and virtual spaces in each symmetry, the correlation energies obtained have converged at least to five figures within the $i$ limit ($L_{max} = 6$). The effect of enlarging the basis sets appears only in the sixth figure or higher. Figure 1 shows the variations of the NR, DC, and DCB second-order correlation energies of the neutral atoms as a function of nuclear charge $Z$. The correlation energies in the neutral atoms increase almost linearly as $Z$ increases, the least deviation from linearity being the NR correlation energies. The DCB correlation energies show the largest deviation from the linearity.

The difference $E_{2(DC)} - E_{2(NR)}$ is the relativistic DC many-body shift that increases in absolute value as $Z$ increases. This increase arises from the use of relativistic single-particle states, but the same two-body interaction, i.e., the classical instantaneous Coulomb interaction. The difference $E_{2(DCB)} - E_{2(NR)}$ in correlation energies is the relativistic DCB many-body shift that arises from the use of relativistic single-particle states and the low-frequency Breit interaction in addition to the classical instantaneous Coulomb interaction in the two-body interactions. Quiney, Grant, and Wilson [5] performed relativistic MBPT calculations on Ar employing $S$ spinors with $L_{max} \leq 3$ and found that the relativistic DCB many-body shift $E_{2(DCB)} - E_{2(NR)}$ is one order of magnitude larger than the relativistic DC many-body shift $E_{2(DC)} - E_{2(NR)}$. In our relativistic MBPT calculations on Ar using up to $L_{max} = 6$, the relativistic DCB many-body shift $E_{2(DCB)} - E_{2(NR)}$ is 0.08763 a.u., an order of magnitude larger than the relativistic DC many-body shift $E_{2(DC)} - E_{2(NR)}$ (=0.00843 a.u.), in agreement with Quiney, Grant, and Wilson. The present results indicate that, for lighter elements, the no-pair DC Hamiltonian accounts for only a fraction of the total relativistic correction to the correlation energy and the Breit interaction results in a significant modification in relativistic many-body effects. In heavy neutral atoms, the increase in the DC correlation energies becomes substantial due to the large number of bound electrons, e.g., in Rn, the relativistic DCB many-body shift ($E_{2(DCB)} - E_{2(NR)} = 0.548$ a.u.) is only 2.8 times larger in magnitude than the relativistic DC many-body shift ($E_{2(DC)} - E_{2(NR)} = 0.195$ a.u.).

A partial-wave analysis of the second-order pair correlation energies for the ground-state mercury atom was performed to examine differences in pair correlation energies based on the NR, DC, and DCB Hamiltonians. In Fig. 2 the differences between the DC and NR pair correlation energies and between DCB and NR pair correlation energies are schematically presented as a bar graph. The shaded and unshaded bars represent, respectively, the differences between the DC and NR pair correlation energies and between the DCB and NR pair correlation energies for a representative set of second-order pair correlation energies. Pair correlation energies that do not appear in the figure are negligibly small in the scale employed. The DC second-order correlation energy $E_{2(DC)}$ of Hg is larger by 0.203 a.u. in magnitude than the NR correlation energy. This is the relativistic DC many-body shift that arises from the use of relativistic single-particle states, but the same two-body interaction, i.e., the classical instantaneous Coulomb interaction. The analysis reveals that the DC many-body shift comes mainly from in-

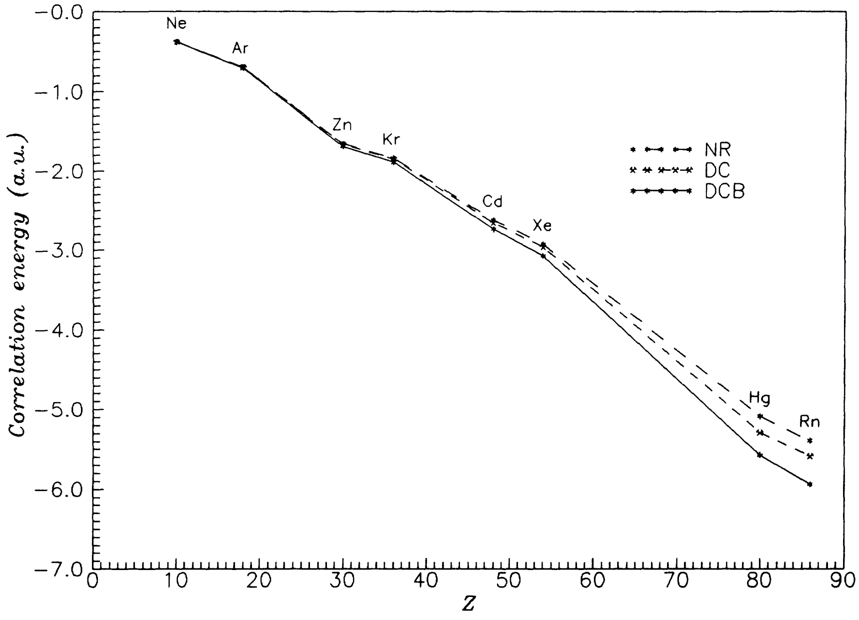

FIG. 1. Variations of the NR, DC, and DCB second-order correlation energies of the neutral atoms as a function of nuclear charge $Z$.

creases in the DC pair correlation energies of the valence-shell electron pairs, e.g., $(5s, 4f)$, $(5p, 4f)$, and $(6s, 5d)$ pairs.

The relativistic DCB many-body shift ($E_{2(DCB)} - E_{2(NR)} = 0.486$ a.u.) in Hg is 2.4 times larger than the relativistic DC many-body shift $E_{2(DC)} - E_{2(NR)} = 0.203$ a.u. A significant increase in magnitude of the pair correlation energies for the inner-shell electron pairs $(1s, 1s)$, $(2p, 2p)$, and $(2p, 1s)$, as well as the increase in pair correlation energies in the valence-shell electron pairs, accounts for the large difference of 0.486 hartree between the DCB correlation energy and the NR correlation energy. Figure 2 clearly demonstrates that the Breit interaction accounts for a significant modification in inner-shell pair correlation energies, whereas the relativistic many-body shifts in the valence-shell pair correlation energies are mainly due to the use of relativistic single-particle states and the instantaneous Coulomb interaction. Thus relativistic many-body effects on the valence spinors are almost entirely accounted for by the no-pair DC Hamiltonian.

The second-order MBPT energies obtained in the present study represent the bulk of the correlation energies obtained by employing all-order methods. Benchmark single- and double-excitation coupled-cluster calculations [25] on the neutral xenon atom employing a medium-sized basis set of $14s13p10d7f6g5h$ $G$ spinors ($L_{max} = 5$) gave a DCB correlation energy of $-2.696$ hartree, whereas the corresponding second-order DCB correlation energy obtained by using the same basis set was $-2.817$ a.u. The DCB second-order correlation energy represents 104% of the all-order result for Xe, the

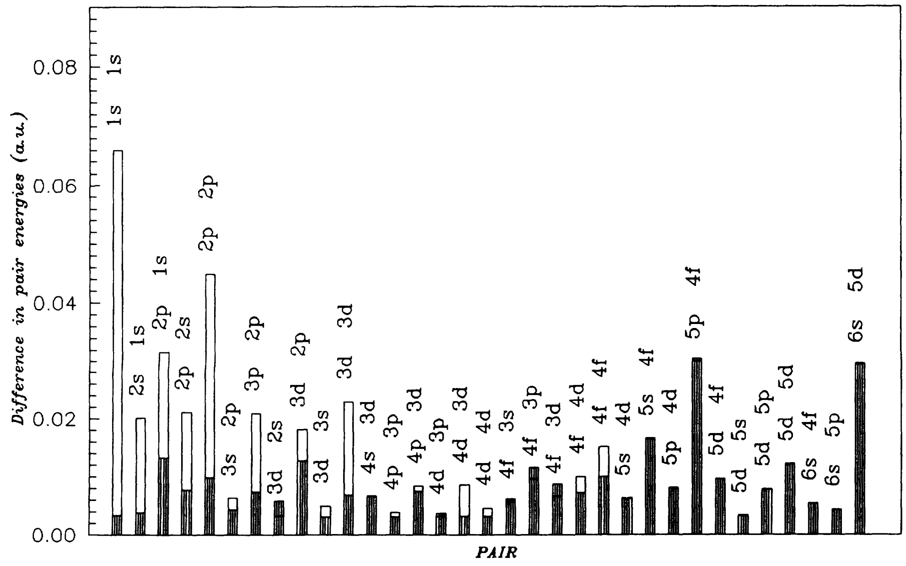

FIG. 2. The differences between the DC and NR pair correlation energies and between the DCB and NR pair correlation energies.

third- and higher-order contribution being 4%.

Table III displays the results of SCF and MBPT calculations on the ions of the Ne isoelectronic sequence $Z \leq 100$. Figure 3 shows the variations in the NR, DC, and DCB correlation energies for Ne and Ne-like ions as a function of nuclear charge. The instantaneous Coulomb correlation energy for Ne and ions of the neon isoelectronic sequence computed by using the DC Hamiltonian remains almost constant, with a slight increase in magnitude as nuclear charge $Z$ increases. In contrast, the DCB correlation energy $E_{2(DCB)}$ increases dramatically as $Z$ increases. For the $s_{1/2}$ and $p_{1/2}$ shells, the contribution is most significant because the magnetic interaction, the dominant term in the low-frequency Breit interaction, is a short-range interaction which, in the classical limit, behaves as $1/r^3$.

Like the highly ionized He-like ions reported previously [6], the nuclear potential dominates electron-electron interactions in highly ionized Ne-like ions and thus the Dirac-Fock independent-particle approximation becomes increasingly accurate as $Z$ increases. In these instances, the MBPT series converges very rapidly and the second-order MBPT energy in general accounts for the total correlation correction to well over 99% accuracy [6].

In their multiconfigurational finite-difference DF calculations on the ions of the He isoelectronic sequence $Ne^{8+}$, $Ca^{18+}$, $Zn^{28+}$, and $Sn^{48+}$, Gorceix, Indelicato, and Desclaux included the magnetic interaction in the self-consistent-field step and computed the electron correlation energies due to both Coulomb and magnetic interactions [27]. They found that the magnetic correlation energy exceeds in magnitude the Coulomb correlation energy in the region $Z \approx 50$ [27]. In a recent study [6], we have computed correlation energies for He and He-like ions employing the DCB Hamiltonian and compared our results with those obtained by Gorceix *et al.* In contrast to the magnetic correlation, the correlation energy due to the low-frequency Breit interaction does not exceed in magnitude the Coulomb correlation

TABLE III. SCF and second-order correlation energies for Ne-like ions.

| Z | Ion | Atomic mass | Method | $E_{SCF}$ | $E_2$ |
|---|---|---|---|---|---|
| 20 | $Ca^{10+}$ | 40.08 | NR | -640.3840658 | -0.3945152 |
| | | | DC | -643.2553506 | -0.3953778 |
| | | | DCB | -643.0721885 | -0.4051025 |
| 30 | $Zn^{20+}$ | 65.39 | NR | -1552.555556 | -0.4038468 |
| | | | DC | -1568.582000 | -0.4063782 |
| | | | DCB | -1567.884988 | -0.4300865 |
| 40 | $Zr^{30+}$ | 91.22 | NR | -2864.782277 | -0.4085616 |
| | | | DC | -2918.746542 | -0.4140520 |
| | | | DCB | -2916.978729 | -0.4578428 |
| 50 | $Sn^{40+}$ | 118.70 | NR | -4577.012941 | -0.4114717 |
| | | | DC | -4715.837068 | -0.4215601 |
| | | | DCB | -4712.211476 | -0.4918780 |
| 60 | $Nd^{50+}$ | 144.24 | NR | -6689.219431 | -0.4133766 |
| | | | DC | -6991.922707 | -0.4301778 |
| | | | DCB | -6985.390129 | -0.5340929 |
| 70 | $Yb^{60+}$ | 173.04 | NR | -9201.367922 | -0.4147801 |
| | | | DC | -9792.611477 | -0.4410812 |
| | | | DCB | -9781.809926 | -0.5868727 |
| 80 | $Hg^{70+}$ | 200.59 | NR | -12113.42456 | -0.4157677 |
| | | | DC | -13183.10081 | -0.4554500 |
| | | | DCB | -13166.27570 | -0.6532587 |
| 90 | $Th^{80+}$ | 232.04 | NR | -15425.33075 | -0.4165655 |
| | | | DC | -17258.51144 | -0.4753647 |
| | | | DCB | -17233.38310 | -0.7387175 |
| 100 | $Fm^{90+}$ | 257.00 | NR | -19137.06139 | -0.4172211 |
| | | | DC | -22163.34260 | -0.5044448 |
| | | | DCB | -22126.87231 | -0.8528151 |

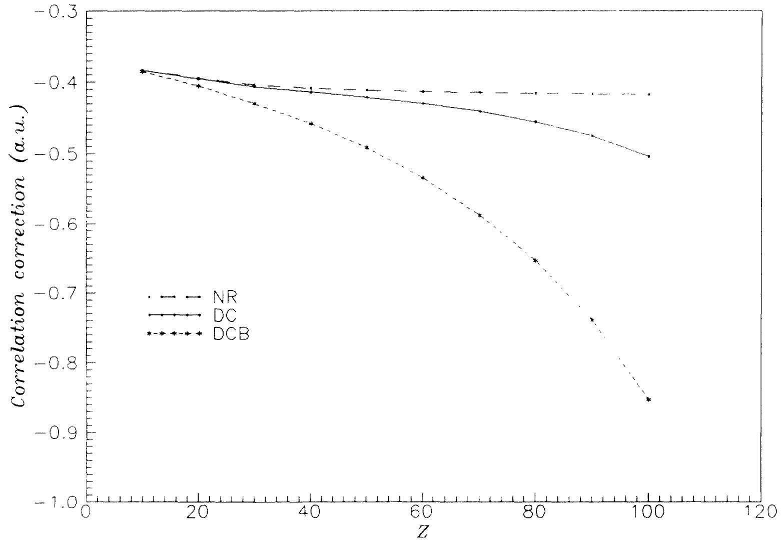

FIG. 3. The variations in the NR, DC, and DCB correlation energies for Ne and Ne-like ions as a function of nuclear charge.

energy even at $Z \approx 50$. Recently, Johnson, Blundell, and Sapirstein performed $B$-spline basis expansion DF SCF and MBPT calculations on the Li atom and Li-like ions [1,3]. Their results show that the second-order contribution of the low-frequency Breit interaction for the Li-like ions exceeds in magnitude the Coulomb correlation energy $E_{2(DC)}$ in the region $Z \approx 74$.

Figure 3 reveals that, unlike the He-like ions where DC correlation energies remain almost constant, the DC correlation energies in Ne-like ions increase noticeably as $Z$ increases. For the Ne-like Fm ion ($Z = 100$), the computed relativistic DCB many-body shift $E_{2(DCB)} - E_{2(NR)}$ amounts to 0.436 a.u., whereas the relativistic DC many-body shift $E_{2(DC)} - E_{2(NR)}$ is 0.087 a.u. The results of DFC, DFB SCF, and MBPT calculations show that the Breit interaction results in a significant modification of relativistic many-body effects in highly ionized Ne-like ions. The DC Hamiltonian accounts for a fraction of the total relativistic correction to the correlation energy for highly ionized high-$Z$ species.

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

[2] M. H. Chen, K. T. Cheng, and W. Johnson, Phys. Rev. A **47**, 3692 (1993).

[3] S. A. Blundell, W. R. Johnson, and J. Sapirstein, Phys. Rev. A **37**, 2764 (1988); **38**, 2699 (1988); **42**, 1087 (1990).

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

[5] H. M. Quiney, I. P. Grant, and S. Wilson, Phys. Scr. **36**, 460 (1987); in *Many-Body Methods in Quantum Chemistry*, edited by U. Kaldor, Lecture Notes in Chemistry Vol. 52 (Springer, Berlin, 1989); J. Phys. B **23**, L271 (1990).

[6] Y. Ishikawa, Phys. Rev. A **42**, 1142 (1990); Y. Ishikawa and H. M. Quiney, *ibid.* **47**, 1732 (1993).

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

[8] A. Rutkowski, J. Phys. B **19**, 3443 (1986); A. Rutkowski and W. H. E. Schwarz, Theor. Chim. Acta **76**, 391 (1990).

[9] E. Eliav, U. Kaldor, and Y. Ishikawa, Phys. Rev. A **49**, 1724 (1994).

[10] A. Rizzo, E. Clementi, and M. Sekiya, Chem. Phys. Lett. **177**, 477 (1991).

[11] P. O. Lowdin, Adv. Chem. Phys. **2**, 207 (1959).

[12] Y.-K. Kim, in *Relativistic, Quantum Electrodynamic, and Weak Interaction Effects in Atoms*, Proceedings of the Program held on Relativistic, Quantum Electrodynamic, and Weak Interaction Effects in Atoms at the Institute of Theoretical Physics, Santa Barbara, CA, 1988, edited by W. R. Johnson, P. Mohr, and J. Sucher, AIP Conf. Proc. No. 189 (AIP, New York, 1989), p. 272; Y.-K. Kim, D. H. Baik, P. Indelicato, and J. P. Desclaux, Phys. Rev. A **44**, 148 (1991).

[13] J. Sucher, Phys. Rev. A **22**, 348 (1980); Phys. Scr. **36**, 271 (1987); J. Phys. B **21**, L585 (1988).

[14] M. H. Mittleman, Phys. Rev. A **24**, 1167 (1981); **4**, 893 (1971); **5**, 2395 (1972).

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

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

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

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

[19] O. Matsuoka and S. Huzinaga, Chem. Phys. Lett. **140**, 567 (1987); S. Okada and O. Matsuoka, J. Chem. Phys. **91**, 4193 (1989).

[20] Y. Ishikawa and H. M. Quiney, Int. J. Quantum Chem. **S21**, 523 (1987); Y. Ishikawa, R. Baretty, and R. C. Binning, Jr., Chem. Phys. Lett. **121**, 130 (1985); Y. Ishikawa, H. M. Quiney, and G. L. Malli, Phys. Rev. A **43**, 3270 (1991).

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

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

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

[24] E. Lindroth and S. Salomonson, Phys. Rev. A **41**, 4659 (1990); E. Lindroth, H. Persson, S. Salomonson, and A.-M. Mårtensson-Pendrill, *ibid.* **45**, 1493 (1992); E. Lindroth and J. Hvarfner, *ibid.* **45**, 2771 (1992).

[25] E. Eliav, U. Kaldor, and Y. Ishikawa, Chem. Phys. Lett. **222**, 82 (1994); Int. J. Quantum Chem. (to be published).

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

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

[28] S. A. Blundell, J. Sapirstein, and W. R. Johnson, Phys. Rev. D **45**, 1602 (1992); S. A. Blundell, W. R. Johnson, and J. Sapirstein, Phys. Rev. Lett. **65**, 1411 (1990); Phys. Rev. A **43**, 3407 (1991).

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

[30] Y. Ishikawa, Int. J. Quantum Chem. **26**, 127 (1992).

[31] A. C. Hartly, E. Lindroth, and A.-M. Mårtensson-Pendrill, J. Phys. B **23**, 1990 (1990); A. C. Hartly and A.-M. Mårtensson-Pendrill, Z. Phys. D **15**, 309 (1990); J. Phys. B **24**, 1193 (1991).

[32] I. Lindgren, in *Many-Body Methods in Quantum Chemistry* (Ref. [5]), p. 293; Nucl. Instrum. Methods Phys. Res. B **31**, 102 (1988).

[33] B. Craseman, K. R. Karim, and M. H. Chen, At. Data Nucl. Data Tables **36**, 356 (1987); M. H. Chen, B. Crasemann, N. Martensson, and B. Johansson, Phys. Rev. A

**31**, 556 (1985); M. H. Chen, B. Crasemann, and H. Mark, *ibid.* **24**, 1158 (1981).

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

[35] B. Klahn and J. Morgan, J. Chem. Phys. **84**, 410 (1984).

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

[37] S. Huzinaga and M. Klobukowski, J. Mol. Struct. Theochem. **167**, 1 (1988); S. Huzinaga, M. Klobukowski, and H. Tatewaki, Can. J. Chem. **63**, 1812 (1985); S. Huzinaga and M. Klobukowski, Chem. Phys. Lett. **212**, 260 (1993).

[38] M. W. Schmidt and K. Ruedenberg, J. Chem. Phys. **71**, 3951 (1979).

[39] J. P. Desclaux, Comput. Phys. Commun. **9**, 31 (1975).