Relativistic Dirac-Fock and many-body perturbation calculations on He, He-like ions, Ne, and Ar

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Relativistic Dirac-Fock and diagrammatic many-body perturbation-theory calculations have been performed on He, several He-like ions, Ne, and Ar. The no-pair Dirac-Coulomb Hamiltonian is taken as the starting point. A solution of the Dirac-Fock equations is obtained by analytic expansion in basis sets of Gaussian-type functions. Many-body perturbation improvements of Coulomb correlation are done to third order.

I. INTRODUCTION

Atomic physics has entered a time of renewed interest in few-electron systems, i.e., highly ionized high-Z ions.[1-3] The interest has been sparked by the development of ion sources and high-energy accelerators. Recently, parity nonconservation in heavy atoms, e.g., Bi, Cs, and Tl, has also generated interest in many-electron systems.[4,5] Ultimately these experiments will have a bearing on the theoretical methods developed to describe many-electron atoms.

Many-body perturbation theory (MBPT), introduced into atomic physics by Kelly,[6] has proven to be a powerful and efficient technique for calculation of atomic and molecular properties. A relativistic version of the MBPT, which accounts for both relativistic and electron correlation effects, was developed by Das *et al.*[7] using a finite-difference Dirac-Fock self-consistent field (DFSCF), and by Johnson and Sapirstein using a "local" basis (Spline basis) expansion DF-SCF.[8] Beck[9] has developed a relativistic configuration-interaction method to calculate spectroscopic transition properties and binding energies.

Theoretical methods developed to describe the electronic structure of truly many-electron atoms must be able to account for relativistic, electron corrrelation, and QED effects. They will have to yield wave functions that can be refined to account for these effects to high accuracy. They must be computationally efficient because they will have to describe eventually electronic states in very-high-Z neutral atoms. And lastly, they should be capable of being extended in a straightforward way to the study of molecules. The present work is one such approach, the solution of the DF-SCF equations by expansion in a "global" basis set of Gaussian-type functions (GTF) and MBPT improvement of the solutions.

The following section outlines methods for determining DFSCF wave functions and of improving them to account for Coulomb correlation energy. In Sec. III, results on He, He-like ions, Ne and Ar will be presented and compared with previous nonrelativistic and relativistic MBPT results obtained by numerical finite-difference methods.

II. BASIS-SET EXPANSION DF-SCF AND MBPT REFINEMENT

Numerical finite-difference solutions of the nonrelativistic and relativistic atomic SCF equations have been developed by a number of workers.[10-14] To date, the majority of relativistic calculations of the electronic structure of atoms and ions have been done using finite-difference numerical methods.[15,16] Recently basis-set expansion DFSCF methods, employing both "local"[17] and "global"[18-21] basis sets, which approach numerical finite-difference calculations in accuracy, have been developed. The unbounded nature of the Dirac Hamiltonian, however, imposes more severe restraints on admissible forms of basis functions than does the Schrödinger Hamiltonian.

A. The Dirac-Fock basis-set expansion method

In the DFSCF scheme, the behavior of an electron in a central field potential V is described by a radial Dirac equation of the form[22]

$$H_r\phi_{nk}=\epsilon_{nk}\phi_{nk} \ , \tag{1a}$$

where

$$H_r=\begin{bmatrix} V & c\pi_k \\ c\pi_k^\dagger & V-2c^2\end{bmatrix} , \tag{1b}$$

with

$$\pi_k=-\frac{d}{dr}+k/r$$

and

$$\pi_k^\dagger=\frac{d}{dr}+k/r \ .$$

Here

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

The radial functions $P_{nk}(r)$ and $Q_{nk}(r)$ are referred to as the large and small components, respectively. c is the speed of light. $P_{nk}(r)$ and $Q_{nk}(r)$ may be expanded in sets of basis functions.

Kim,[22] in his pioneering work on the basis-set expansion DFSCF method, revealed a tendency for calculated energies to fall below the variational limit. The origin of this "variational failure" is associated with an improper relationship between the basis sets[18,19,21] which represent the large and small components of the wave function and with failure to insure that the wave function behaves properly in the region near the nucleus.[19–23] The failure of the basis-set expansion DF method can be avoided if a well-defined set of constraints is used in the definition of "global" basis sets. The constraints impose physical boundary conditions on the four-spinor solutions of the DF equations[20,21] and ensure that the basis sets in which the large and small components are expanded may be systematically extended to completeness. Analysis shows that the failure to impose the correct constraints on the large and small component basis sets results in a deficiency in the computed kinetic energy[24] as well as the appearance of spurious solutions among the physical ones.[19,23]

Among the types of functions employed in basis-set expansions have been exponential or Slater-type functions[18–25] (STF), piecewise polynomials,[17] orthogonal Laguerre functions,[26] and Gaussian-type functions[27,28] (GTF). No type is yet preeminent in relativistic atomic calculations as STF are in atomic and GTF in molecular nonrelativistic calculations, but the advantages and disadvantages of each are understood.

STF are employed in nonrelativistic atomic calculations because, in the point nucleus approximation, they correctly represent the wave-function singularity at the origin. They have also been used successfully in relativistic atomic calculations but, in these, noninteger quantum numbers are employed in order to fit the more severe relativistic cusp condition.[19–23] In heavy atoms, the point representation of the atomic nucleus is better replaced by a finite model. With the finite nucleus, the cusp condition changes and the use of STF as basis functions loses some relevance. Basis sets of STF are also prone to near-linear dependence.[26] This characteristic is more significant for matrix DF equations than for Hartree-Fock equations. In recent work, Goldman[26] has employed orthogonal Laguerre functions. This type of basis set was shown to be free of linear dependency and therefore promising.

Piecewise polynomial basis sets[8,17,29] are largely free of computational linear dependence problems because of their "local" nature. Basis sets of B splines have been successfully used by Johnson and Sapirstein[8] in relativistic DF and MBPT calculations. Hermite interpolation functions have also been employed as basis functions in relativistic calculations.[30] A restriction on the use of piecewise polynomial basis sets in relativistic atomic calculations is the difficulty in imposing the proper relationship between the "local" basis sets for the large and small components in order to avoid variational failure.[30]

Basis sets of Gaussian functions have a number of advantages in relativistic SCF calculations: (i) Although GTF are at a disadvantage with respect to STF in nonrelativistic calculations because they behave improperly near a point nucleus, the advantage of STF dissipates in heavy-atom systems when a finite nucleus is employed. In fact, when the nucleus is modeled as a finite body of uniform proton-charge distribution, the wave function near the origin is Gaussian.[27,31] (ii) Basis sets of GTF are less prone to near-linear dependence than are basis sets of STF. The use of large basis sets of GTF has been shown to be feasible in relativistic calculations.[32,33] (iii) In comparison with piecewise polynomial basis, fewer GTF are needed to attain accurate energies. (iv) The ease with which multicenter two-electron integrals over GTF are evaluated makes their use in molecular calculations preferred. (v) The Fourier transform of a GTF is Gaussian, of possible use in calculations of QED and related dynamical effects directly in momentum space.

In recent studies, we have performed DF Gaussian basis-set expansion calculations on one- and many-electron systems with a finite nucleus model.[27,31,32] These studies have explored ways of accelerating convergence of the basis-set expansions. In those studies, the large- and small-component radial functions, $P_{nk}(r)$ and $Q_{nk}(r)$, respectively, were expanded in GTF, for $k<0$ states, as

$$P_{nk}(r) = \sum_{i=1}^{N_k} r^{m}\exp(-\zeta_{ki}r^2)\xi_{nki} , \tag{2a}$$

$$Q_{nk}(r) = \sum_{i=1}^{N_k} r^{m-1}\exp(-\zeta_{ki}r^2)\eta_{nki} , \tag{2b}$$

where $m=-k$. Here N_k is the number of GTF in the basis set. For $k>0$ states,

$$P_{nk}(r) = \sum_{i=1}^{N_k} r^{m}\exp(-\zeta_{k_i}r^2)\xi_{nki} , \tag{3a}$$

$$Q_{nk}(r) = \sum_{i=1}^{N_k} r^{m-1}\exp(-\zeta_{ki}r^2)\eta_{nki} + \sum_{j=1}^{N_k} r^{m+1}\exp(-\zeta_{kj}r^2)\omega_{nkj} , \tag{3b}$$

where $m=k+1$. The $\{\xi_{nki}\}$, $\{\eta_{nki}\}$, and $\{\omega_{nkj}\}$ are linear variation parameters.

GTF are chosen to satisfy the condition of kinetic balance and relativistic boundary conditions associated with a finite nucleus.[27,31] In previous numerical studies, these expansion schemes have achieved accuracy comparable to that attained with the finite-difference DF method. In the present study, we have also performed DF basis-set calculations using expansions (2) and (3).

B. Relativistic MBPT refinements

The starting point for our development of relativistic MBPT calculations is the relativistic "no-pair" Dirac-

Coulomb (DC) Hamiltonian,[34,35] originally introduced to avoid the "continuum dissolution" problem associated with relativistic many-body calculations:

$$H=\sum_{i=1}^{N} h_D(i)+L_+\left[\sum_{\substack{i=1\\ i<j}}^{N} 1\Big/ r_{ij}\right]L_+ , \tag{4}$$

where $L_+=L_+(1)\cdots L_+(N)$, with $L_+(i)$ the projection operator onto the space spanned by the positive-energy eigenfunctions of the DF operator.[35]

Negative-energy states, as part of the complete set of states, play a role in many-body calculations. However, contributions from the negative energy states due to creation of virtual electron-positron pairs are small, of the order α^3, and are neglected in the present study. Neglecting interactions with the filled negative-energy sea, i.e., neglecting virtual electron-positron pairs in summing the MBPT diagrams, we have a straight-forward extension of nonrelativistic MBPT. The "no-pair" Dirac-Coulomb Hamiltonian may be expressed in terms of normally ordered products of the spinor operators, $[r^+s]$ and $[r^+s^+ut]$,[34,21]

$$H_N=\sum_{r,s} f_{rs}[r^+s]+\tfrac{1}{4}\sum_{\substack{r,s\\ t,u}}\langle rs\|tu\rangle[r^+s^+ut] \tag{5}$$

where

$$\langle rs\|tu\rangle=\langle rs|tu\rangle-\langle rs|ut\rangle$$

and

$$\langle rs|tu\rangle=\int d\mathbf{x}_1 d\mathbf{x}_2\phi_r(\mathbf{x}_1)\phi_s(\mathbf{x}_2)r_{12}^{-1}\phi_t(\mathbf{x}_1)\phi_u(\mathbf{x}_2) .$$

Here f_{rs} and $\langle rs\|tu\rangle$ are, respectively, one-electron DF and antisymmetrized two-electron Coulomb 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.[21] In this form the no-pair Hamiltonian is restricted to contributions from the positive-energy branch of the spectrum.

The correlation energy induced by the Breit interaction is significant for inner-shell spinors of heavier systems.[36,37] In the present study, however, we neglect the Breit interaction along with radiative corrections, mass polarization, and reduced-mass effects.

C. Computation

For He and He-like ions, even-tempered[38] basis sets of GTF were used. In basis sets of even-tempered GTF, the exponents, $\{\zeta_{ki}\}$ are given in terms of the parameters α, β according to the geometric series

$$\zeta_{ki}=\alpha\beta^{i-1},\quad i=1,2,\ldots,N_k .$$

In DF calculations on He and He-like species, the parameters α and β are optimized until a minimum in the DF total energy is found. The optimal α and β values thus determined for He are, respectively, 0.124 49 and 2.3905: for Sn^{+48} ($Z=50$), they are 170.5065 and 2.476 41, respectively. For the Ne and Ar atoms, well-tempered GTF basis sets of Huzinaga[39] were chosen because of their compactness. In this case, the exponents are initially energy-optimized in terms of four parameters, α, β, γ, and δ according to the formula

$$\zeta_{ki}=\alpha\beta^{i-1}[1+\gamma(i/N_k)\delta],\quad i=1,2,\ldots,N_k .$$

The exponents thus determined are further optimized individually in nonrelativistic Hartree-Fock calculations. The exponents for atoms up to Kr are tabulated in Ref. 39. They are employed without further optimization in our DFSCF and MBPT calculations. The radial functions that possess different k quantum number but with the same l quantum number are expanded in terms of the same set of basis functions (e.g., the radial functions of $p_{1/2}$ and $p_{3/2}$ symmetries are expanded in the same set of p-type radial GTF). The speed of light used in calculating the relativistic energies was 137.037 a.u. A value of c of 10 000.0 a.u. was chosen in the calculations which simulated the nonrelativistic limit.

The nuclei were modeled as spheres of uniform proton charge in every calculation. The model has been discussed in Ref. 27. The atomic masses used for the He, Ne^{8+} ($Z=10$), Ca^{18+} ($Z=20$), Zn^{28+} ($Z=30$), Zr^{38+} ($Z=40$), Sn^{48+} ($Z=50$) ions, Ne, and Ar are, respectively, 4.0, 20.18, 40.08, 65.37, 91.22, 118.71, 20.0, and 39.948.

In the present MBPT calculations, Goldstone diagrams[40] have been summed to compute Dirac-Coulomb correlation corrections up to third order. Single-configuration Dirac-Fock wave functions were used as reference states for the MBPT refinements. Second- and third-order Coulomb correlation corrections were computed by systematically enlarging the virtual space. Virtual spinors used in the study were generated in the field of the nucleus and all electrons (V^N potential). The basis-set exponents for the virtual spinors were taken from a single, "saturated" set of GTF exponents used in the DFSCF calculations.

III. RESULTS AND DISCUSSION

Table I shows the DF energies as well as the second-order (E_2) and third-order (E_3) electrostatic correlation energies for He and for several He-like ions which have nuclear charge Z up to 50. Dirac-Fock and second- and third-order correlation energies computed with three GTF basis sets, $14s10p8d7f6g$, $14s10p8d7f6g5h$, and $14s10p8d7f6g5h4i$, respectively, are presented in rows A, B, and C. The basis-set exponents used for these cal-

TABLE I. Energies of He and He-like ions (a.u.). Square brackets denote powers of 10.

		E_{DF}	E_2	E_3	E_2 from pair equation[a]
$Z=2$	A	−2.861 812	−3.6911[−2]	−3.898[−3]	−3.6965[−2]
	B		−3.7059[−2]	−3.815[−3]	
	C		−3.7132[−2]	−3.772[−3]	
$Z=10$	A	−93.982 693	−4.4055[−2]	−1.099[−3]	−4.4095[−2]
	B		−4.4215[−2]	−1.081[−3]	
	C		−4.4294[−2]	−1.072[−3]	
$Z=20$	A	−389.665 326	−4.4949[−2]	−5.925[−4]	−4.4922[−2]
	B		−4.5104[−2]	−5.836[−4]	
	C		−4.5180[−2]	−5.791[−4]	
$Z=30$	A	−892.065 124	−4.5293[−2]	−4.187[−4]	−4.5113[−2]
	B		−4.5444[−2]	−4.130[−4]	
	C		−4.5517[−2]	−4.101[−4]	
$Z=40$	A	−1609.865 286	−4.5716[−2]	−3.334[−4]	−4.5320[−2]
	B		−4.5864[−2]	−3.292[−4]	
	C		−4.5936[−2]	−3.270[−4]	
$Z=50$	A	−2556.308 720	−4.6439[−2]	−2.845[−4]	−4.5832[−2]
	B		−4.6587[−2]	−2.811[−4]	
	C		−4.6661[−2]	−2.794[−4]	

[a]Second-order electrostatic correlation energies obtained by using the relativistic pair equation ($L_{\max}=4$): Ref. 41.

culations are tabulated in Table II. The DF energies computed with the three basis sets are identical because all of them contain the same 14s GTF's. They differ only in the order of partial-wave expansion, $L_{\max}$, the highest angular momentum of the spinors included in the virtual space.

Lindroth[41] used relativistic pair equations to compute second-order energies of He and He-like ions using $L_{\max}=4$. For all the systems considered, our second-order results obtained with $L_{\max}=4$ agree well with those reported by Lindroth. For lower-Z cases, in particular, the agreement is excellent. Thus the error in the second-order energies due to basis-set truncation is small (0.15 and 0.10%, respectively, for the $Z=2$ and 10 cases). With increasing Z, however, there is a systematic deviation between our E_2 and those obtained by Lindroth. This deviation may be attributable to the fact that our calculations treat the nucleus as a finite body of uniform proton charge distribution, whereas Lindroth uses a point nucleus approximation.

Along the entire He isoelectronic series, the second-order electrostatic correlation energy remains almost constant, with a slight increase in magnitude as nuclear charge increases. The magnitude of the third-order energy, however, decreases dramatically as Z increases, indicating that the perturbation series converges faster at

TABLE II. Basis-set composition for He.[a]

ζ	Symmetry $s_{1/2}$	$p_{1/2,3/2}$	$d_{3/2,5/2}$	$f_{5/2,7/2}$	$g_{7/2,9/2}$	$h_{9/2,11/2}$	$i_{11/2,13/2}$
10 362.85	A,B,C						
4335.033	A,B,C						
1813.450	A,B,C						
758.6100	A,B,C						
317.3450	A,B,C	A,B,C					
132.7531	A,B,C	A,B,C	A,B,C				
55.533 86	A,B,C	A,B,C	A,B,C	A,B,C			
23.231 16	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C		
9.718 158	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C	B,C	C
4.065 342	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C	B,C	C
1.700 631	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C	B,C	C
0.711 415	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C	B,C	C
0.297 602	A,B,C	A,B,C	A,B,C	A,B,C	A,B,C	B,C	
0.124 494	A,B,C	A,B,C					

[a] A, B, and C specify the exponents of the basis sets, 14s10p8d7f6g, 14s10p8d7f6g5h, and 14s10p8d7f6g5h4i, respectively.

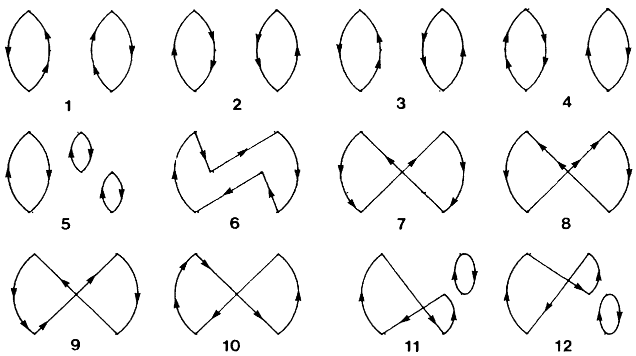

FIG. 1. Third-order Goldstone diagrams.

higher Z. For highly ionized species ($Z>30$), the second-order perturbation correction alone is capable of accounting for over 99% of the correlation energy, and the third-order correlation correction may not be necessary at all for correlation corrections in most applications. The DF independent-particle approximation is an accurate approximation to the exact N-particle eigenfunction of the no-pair Hamiltonian in highly ionized species.

We have explored the dependence of the partial wave contributions on the number of basis functions per k value for up to $L_{max}=5$. Table III shows the effect on the second-order energy in He of using a larger basis set for each symmetry species. ΔE_2 represents the increase in second-order energy due to the use of a larger basis set. The reference E_2 used for the comparative study is the value obtained by using $14s\,10p\,8d\,7f\,6g\,5h$ basis given in row B, Table I, which is reproduced in the first row of Table III. The effect on the E_2 of using, respectively, $16s$, $12p$, and $10d$ instead of using $14s$, $10p$, and $8d$ is seen to be negligible. This implies that the basis sets used for these symmetry species are nearly saturated. However, the effect of using larger basis sets in f, g, and h symmetry is noticeable, the improvement in E_2 being on the order of 10^{-5} a.u. The basis sets used for f, g, and h symmetries are not saturated. This is a consequence of using smaller basis sets for the f, g, and h partial-wave expansions.

TABLE III. The effects of the basis-set size on the second-order energy in He (a.u.).

Basis set	E_2	ΔE_2
$14s\,10p\,8d\,7f\,6g\,5h$	$-0.037\,059\,3$	
$16s\,10p\,8d\,7f\,6g\,5h$	$-0.037\,059\,3$	$0.000\,000\,0$
$14s\,12p\,8d\,7f\,6g\,5h$	$-0.037\,059\,4$	$-0.000\,000\,1$
$14s\,10p\,10d\,7f\,6g\,5h$	$-0.037\,059\,5$	$-0.000\,000\,2$
$14s\,10p\,8d\,9f\,6g\,5h$	$-0.037\,059\,9$	$-0.000\,000\,6$
$14s\,10p\,8d\,7f\,8g\,5h$	$-0.037\,061\,9$	$-0.000\,002\,6$
$14s\,10p\,8d\,7f\,6g\,7h$	$-0.037\,068\,9$	$-0.000\,009\,6$

Table IV displays results for He atom together with the numerical limits calculated by Blundell *et al.*[42] Our DFSCF total energy and nonrelativistic limit agree well with the results of Blundell *et al.* In particular, the difference between the DF energy and the nonrelativistic limit, $E_{rel}-E_{nr}$, is in excellent agreement with the numerical limit.

The Coulomb correlation corrections computed with the $14s\,10p\,8d\,7f\,6g\,5h\,4i$ set ($L_{max}=6$) do not appreciably improve on those obtained with the $14s\,10p\,8d\,7f\,6g$ set ($L_{max}=4$). E_2+E_3 obtained in both these calculations account for approximately 97% of the limiting electrostatic correlation energy of $-0.042\,043$ a.u. The results of Blundell *et al.* (Ref. 42, Table V) show that improvement in the computed all-order correlation energy obtained using a partial wave expansion with $L_{max}=7$ over that obtained with $L_{max}=4$ is only 0.4%. The relativistic MBPT correlation corrections, then, would probably not improve with a higher-order partial-wave expansion ($L_{max}>6$). The [2/1] Padé approximant, $E_{[2/1]}$, improves the computed correlation correction by another 1%, thereby accounting for 98.3% of the total correlation correction. Obtaining the remaining fraction of the correlation energy of the He atom requires perturbation corrections of fourth or higher order.

Tables V and VI show results for Ne and Ar computed with increasing L_{max}. For both Ne and Ar, the second- and third-order electrostatic correlation corrections improve noticeably as L_{max} increases. Basis-set compositions of some representative GTF basis sets for Ar are given in Table VII. Table VIII summarizes the relativis-

TABLE IV. Comparison of calculated MBPT energies of He with the numerical limits (Ref. 42).

	E_{rel}	E_{nr}	$E_{rel}-E_{nr}$
Present work[a]			
DF energy	$-2.861\,812\,04$	$-2.861\,678\,74$	$-0.000\,133\,30$
E_2+E_3	$-0.040\,904\,16$	$-0.040\,904\,97$	$0.000\,000\,81$
$E_{[2/1]}$	$-0.041\,330\,63$	$-0.041\,330\,98$	
Numerical limit[b]			
DF energy	$-2.861\,813\,34$	$-2.861\,679\,99$	$-0.000\,133\,35$
Correlation	$-0.042\,043\,15$	$-0.042\,044\,39$	$0.000\,001\,24$

[a]Computed with a $14s\,10p\,8d\,7f\,6g\,5h\,4i$ GTF basis set.
[b]Reference 42.

TABLE V. Calculated energies of the neon atom (a.u.) (Refs. a and b).

Basis set	E_2		E_3	
	Relativistic	Nonrelativistic	Relativistic	Nonrelativistic
$14s\,10p\,8d$	−0.322 010	−0.321 735	+0.001 400	+0.001 358
$14s\,10p\,8d\,6f$	−0.358 897	−0.358 646	+0.000 410	+0.000 366
$14s\,10p\,8d\,6f\,5g$	−0.372 847	−0.372 607	+0.001 099	+0.001 054
$14s\,10p\,8d\,6f\,5g\,4h$	−0.378 067	−0.377 832	+0.002 058	+0.002 015
$14s\,10p\,8d\,6f\,5g\,4h\,4i$	−0.380 411	−0.380 180	+0.002 652	+0.002 609

[a]DF energy and the nonrelativistic limit ($c=10^4$ a.u.) computed with GTF basis sets are, respectively, −128.691 639 and −128.546 839 a.u.
[b]DF energy and the nonrelativistic limit computed with the numerical finite difference computer program of Desclaux are, respectively, −128.6919 and −128.5471 a.u.

tic MBPT results for these systems and results of previous nonrelativistic calculations in which correlation corrections have been calculated. In contrast to the He case, the [2/1] Padé approximants do not improve the correlation energy. Convergence of the perturbation expansion is good. More accurate correlation energies for these systems require higher-order partial-wave expansion calculations rather than higher-order perturbation corrections. That is gratifying because, for truly many-electron systems, such as Ar, computation of the fourth-order perturbation correction becomes time consuming.

Using a finite-difference pair equation approach,[43] Lindgren and Salomonson computed the nonrelativistic second-order correlation energy of Ne using a partial-wave expansion with $L_{\max}$ up to 6. A V^N potential was employed in their calculations. With $L_{\max}=6$, they obtained $E_2=-0.383\,55$ a.u. This value is to be compared with our nonrelativistic limit, $-0.380\,180$ a.u.

Jankowski *et al.*[44] used a large basis of STF to calculate nonrelativistic second- and third-order correlation energies for the Ne atom. Our nonrelativistic correlation correction, E_2+E_3 ($-0.377\,57$ a.u.), compares well with their reported value of $-0.379\,80$ a.u. obtained with a partial-wave expansion employing up to *i*-type STF. Das *et al.* have estimated the "experimental" correlation energy of Ne to be -0.3890 a.u.[45] Our computed correlation energy accounts for 97% of this estimated energy.

Quiney *et al.*[46] have computed the second-order Dirac-Coulomb correlation energy of Ar. They used a large basis set of 17 STF of noninteger quantum number in each symmetry with up to *f*-type basis functions. A V^N potential was used to generate virtual spinors up to $L_{\max}=3$. The point nucleus approximation was employed in the calculations. E_2 thus obtained was $-0.639\,424$ a.u. This is to be compared with our second-order energy, $-0.633\,833$ a.u. obtained with $L_{\max}=3$. Assuming that the effect on E_2 of treating the nucleus differently is small, the discrepancy of 0.0056 a.u. between the two results is best attributed to basis-set truncation error in our calculations. Expansion of a GTF basis set to a size necessary to eliminate truncation as the primary source of error effectively restricts the MBPT calculations to second order without the use of a supercomputer. Recalling that accurate correlation calculations on this system require inclusion of a partial-wave expansion with $L_{\max}\gg 3$, evaluation of even the third-order term may be expected to be time consuming.

Cooper and Kelly[47] performed a nonrelativistic MBPT study on the Ar atom. In their numerical finite-difference Hartree-Fock scheme, a V^{N-1} potential was used to generate the virtual single-particle states with a partial-wave expansion of $L_{\max}$ through 3. A correlation energy of -0.685 a.u. was determined. This value includes an estimate of the fourth-order four-body contribution of -0.01 a.u. This value may be compared to our Dirac-Coulomb correlation energy (E_2+E_3) of $-0.695\,126$ a.u., obtained with a partial-wave expansion of $L_{\max}$ through 5.

Taking the first eight ionization potentials reported by Moore[48] together with theoretical results on Ar^{+8} reported by Sherr *et al.*,[49] Cooper and Kelly estimated the correlation energy of Ar to be -0.73 a.u. In another study, Clementi estimated the value to be -0.692 a.u.[50] Taking into account errors of basis-set and partial-wave expansion truncation, we estimate that our computed

TABLE VI. Calculated energies of argon atom (a.u.) (Refs. a and b).

Basis set	E_2		E_3	
	Relativistic	Nonrelativistic	Relativistic	Nonrelativistic
$16s\,11p\,9d$	−0.542 645	−0.541 450	−0.009 512	−0.009 571
$16s\,11p\,9d\,7f$	−0.633 833	−0.632 753	−0.014 637	−0.014 721
$16s\,11p\,9d\,7f\,6g$	−0.669 685	−0.668 673	−0.014 770	−0.014 858
$16s\,11p\,9d\,7f\,6g\,5h$	−0.682 257	−0.681 283	−0.012 869	−0.012 953

[a]DF energy and nonrelativistic limit obtained with GTF basis sets are, respectively, −528.681 482 and −526.815 735 a.u.
[b]DF energy and nonrelativistic limit calculated with the numerical finite difference program of Desclaux are respectively, −528.683 and −526.818 a.u.

TABLE VII. Basis-set composition for Ar (Ref. a).

ζ	$s_{1/2}$	$p_{1/2}$ $_{3/2}$	$d_{3/2}$ $_{5/2}$	$f_{5/2}$ $_{7/2}$	$g_{7/2}$ $_{9/2}$	$h_{9/2}$ $_{11/2}$
1192 038.6	A,B,C					
176 715.15	A,B,C					
40 309.619	A,B,C					
11 089.577	A,B,C					
3461.2322	A,B,C					
1163.6413	A,B,C	A,B,C				
409.939 44	A,B,C	A,B,C	A,B,C			
153.084 37	A,B,C	A,B,C	A,B,C	A,B,C		
60.6375 11	A,B,C	A,B,C	A,B,C	A,B,C	B,C	
25.040 039	A,B,C	A,B,C	A,B,C	A,B,C	B,C	C
10.550 746	A,B,C	A,B,C	A,B,C	A,B,C	B,C	C
4.571 726	A,B,C	A,B,C	A,B,C	A,B,C	B,C	C
2.015 611	A,B,C	A,B,C	A,B,C	A,B,C	B,C	C
0.836 350	A,B,C	A,B,C	A,B,C	A,B,C	B,C	C
0.332 530	A,B,C	A,B,C	A,B,C			
0.125 515	A,B,C	A,B,C				

[a] A, B, and C specify the exponents of the GTF basis sets, $16s11p9d7f$, $16s11p9d7f6g$, and $16s11p9d7f6g5h$, respectively.

Coulomb correlation energy of argon is accurate to within 4%.

Table VIII also shows the breakdown of E_3 into hole-hole (h-h), particle-particle (p-p), and hole-particle (h-p) contributions. For both Ne and Ar, h-p contributions are as large as the sum of p-p and h-h in magnitude, but with opposite sign. Cancellation of terms makes E_3 an order of magnitude smaller than the h-p contributions. Table IX shows the breakdown by diagram of E_3 of argon. See Fig. 1.

For all the systems studied, the Coulomb correlation energies computed with the Dirac-Coulomb Hamiltonian are different from those computed at the nonrelativistic limit, simulated by setting the speed of light c to 10^4. The difference represents the "interference" between relativistic and correlation effects. Comparison of the He, Ne, and Ar results shows that nonadditivity increases in magnitude with increasing Z. In helium the nonadditive contribution is about 10^{-6} a.u., increasing in argon to 10^{-3} a.u.

IV. CONCLUSIONS

The aim of this study has been to develop a relativistic MBPT scheme which can practically be applied to truly many-electron atoms and molecules. The Gaussian basis-set calculations have yielded accurate results for highly ionized systems, and show none of the signs of near linear dependence problems reported with Slater

TABLE VIII. Coulomb correlation energies of Ne and Ar (a.u.).

	Ne[a]		Ar[b]	
	Relativistic	Nonrelativistic	Relativistic	Nonrelativistic
$E_{\rm DF}$	−128.691 639	−128.546 839	−528.681 482	−526.815 735
E_2	−0.380 411	−0.380 180	−0.682 257	−0.681 283
$E_3(h\text{-}h)$	+0.040 030	+0.039 974	+0.056 905	+0.056 882
E_3 $(p\text{-}p)$	+0.052 307	+0.052 257	+0.083 854	+0.083 862
E_3 $(p\text{-}h)$	−0.089 684	−0.089 622	−0.153 629	−0.153 696
E_3	+0.002 652	+0.002 609	−0.012 869	−0.012 953
E_2+E_3	−0.377 759	−0.377 571	−0.695 126	−0.694 236
$E_{[2/1]}$	−0.377 777	−0.377 588	−0.695 373	−0.694 487
Previous work		−0.379 80[c]		−0.685[e]
		−0.3890[d]		−0.73[e]

[a]Computed with $14s10p8d6f5g4h4i$ basis set.
[b]Computed with $16s11p9d7f6g5h$ basis set.
[c]Reference 44.
[d]Reference 45.
[e]Reference 47.

TABLE IX. Third-order correlation energies of Ar (Ref. a).

Diagram of Fig. 1	Value (in a.u.)
1	+0.133 614 6
2	+0.088 651 1
3	−0.181 727 0
4	−0.190 691 0
5	+0.153 447 8
6	+0.013 597 5
7	−0.031 746 2
8	−0.049 760 3
9	+0.061 960 9
10	+0.061 960 9
11	−0.036 088 9
12	−0.036 088 9

[a]Computed with a $16s11p9d7f6g5h$ GTF basis set.

function basis sets.[26,21] Thus the use of GTF basis sets in relativistic SCF and MBPT calculations on atoms and molecules seems more appropriate that STF. The results reported in the present study indicate that a moderately large GTF basis set is sufficient to account for 97% of the total electrostatic correlation energy for the species considered in the present study. Third-order MBPT has proven to be adequate to recover almost all electrostatic correlation energy in neutral atoms, and second order suffices for highly ionized species. For Ne and Ar, the remaining error is due more to truncation of the partial-wave expansion than to termination of the perturbation expansion.

In the present study, the Breit interaction has been neglected; the two-electron interaction has been treated "nonrelativistically" as the instantaneous Coulomb repulsion. The leading effects of transverse photon exchange may be included in the Hamiltonian by adding the frequency-independent Breit operator to the instantaneous Coulomb operator. Such an approach has been taken in recent studies by Johnson *et al.*,[51] Lindroth,[41] and Quiney *et al.*[52] As argued by Sucher,[34] such an approach has the advantage that all effects through order α^2 are included in the zero-order Hamiltonian. Work along these lines is already in progress.[32]

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