

Relativistic correlation energies of heliumlike atoms

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The dependence of the relativistic correlation energy in the ground states of helium isoelectronic series ions on the atomic number, for $1 \leq Z \leq 118$, is investigated. The correctness of the results derived from large-scale Hylleraas configuration-interaction calculations has been confirmed by analyzing the results of numerical multiconfiguration Dirac-Fock calculations. In particular, the relativistic correlation energy is a nonmonotonic function of Z . It has a minimum at $Z=20$ and a maximum at $Z=68$ and rapidly decreases for larger Z values.

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The nonrelativistic correlation energy is usually defined as [1]

$$E_{\text{nr}}^{\text{corr}} = E_{\text{Schr}} - E_{\text{HF}}, \quad (1)$$

where E_{Schr} is the eigenvalue of the Schrödinger Hamiltonian and E_{HF} is the corresponding Hartree-Fock energy. A relativistic generalization of this definition is not unique since the “exact” relativistic energy of an atom or a molecule is not uniquely defined. The most straightforward definition of the relativistic correlation energy, also used in this paper, reads

$$E_{\text{rel}}^{\text{corr}} = E_{\text{DC}} - E_{\text{DF}}, \quad (2)$$

where E_{DC} is the eigenvalue of the Dirac-Coulomb (DC) Hamiltonian and E_{DF} is the corresponding Dirac-Fock energy. By the DC Hamiltonian we understand a Hamiltonian in which the one-electron part is taken as a sum of appropriate one-electron Dirac Hamiltonians and the interaction is described by the nonrelativistic, Coulomb, $1/r_{ij}$ operators. Of particular interest is the part of the relativistic correlation energy referred to as the *relativity-correlation cross terms* [2] and defined as

$$E_x = E_{\text{rel}}^{\text{corr}} - E_{\text{nr}}^{\text{corr}}. \quad (3)$$

This quantity, very small for small- Z atoms, becomes a dominant part of the relativistic correlation energy for extremely large Z .

The nonrelativistic electron correlation energies for heliumlike ions have been evaluated by Midtdal and Aashamar using a $1/Z$ expansion [3], by Drake using a variational approach [4], and by Kutzelnigg and Morgan using a partial-wave expansion [5]. Accurate determination of the relativistic correlation energies, particularly for large Z , remains a difficult and elusive problem. The difficulty is both numerical and methodological. For large- Z ions the correlation energy constitutes a very small fraction of the total energy. For example, in the ground state of a $Z=80$ two-electron ion the correlation energy affects the sixth significant figure of the total energy. This means that in order to estimate the relativistic correction to the correlation energy one has to evaluate the eigenvalue of the Dirac-Coulomb Hamiltonian with an accuracy of at least eight figures. This task, rather straight-

forward in the case of the Schrödinger equation, is hard to accomplish with the unbounded-from-below Dirac-Coulomb Hamiltonian.

The simplest way to calculate the DC energies is to solve numerically the multi-configuration Dirac-Fock (MCD) equations with a sufficiently large basis of configurations. The exact fulfillment of the boundary conditions and of the relations between the large and small components of the numerical orbitals makes the numerical Dirac-Fock energies upper bounds to the exact ones [6]. In the multiconfigurational case the relations between the components of the wave function are only approximately correct. Therefore the bound properties of the energies, particularly for extremely large Z , are not necessarily obtained. However, one should expect the MCD energies to be close to the exact DC Hamiltonian eigenvalues. MCD calculations have been performed for the ground states of heliumlike ions with $2 \leq Z \leq 20$ [7] and $1 \leq Z \leq 26$ [8] using the the DHF programs developed by Grant *et al.* [9]. The calculations for larger values of Z are hindered by convergence problems and by the limits of numerical accuracy. Recently, a relativistic Hylleraas configuration-interaction (Hy-CI) approach [10,11] has been applied to solving the DC equation for He-like ions with point nucleus and $1 \leq Z \leq 118$ [11]. The results were rather unexpected. While the nonrelativistic correlation energy changes in a monotonic way from -39.8 mhartrees for $Z=1$ to -46.5 mhartrees for the largest values of Z (it reaches this value at $Z=48$ and remains approximately constant up to the largest physically acceptable values of Z), the relativistic correlation energy has a minimum of about -46 mhartrees at $Z=20$, reaches a maximum (equal to -45 mhartrees) at $Z=68$ and then rapidly decreases down to -70 mhartrees for $Z=118$. The dependence of $E_{\text{nr}}^{\text{corr}}$ on Z may be easily explained in terms of $1/Z$ expansion [3]. The problem is much more difficult in the relativistic case. It has been shown that the lowest-order contribution to the correlation-relativity cross term energy, E_x , vanishes [2]. The third-order correction is positive and proportional to $\alpha^2 Z^2$. The higher-order corrections are, to the authors' knowledge, unknown.

The Hy-CI calculations are performed in a basis of analytical functions. Then, for reasons of principle, the relations between large and small components of the wave function can be satisfied only in an approximate way. Also the two-electron generalizations of the one-electron exact kinetic bal-

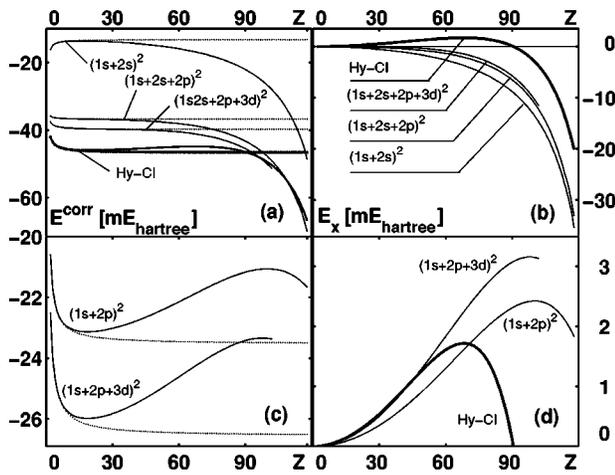


FIG. 1. (a) and (c) Electron correlation energies E^{corr} , relativistic (solid lines) and nonrelativistic (dotted lines), obtained in several MCDF calculations compared with Hy-CI results derived from a 502-parameter trial function (thick solid line) [11]. (b) and (d) Relativity-correlation cross-term energies E_x derived from the correlation energies displayed, respectively, in (a) and (c). All energies are in mhartrees.

ance conditions, necessary to secure the bound properties of the Hamiltonian eigenvalues [12], are represented by an infinite sequence of conditions and can never be satisfied exactly [11]. Therefore the authors of these calculations [11] concluded: “We cannot exclude that the behavior of the relativistic correlation energy for very large Z (strong decrease with increasing Z) may be an artifact resulting from a slight departure of the eigenvalue of the DC Hamiltonian describing the ground state from the Hylleraas-Undheim-MacDonald theorem conditions (the effect concerns the 7th significant figure in the energy).” In this Brief Report we demonstrate that these results are not an artifact but they

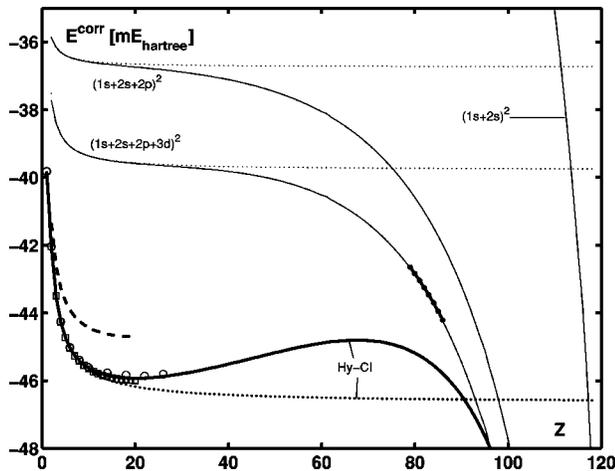


FIG. 2. A comparison of the results displayed in Fig. 1(a) with those in the literature: MCDF $(1s+2s+2p+3d)^2$, $78 < Z < 87$ (full circles) [14], MCDF $(1s+2s+2p+3s+3p+3d+4s+4p+4d+4f+5g)^2$, $Z < 21$ (broken line) [7], MCDF results based on an 11-configuration expansion extrapolated to a complete basis, $Z < 21$ (squares) [7], and based on a 21-configuration expansion, $Z < 27$ (circles) [8]. All energies are in mhartrees.

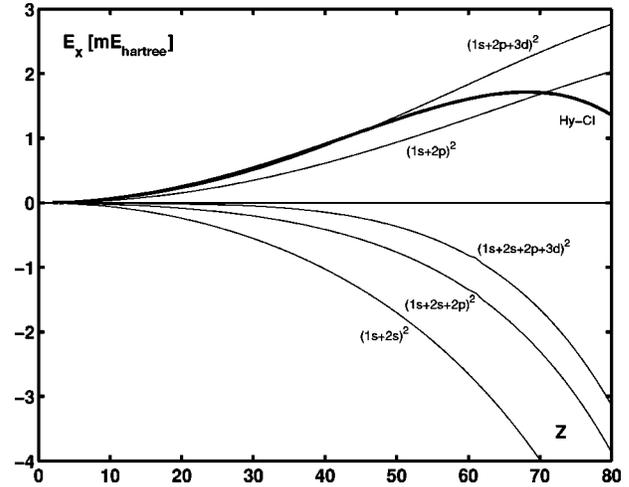


FIG. 3. Pattern of convergence of the MCDF relativity-correlation cross-term energies (thin lines) to the Hy-CI values represented by the thick line. All energies are in mhartrees.

reflect the real behavior of the relativistic correlation energy in the ground states of heliumlike ions.

As it is known [2,8,13], the cross-term corrections in $(1s)^2$ shells of heavy-nuclei atoms are much larger than the nonrelativistic correlation energies and the major part of the contribution to the total two-electron relativistic correction is due to the Breit interaction. Nevertheless, the demonstration of the correctness of the Hy-CI results for large- Z ions is important for at least two reasons. First, establishing the reliability of the relativistic Hy-CI approach opens a way to very accurate relativistic calculations for several-electron systems, in particular, to precise estimates of the Breit corrections for superheavy ions using the Hy-CI wave functions. Second, it shows that the relation between relativistic and

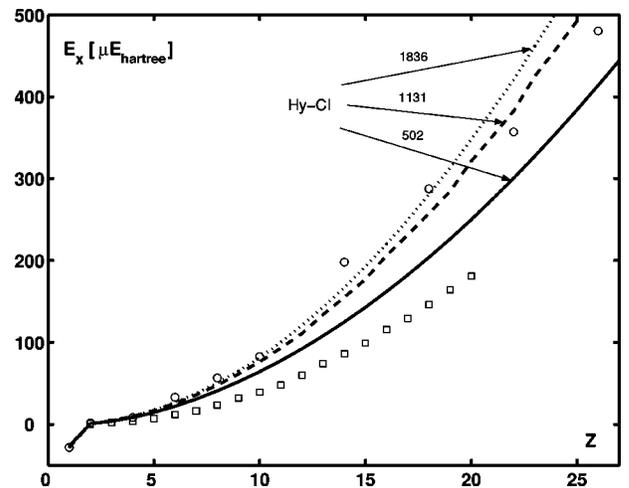


FIG. 4. Relativity-correlation cross-term energies E_x (in μ hartrees) derived from Hy-CI calculations with trial functions containing 502 parameters (solid line), 1131 parameters (broken line), and 1836 parameters (dotted line), compared with MCDF results extrapolated to the limit of a complete expansion taking as a base for the extrapolation results including all $(nl)^2$ configurations with $n < 5$ and $(5g)^2$ (squares) [7] and with $n < 7$ (circles) [8].

nonrelativistic correlation energy for large- Z ions is entirely different from that of the small- Z ones.

The Hy-CI trial functions are composed of 502 terms (they contain 502 linear variational parameters). The spaces of large-large and small-small components are spanned by 120 two-electron functions each. The combined space of large-small and small-large components is spanned by 262 two-electron functions. In the expansion correlation factors with r_{12}^n , $n=0,1,2$, have been included. The resulting wave functions exactly satisfy the boundary conditions in all singular points of the DC Hamiltonian and the two-electron kinetic balance conditions are satisfied up to the second order. A detailed description of the structure of the trial wave function is given in [11]. The Hy-CI correlation energies and relativity-correlation cross terms are compared with MCDF results in Fig. 1. It is interesting to note that the strong decrease of the relativistic correlation energy for large Z is caused by an s -type partial wave [by $(2s)^2$ configuration]. The contributions due to configurations $(2p)^2$ and $(3d)^2$ are entirely different. On one hand they lead to a decrease of the correlation energy, approximately uniform for all Z values and, on the other, they are responsible for the maximum in Z dependence of $E_{\text{rel}}^{\text{corr}}$. This can clearly be seen in Figs. 1(c) and 1(d). A comparison of our results with the ones in the literature is shown in Fig. 2. The convergence of the MCDF expansion is seen to be painfully slow—only the extrapolated MCDF results are comparable with those of Hy-CI. A

simple pattern of convergence of the MCDF results to the Hy-CI is very well seen in Fig. 3. Finally, in Fig. 4 the Hy-CI results obtained in three different basis sets of explicitly correlated trial functions for $Z < 30$ are compared with the extrapolated energies derived from two sets of MCDF calculations: Taking into account all configurations $(nl)^2$ with $n < 5$ and $(5g)^2$ (squares) [7]; and taking into account all configurations $(nl)^2$ with $n < 7$ (circles) [8].

The three sets of Hy-CI calculations correspond to 502-, 1131-, and 1836-function basis sets [11]. The results obtained with the smallest set, the same as in the cases displayed in Figs. 1–3, are represented by the solid line, the remaining two, respectively, by the broken and the dotted lines. The agreement between Hy-CI results and the most accurate extrapolations of MCDF calculations is perfect. Also, the convergence pattern of the Hy-CI calculations is correct.

We conclude that the Hy-CI relativistic correlation energies are correct and the influence of the approximate satisfaction of the relations between components of the two-electron wave function is negligibly small. Consequently, the Hy-CI approach proves to be applicable to relativistic calculations, and also for superheavy elements.

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