Effect of the complete Breit interaction on two-electron ion energy levels

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The effect of the fully relativistic Breit term upon atomic energy levels is investigated. The gauge dependence of the retarded electron-electron interaction in a self-consistent-field scheme is studied both theoretically and numerically. The complete Breit operator mean values are computed in Lorentz gauge and compared with those of the semirelativistic retarded interaction in covariant and radiation gauges for high-Z heliumlike ion singly excited states. The off-shell energy case is considered in detail even for a perturbative approach.

I. INTRODUCTION

Experiments measuring transition energies and level lifetimes in two- or three-electron ions have been extended to the relativistic domain. For example, $\Delta n=0$ $2\,^3P_J-2\,^3S_1$ transitions and $\Delta n=1$ $2\,^{3,1}P_J-1\,^1S_0$ transitions have been studied in heliumlike krypton ions produced at the Grand Accélérateur National d'Ions Lourds in Caen, France[1,2] (GANIL) with precisions of 180 and 20 ppm, respectively. The Lyman transitions have been studied in heliumlike xenon[3] at the same accelerator. It is now possible to study uranium ions at the Super-HILAC (heavy-ion linear accelerator in Berkeley, California) and a lifetime measurement has been carried out[4] on the $2\,^3P_0$ state. Experiments with increased precision are being planned; lifetime measurements using hyperfine quenching in heliumlike silver ($Z=47$) will hopefully give the fine-structure splitting $2\,^3P_0-2\,^3P_1$ for that system[5] while spectroscopic studies are in progress on uranium.[6]

Those measurements, when compared with *ab initio* theoretical calculations, provide hints that previously neglected effects might have to be considered due to their now measurable influence on the atomic structure. A detailed description of the atomic properties must include a wealth of contributions and one is rapidly faced with intricate mixings among them. To be more specific, let us recall that in few-electron ions of high Z one is compelled to include correlations induced by the electron-electron interaction, QED corrections, and, of course, relativistic corrections. In two preceding papers,[7,8] hereafter referred to as I and II, correlation and Lamb shift corrections were considered in two-electron systems. It has been demonstrated, in these papers, that electrostatic correlations were exhibiting a relativistic behavior in the middle- and high-Z ranges and that the instantaneous magnetic interaction was inducing important correlations. Those results have been confirmed by a relativistic treatment of the correlations using the pair equation.[9] In the same spirit, searching for a complete mixing of relativistic effects and correlation treatment, Quiney, Grant, and Wilson[10] argued that the Breit interaction can be included in self-consistent-field (SCF) calculations. It will be demonstrated that this statement is only partially valid. The inclusion of the magnetic instantaneous interaction, or Gaunt term, in the SCF is free of ambiguity and has already been performed in I and II as well as in previous calculations of binding energies in superheavy elements.[11] On the contrary, it has been demonstrated in I that the retardation terms are subject to gauge ambiguity when coupled to SCF calculations. The main difficulty (or even impossibility) in such a scheme is to define one-electron energy. This one-electron energy is, in turn, crucial in the calculation of retardation effects even for the well-known and widely used nonlocal Breit term. In Coulomb gauge, the one-electron energy of decisive importance is concealed by the gradient operators and might be restored by usual algebraic transformations. In this work, neither correlation nor Lamb shift calculations are considered (cf. papers I and II); we focus on the relativistic complete two-body interaction. While results are valid for any multielectron system, numerical data are given for heliumlike ions due to the challenging questions presented by experimental developments.

In Sec. II, the basic treatments for magnetic and retarded interactions are recalled and notations are specified. In the framework of Dirac-Fock methods[12,13] the numerical importance of the already mentioned gauge dependence is given for singly excited states; the discrepancy in level energy between Coulomb and Lorentz gauge is found to have a numerical contribution of $k\alpha^5Z^2m_ec^2$ (m_e being the electron mass and k a numerical factor depending on the level).

In Sec. III, the high-order (in $1/c$) retardation terms are considered in Lorentz gauge and numerical data are given for singly excited states of various heliumlike ions. A $k'\alpha^6Z^5m_ec^2$ energy contribution is found for those relativistic terms. Among the studied state levels, the $2\,^3P_2$ state matrix elements are the most important. Their values point out that $\Delta n=0$ $2\,^3P_2-2\,^3S_1$ transitions are now precise enough to make it mandatory to include this contribution in theoretical calculations.

In Sec. IV, the problems associated with off-shell energy matrix elements for retardation are studied both theoretically and numerically in the case of $1s2p$ $J=1$ states. An intrinsic gauge dependence is established and its relevance to the previously SCF-induced gauge dependence is discussed.

II. GAUGE DEPENDENCE OF RETARDED INTERACTION IN SCF CALCULATIONS

This section is an extension of results given in paper I, notations will be similar to those previously used, and demonstrations that were already given in I will not be reiterated here. To begin with, the different stages at which the retardation might be taken into account are briefly reviewed. Two distinct features should be stressed from the beginning: on the one hand, the necessity to go beyond the second order in $1/c$ to reach the precision of recent experiments (see, e.g., Ref. 1 or Table VI in paper II); and on the other hand, the necessity to perform actual calculations in a specific gauge.

Of course, there is a total freedom in the choice of the gauge condition to be satisfied by the vector potential $\mathbf{A}$ and by the electric potential V, while the true solution of the physical problem has to be independent of this choice. Only the two most commonly used gauges are considered here: the Coulomb (or radiation) gauge in which $\mathbf{A}$ and V satisfy

$$\operatorname{div}\mathbf{A}=0 , \tag{1}$$

and the Lorentz (or covariant) gauge in which one has

$$\operatorname{div}\mathbf{A}+\frac{1}{c^2}\frac{\partial V}{\partial t}=0 . \tag{2}$$

The photon propagator has a given expression in each gauge corresponding to a given propagation equation. This expression for the propagator, in turn, is used to obtain an effective potential g describing the interaction between two electrons. This potential has the same matrix elements as the S matrix.[14] Its expression is obtained by means of standard QED rules in the bound-state picture. In Coulomb gauge one obtains

$$g_{\omega C}=\frac{1}{R}-\frac{\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2}{R}\cos(\omega R)+(\boldsymbol{\alpha}_1\cdot\boldsymbol{\partial}_1)(\boldsymbol{\alpha}_2\cdot\boldsymbol{\partial}_2)\frac{\cos(\omega R)-1}{\omega^2 R} , \tag{3}$$

while in Lorentz gauge the following expression is obtained:

$$g_{\omega}=\frac{1-\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2}{R}\cos(\omega R) . \tag{4}$$

These two expressions define the electron-electron interaction operator in each gauge to all orders in $1/c$. The α_i's stand for the Dirac matrices of the interacting electrons, R for the electron-electron separation, and ω for the energy of the exchanged virtual photon (formulas are given in atomic units throughout this paper).

For weakly relativistic problems like the study of excited states in a heliumlike ion (i.e., when the excited electron has a velocity far from being relativistic), it seems wise to limit oneself to the first nonzero order in $1/c$. The following incomplete Breit operators are obtained:

$$g_{Ci}=g_e+g_m+g_{\mathrm{RC}} , \tag{5}$$

where

$$g_e=\frac{1}{R} , \tag{6}$$

$$g_m=-\frac{\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2}{R} , \tag{7}$$

and

$$g_{\mathrm{RC}}=\frac{\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2}{2R}-\frac{(\boldsymbol{\alpha}_1\cdot\mathbf{R})(\boldsymbol{\alpha}_2\cdot\mathbf{R})}{2R^3} \tag{8}$$

in Coulomb gauge and

$$g_{Li}=g_e+g_m+g_{\omega 2} , \tag{9}$$

where

$$g_{\omega 2}=-\frac{\omega^2}{2}R \tag{10}$$

in Lorentz gauge. In formulas (5) and (9), g_e and g_m are, respectively, the instantaneous electric and magnetic interactions; these two terms appear in Lorentz gauge as well as in Coulomb gauge. In both expressions the last term is the retardation in the electric interaction due to the finiteness of light velocity. In Eqs. (5) and (8), the subscripts in g_{RC} stand for "retardation in Coulomb gauge;" in Eqs. (9) and (10), the subscripts in $g_{\omega 2}$ recall that the photon energy is explicitly present and that we restrict ourselves to the second $1/c$ order. It has been demonstrated in paper I that even to this order the gauge dependence is present when Dirac-Fock wave functions are used to calculate the retarded interaction as a first-order perturbation.

Due to the explicit or hidden presence of the photon energy in expressions obtained for g_{ω}, $g_{\omega 2}$, $g_{\omega C}$, and g_{RC}, those expressions are only valid for matrix elements satisfying energy conservation (the S-matrix elements actually comprise a δ-function factor in the energy). The distinction between g_{ω} and $g_{\omega C}$ or between $g_{\omega 2}$ and g_{RC} are physically meaningless as far as the matrix elements for those operators are equal. It has been demonstrated in previous works (e.g., Ref. 15 and paper I) that the choice of a particular class of wave functions is determinant to satisfy gauge invariance. Effective operators in distinct gauges have equal mean values if, and only if, the used wave functions are solutions of a Dirac one-electron equation in a local potential. If the wave functions of the Dirac-Fock model are to be used, the two potentials corresponding to the two gauges lead to two distinct interaction energies. The SCF treatment of the mean contribution to the interaction (the instantaneous electrostatic repulsion between the electrons or, as well, the sum of this interaction and of the magnetic instantaneous interaction) gives a precise value for the total energy more rapidly and more elegantly than any perturbative scheme. Unfortunately, this efficacious treatment of the instantaneous interaction comes into conflict with an unambiguous treatment of the retardation. The gauge ambiguity traces back to the nature of the SCF wave function that should only be considered as a mathematical tool used to approximate the eigenstate wave function. Two questions, among others, remain open. The Dirac-Fock calculations are based on a

many-electron Hamiltonian that is deduced from QED by means of a no-pair approximation.[16] The effect of virtual electron-positron pairs (vacuum polarization) is thus neglected and the corrections to be introduced behave as higher order in $Z\alpha$. Furthermore, the relation between the no-pair approximation and the boundary conditions imposed in numerical calculations needs to be clarified. The numerical differences between the mean values of $g_{\omega 2}$ and g_{RC} are now studied in detail to show whether or not this gauge dependence is important compared with experimental precisions and with other QED contributions.

Heliumlike ions are chosen to avoid the complexity of dealing with many electrons. Having pointed out the present inability to calculate retardation correlation, the most relativistic case, that of the ground state, has to be discarded. We focus on singly excited states in ions for which experimental data are, or are becoming, available. Desclaux's code[13] is used to generate the SCF wave functions and subroutines to calculate $g_{\omega 2}$ or, as below, $g_{\omega}-(g_e+g_m+g_{\omega 2})$ mean values were implemented using standard angular moment algebra. Mean values for the gauge dependence operator $g_{\Delta j}$ whose expression is

$$g_{\Delta j}=g_{\omega 2}-g_{\mathrm{RC}}=-\frac{\omega^2 R}{2}-\frac{\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2}{2R}+\frac{(\boldsymbol{\alpha}_1\cdot\mathbf{R})(\boldsymbol{\alpha}_2\cdot\mathbf{R})}{2R^3} \quad (11)$$

are given in Tables I–V for the four $1s2p$ states and for the $1s2s\ ^3S_1$ state. The Z dependences for these states are plotted on a log-log scale in Figs. 1–5. Gauge dependence values (second column in tables and solid squares in figures) are given together with high-order retardation values to be discussed in Sec. III (third column in tables and open squares in figures). Numerical values smaller than 10 μeV are not reported. We made a test of our code by calculating $g_{\Delta j}$ mean values with purely hydrogenic wave functions. As expected in a local potential, the $g_{\Delta j}$ mean values vanish and the nonzero data reported in Tables I–V are originating only from the nature of the Dirac-Fock wave functions.

The calculated values for gauge dependence in the Dirac-Fock scheme show that this previously unmentioned effect is important compared with experimental precision at low or medium Z. For example, $\Delta n=0$ $2\ ^3P_2-2\ ^3S_1$ transition energy in heliumlike argon has been measured with a precision of 4 meV (or 32 cm^{-1}),[17] while the gauge effect value reported here is more than 2.5 meV (or 20 cm^{-1}). In Paper II, we estimated, by a phenomenological method based on the Welton picture, the importance of self-energy screening and found, for this particular example, a 9-meV (or 72-cm^{-1}) contribution.

For this gauge dependence ambiguity, a $k\alpha^5Z^2m_ec^2$ dependence is shown by Figs. 1–5 and by changing arbitrarily the value of the fine structure in the code. The second-order terms in both gauges grow approximately as Z^3; thus, the gauge ambiguity in SCF schemes has a decreasing relative importance. The values taken by the constant k or equivalently by the mean values show that this effect is semirelativistic; indeed, at low Z, the ambiguity is the same for all $1s2p$ triplet states. Besides, the considered effect clearly has a more involved behavior for $1s2p$ states having $J=1$ (Figs. 2 and 4) than for the other states (Figs. 1,3, and 5). This is related to the description of the $J=1$ states as a sum of two $j-j$ configurations [see below, Eqs. (19) and (20)] treated in intermediate coupling; it has been established that if single configurations are used ($1s_{1/2}2p_{1/2}$ $J=1$ and $1s_{1/2}2p_{3/2}$ $J=1$) the monotonic variation and the quadratic scaling law encountered for the other states are restored.

Lastly, this gauge ambiguity is not shaded off in multiconfiguration Dirac-Fock (MCDF) calculations. Discarding the questions associated with a sensible definition of one-electron energy, one might be tempted to associate the gauge difficulties with the approxima-

TABLE I. Mean values for $g_{\Delta j}$ (gauge dependence) and $g_{\omega 4}$ (high-order retardation) operators for the $1s2p\ ^3P_0$ state in heliumlike ions. Dirac-Fock wave functions are used and values are given in meV.

Z	Gauge dependence	High-order retardation
6	−0.33	
10	−1.00	
18	−3.46	−0.16
26	−7.36	−1.05
36	−14.3	−5.07
54	−32.2	−28.5
92	−89.7	+349

TABLE II. Mean values for $g_{\Delta j}$ (gauge dependence) and $g_{\omega 4}$ (high-order retardation) operators for the $1s2p\ ^3P_1$ state in heliumlike ions. Two-configuration Dirac-Fock wave functions are used and values are given in meV.

Z	Gauge dependence	High-order retardation
6	−0.33	
10	−1.00	−0.04
18	−3.31	−0.83
26	−5.56	−4.43
36	−6.06	−14.0
54	−4.73	−42.4
92	−2.03	+29.3

TABLE III. Mean values for $g_{\Delta j}$ (gauge dependence) and $g_{\omega 4}$ (high-order retardation) operators for the $1s2p\ ^3P_2$ state in heliumlike ions. Dirac-Fock wave functions are used and values are given in meV.

Z	Gauge dependence	High-order retardation
6	−0.33	
10	−1.00	−0.09
18	−3.46	−1.87
26	−7.39	−12.1
36	−14.3	−63.0
54	−32.9	−486
92	−97.2	−7049

TABLE IV. Mean values for $g_{\Delta j}$ (gauge dependence) and $g_{\omega 4}$ (high-order retardation) operators for the $1s2p\ ^1P_1$ state in heliumlike ions. Two-configuration Dirac-Fock wave functions are used and values are given in meV.

Z	Gauge dependence	High-order retardation
6	0.33	
10	1.00	0.07
18	3.53	1.47
26	7.21	8.67
36	12.4	36.6
54	23.8	225
92	60.8	2998

tions made in the wave-function determination and think that a "better" wave function would reduce the ambiguity. This is not true, as is demonstrated by calculating retarded interaction elements with an extended sum of determinants (the half sum rule derived by Mittleman[18,19] was adopted for off-shell elements). For the $1s2p\ ^3P_2$ state in heliumlike aluminium ($Z=13$) the single-configuration Dirac-Fock calculation leads to a 1.8-meV ambiguity and the multiconfiguration calculation (on the same extended basis set as in paper I, Secs. III and IV) leads to a 3.9-meV ambiguity. Far from correcting for these gauge difficulties, the MCDF treatment worsens them. The gauge ambiguity is unavoidable in any SCF scheme (and in any scheme for which no one-electron energy is clearly defined).

A complete relativistic calculation in Coulomb gauge will have to be performed in the future to give more reliable data for heavy ions but it has been demonstrated that the gauge ambiguity is still present for the whole v/c series and it is expected that the present results are giving the main contribution to this effect in the studied Z range. From the given examples, the gauge ambiguity is seen to be nonnegligible compared both to experimental precision and to theoretical uncertainties in the calculation of the two-electron Lamb shift. Thus extracting information on the screening of QED corrections from experimental data demands a clarification of this gauge dilemma.

TABLE V. Mean values for $g_{\Delta j}$ (gauge dependence) and $g_{\omega 4}$ (high-order retardation) operators for the $1s2s\ ^3S_1$ state in heliumlike ions. Dirac-Fock wave functions are used and values are given in meV.

Z	Gauge dependence	High-order retardation
6	−0.08	
10	−0.24	
18	−0.83	0.06
26	−1.80	0.41
36	−3.57	2.16
54	−8.66	16.50
92	−32.70	217.10

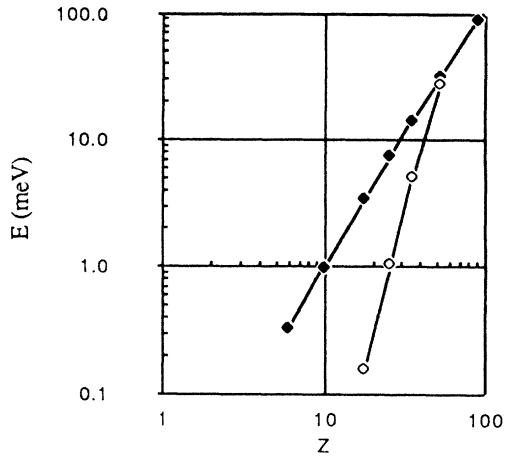

FIG. 1. $g_{\Delta j}$ gauge dependence (solid squares) and $g_{\omega 4}$ high-order retardation (open squares) operator mean value Z dependence for the $1s2p\ ^3P_0$ energy level in Dirac-Fock calculations.

III. RETARDATION TO ALL v/c ORDERS IN TWO-ELECTRON SYSTEMS

In Sec. II, the semirelativistic (or incomplete) electron-electron interaction has been studied in two different gauges. This approach is, as will soon appear, limited to elements lighter than iron ($Z=26$). Indeed, for heavier systems the complete operators $g_{\omega C}$ and g_{ω} [Eqs. (3) and (4)] have to be used instead of their incomplete counterparts g_{Ci} and g_{Li} [Eqs. (5) and (9)]. The calculation of retarded interaction is then made to all orders in $1/c$ (i.e., to all orders in the exchanged photon energy). The numerical importance of high-order retardation, in Lorentz gauge, is demonstrated by calculating

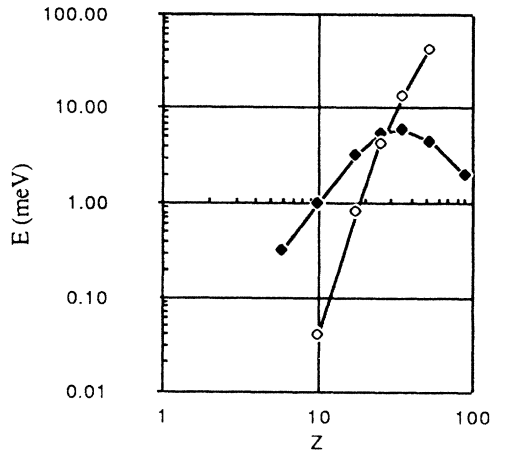

FIG. 2. $g_{\Delta j}$ gauge dependence (solid squares) and $g_{\omega 4}$ high-order retardation (open squares) operator mean value Z dependence for the $1s2p\ ^3P_1$ energy level in two-configuration Dirac-Fock calculations.

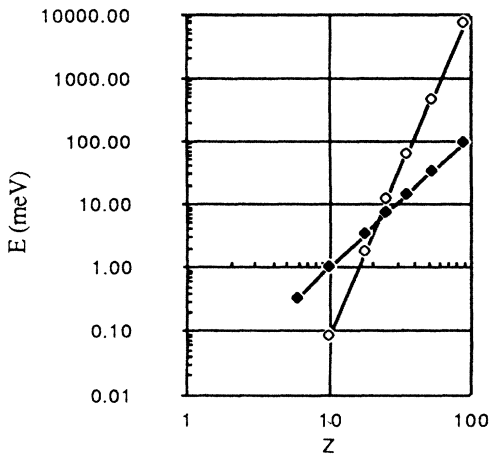

FIG. 3. $g_{\Delta j}$ gauge dependence (solid squares) and $g_{\omega 4}$ high-order retardation (open squares) operator mean value Z dependence for the $1s2p\ ^3P_2$ energy level in Dirac-Fock calculations.

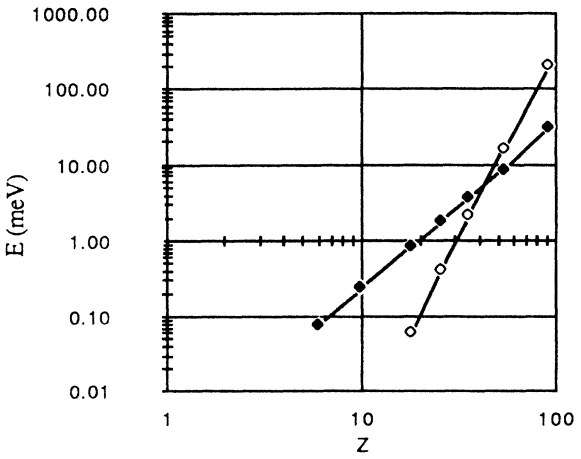

FIG. 5. $g_{\Delta j}$ gauge dependence (solid squares) and $g_{\omega 4}$ high-order retardation (open squares) operator mean value Z dependence for the $1s2s\ ^3S_1$ energy level in Dirac-Fock calculations.

mean values of the following operator:

$$g_{\omega 4}=g_{\omega}-(g_e+g_m+g_{\omega 2})$$
$$=\frac{1}{R}\left[\cos(\omega R)-1+\frac{\omega^2R^2}{2}\right]-\frac{\alpha_1\cdot\alpha_2}{R}[\cos(\omega R)-1]\ . \tag{12}$$

Magnetic retardation (last term in the preceding expression) is described by this operator while it was neglected by means of incomplete operators. As in Sec. II, mean values have been calculated for several heliumlike ions using Dirac-Fock wave functions. Results are reported in Tables I–V (third column) and the Z dependence is plotted on a log-log scale in Figs. 1–5 (open squares). Compared with gauge dependence, this relativistic effect is seen to grow much more rapidly. For medium Z, its energy contribution is found to be well fitted by a $k\alpha^6Z^5m_ec^2$ scaling law. This scaling law has already been quoted and interpreted in terms of fourth-order leading terms by Hata and Grant.[15] In this work, calculations were performed in Coulomb gauge and the gauge dependence in SCF schemes was not discussed (as in earlier works like the study of $1s$ binding energy for heavy atoms.[20] Calculations to all orders in Lorentz gauge are done for the first time in the present paper.

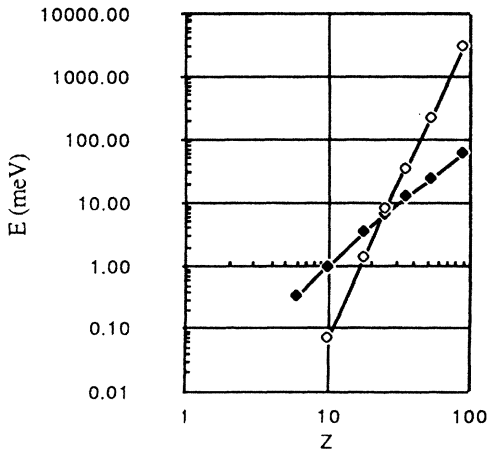

FIG. 4. $g_{\Delta j}$ gauge dependence (solid squares) and $g_{\omega 4}$ high-order retardation (open squares) operator mean value Z dependence for the $1s2p\ ^1P_1$ energy level in two-configuration Dirac-Fock calculations.

Hata and Grant[15] have considered elements lighter than molybdenum ($Z=42$) and the Z^5 scaling law is then valid. For heavier elements, Figs. 1–5 show that higher-order terms become important and that no scaling law fits to the data. In the case of $1s2p\ J=1$ states, the Z dependence is strongly distorted by the superposition of two different effects, the studied relativistic retardation and the intermediate coupling effect. If calculations are performed on a pure j-j single configuration, results are similar to those obtained for $1s2p\ J=0$ or $J=2$. Besides, we have verified that for heavy elements, numerical results for $g_{\omega 4}$ mean values are nearly equal whether Dirac-Fock or hydrogenic wave functions are used.

As for the gauge dependence, values for the three $1s2p$ triplet states are roughly equal in the low-Z range. When Z increases, high orders become more and more important so that states with different J act very differently (in the $1s2p\ J=0$ case there occurs a change in sign for high Z; for that reason the gauge dependence is not plotted for elements heavier than xenon in Fig. 1).

It is clear from Tables I–V that relativistic effects are quite different on various states due to different magnetic properties. The state on which this effect is the most important is the $1s2p\ ^3P_2$ state (Table III and Fig. 3). Relativistic high-order effects in the retarded interaction have to be looked for in transitions involving this state. The 7-eV $g_{\omega 4}$ mean value for uranium is striking because of the availability of this ion and the experimental precision that is anticipated. A high-Z experiment to mea-

sure the $\Delta n=0$ $2\,^3P_2-2\,^3S_1$ transition in krypton has been performed by Martin *et al.*[1] with a precision of 20 meV, while the $g_{\omega 4}$ mean values give a -65-meV contribution to the energy. The self-energy screenings have an estimated contribution of 47 meV to the considered transition energy (Paper II, Table VI) and this comparison shows that both effects have to be considered to get information on the many-electron self-energy problem from experiments. Further comparisons between experimental precision, Lamb shift screening, gauge ambiguity, and relativistic retardation and comparisons between the scaling laws for these contributions to the energy show qualitatively the following.

(a) For semirelativistic systems (lighter than argon ion) high-order retardation is negligible compared to gauge ambiguity; this term is then small compared to the self-energy screening.

(b) For ions ranging from argon to krypton the three quoted effects have the same order of magnitude.

(c) For heavy ions (like xenon or uranium ions) the relativistic high-order retardation (scaling as Z^5) dominates over the self-energy screening (scaling as Z^3).

In paper II and in Ref. 21, a detailed analysis of the different contributions to transition energies is given for various ions. The interested reader is referred to these articles for more quantitative information.

Lastly, we would like to clarify the notation used in papers I and II. We used the expression "higher order" in the tables to designate the mean values of $g_{\omega 4}+g_{\Delta j}$. This terminology is seen from the above discussion to be misleading for light elements because, at low Z, gauge dependence (or, more precisely, changing from Coulomb to Lorentz gauge in second order) dominates high-order terms.

IV. RETARDATION TERMS AND OFF-SHELL MATRIX ELEMENTS

In this section, the treatment of the retarded electron-electron interaction is discussed in the case of the complex states for which the multiconfiguration scheme has to be used. In two-electron systems, the prototype of such states is given by the two singly excited $1s2p$ states having $J=1$. For those states the intermediate coupling is handled by considering a linear combination of $1s_{1/2}2p_{1/2}$ and $1s_{1/2}2p_{3/2}$ states. While introducing retarded interaction, one has to compute an off-shell energy matrix element (owing to the relativistic energy separation between $2p_{1/2}$ and $2p_{3/2}$ states). A generalization of the Breit operator has been introduced by Mittleman.[18,19] This generalized Breit operator has, as already briefly mentioned,[22] the flaw that it is intrinsically gauge dependent. This point needs to be somehow clarified. It can be demonstrated that even on a hydrogenic basis set the mean values of the retarded interaction are different when two different gauges are used. The same result holds true whatever local potential is used.

When applied to single-configuration states, the gauge dependence discussed in paper I and in Sec. II was only a consequence of the mean-field approximation used to determine the wave functions. In the MCDF scheme[7,13] this type of gauge dependence is, of course, still present and is far more important numerically (see below) but, from a theoretical point of view, the gauge dependence arising from the operator itself shows that the treatment of retardation is lacking consistency for states as common as $1s2p$ triplet and singlet P_1 states in heliumlike ions. Perturbative schemes on an extended basis set are also subject to this gauge ambiguity and, to our knowledge, this fact has never been clearly mentioned.

In Sec. II, the on-shell S-matrix elements were used to derive an effective interaction potential. This potential reproduces the scattering amplitude from state $|AB\rangle$ to state $|CD\rangle$ to first order in α (paper I, Sec. II) when the energy is conserved. This deduction demands that the exchanged photon energy satisfies

$$\omega=\omega_{AC}=\alpha\,|\,\epsilon_A-\epsilon_C\,|=\omega_{BD}=\alpha\,|\,\epsilon_B-\epsilon_D\,|\ . \tag{13}$$

This condition restricts our ability to determine interaction matrix elements to the direct and thereby retardless case for which $C=A$ and $B=D$, or to the exchanged case in which $C=B$ and $A=D$. Thus the matrix element between $1s_{1/2}2p_{1/2}$ $J=1$ and $1s_{1/2}2p_{3/2}$ $J=1$ states is not manageable due to the fine-structure splitting between $2p_{1/2}$ and $2p_{3/2}$. Generally speaking, to perform any nonperturbative calculation or any perturbative calculation on an extended basis, one has to consider off-shell matrix elements. To handle those elements Mittleman introduced the generalized Breit operator

$$g'=\tfrac{1}{2}[g(\omega_{AC})+g(\omega_{BD})]\ , \tag{14}$$

in which $g(\omega_{AC})$ stands for the operators given in (3) and (8), or in (4) and (10), depending on the gauge. These operators semirelativistic or fully relativistic) have been used in published calculations (for example, Ref. 15, 23, 24, and paper II) regardless of their known intrinsic gauge ambiguity.[22] Our purpose is to clarify the status of this gauge ambiguity. Mean values for the operator that corresponds to the difference between the two gauges are given. An important consequence of the gauge dependence is made more explicit: the well-known classical retardation operator (8) is definitely restricted to the Coulomb gauge. This fact seems to have been ignored in the past. Even for purely hydrogenic wave functions the off-shell matrix elements of this g_{RC} operator are distinct from those of its Lorentz gauge counterpart $g_{\omega 2}$.

To get an expression for the difference between operators in the two gauges, the usual double commutator transformation has to be performed to change factors including photon frequencies ω_{AC} and ω_{CD} in Lorentz gauge formulas into gradient factors in Coulomb gauge formulas (see paper I, Sec. II). Starting from a general matrix element for the retardation in Lorentz gauge

$$\begin{aligned}\Gamma=\int d1\,d2\,&\overline{\Phi_A(1)}\,\overline{\Phi_B(2)}\\ &\times\tfrac{1}{2}[\omega_{AC}^2F_{\alpha AC}(1,2)+\omega_{BD}^2F_{\alpha BD}(1,2)]\\ &\times\Phi_C(1)\Phi_D(2)\ ,\end{aligned} \tag{15}$$

in which 1 and 2 are the electron locations and

$$F_{\alpha AC}(1,2)=\frac{\cos(\omega_{AC}R)-1}{\omega_{AC}^2 R} , \tag{16}$$

one is willing to recover the retardation in Coulomb gauge. For semirelativistic systems, the same reasoning to second order in $1/c$, one has to consider the matrix element obtained from (15) by replacing F_α by F_β with

$$F_{\beta AC}(1,2)=-\tfrac{1}{2}R . \tag{17}$$

Using (13), the matrix element Γ in (15) is found to be half the mean value of the sum

$$[h_1,[h_1,F_\alpha]]+[h_2,[h_2,F_\alpha]] . \tag{18}$$

A tedious calculation demonstrates that this last expression has distinct mean values as the $2[h_1,[h_2,F_\alpha]]$ operator required to satisfy gauge independence whatever basis set is used for the wave functions. The retarded interaction energy is found to be gauge dependent. This result holds true either for the full series or for the second-order term. This ambiguity is not related to the nature of the wave functions; its origin is more fundamental than that of previously discussed gauge ambiguity due to the SCF scheme used to obtain the wave functions.

To determine what the importance of this effect is for heliumlike ions, we carried out calculations of second-order retardation in both gauges on the example of $1s2p$ $J=1$ states. The two levels are described by linear combinations

$$|2\,^3P_1\rangle=c_1\,|1s_{1/2}2p_{1/2}\rangle+c_2\,|1s_{1/2}2p_{3/2}\rangle , \tag{19}$$

$$|2\,^1P_1\rangle=c_2\,|1s_{1/2}2p_{1/2}\rangle-c_1\,|1s_{1/2}2p_{3/2}\rangle , \tag{20}$$

where the coefficients are obtained by diagonalization of the Dirac-Coulomb Hamiltonian

$$H=h_{D1}+h_{D2}+g_e \tag{21}$$

on the purely one-electron hydrogenic wave-function basis set. The retarded interaction energy is then treated as a perturbation on these states. The numerical results for the singlet state of several heavy ions are given in Table VI (for triplet states, results are exactly the opposite). Values lower than 10 μeV are discarded so that the lightest ions in the table have Z equal to 50. Comparing the values in Table VI to those in Table IV shows that this gauge ambiguity is much smaller than the one discussed in Sec. II. More precisely from data in Table VI, this gauge dependence is found to behave as $2.58Z^4$ peV. For heavy ions, this effect is negligible compared to other sources of uncertainties and also to the expected experimental precision; for example, the second-order retardation energy in the uranium $2\,^1P_1$ state differs by only 60 meV according to the gauge. The smallness of this effect in the problem under study is of course related to the smallness of the fine-structure splitting but in perturbative calculations on an extended basis set the discrepancy between the two gauges might be strongly enhanced by the importance of the energy nonconservation involved in calculated matrix elements. This question will have to be studied in the future.

TABLE VI. Mean values for $g_{\Delta j}$ (gauge dependence) operator for the $1s2p\ ^1P_1$ state. Hydrogenic wave functions are used and values are given in μeV.

Z	Gauge dependence (μeV)
50	15.9
55	23.5
60	33.5
65	46.4
70	62.4
75	82.2
80	106.4
85	134.6
90	167.9

V. CONCLUSIONS

We hope that the results given in the present paper, though incomplete, will throw some light on the difficulties one is faced with when judiciously handling the complete Breit operator. Let us recall that difficulties are encountered as soon as noninstantaneous interactions are involved. New theoretical methods will have to be developed if such phenomena as retardation correlation are to be included in atomic structure calculations. We also hope that numerical data concerning high-order retardation effects, reported here, will encourage further experimental investigations in the highly relativistic region.

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