Gauge dependence in relativistic calculations of the correlation energy of helium-like atoms

V. G. Pal'chikov

State Enterprise "All-Russian Scientific-Research Institute for Physical-Mechanical and Electronic Measurements, 141570 Mendeleevo, Moscow Region, Russia

G. von Oppen

Technical University, D-10623 Berlin, Germany.

(Submitted 8 February 1996)
Zh. Éksp. Teor. Fiz. **110**, 1608–1615 (November 1996)

A quantum electrodynamic perturbation theory is developed for two-electron systems in which the interaction between bound electrons is treated as a first order perturbation. The effects of the gauge dependence in calculations of terms in the $1s3l$-configuration of helium-like atoms are discussed for the first time based on the principles of quantum electrodynamics. It is shown that the relativistic Breit operator in the Coulomb and Feynman gauges yields identical results for the diagonal matrix elements in a local potential, but different values for the nondiagonal matrix elements. Numerical estimates are presented and a physical interpretation is given for the nondiagonal matrix elements. © *1996 American Institute of Physics.* [S1063-7761(96)00511-2]

1. INTRODUCTION

Progress in increasing the accuracy of spectral measurements of helium-like atoms has become a steady trend over the last few years.[1,2] Thus, measurements of the frequency of the $2^3S_1-3^3P_0$ transition of neutral helium ^{4}He with an accuracy of 2.4×10^{10} have recently been reported[1] which make it possible, on one hand, to verify quantum electrodynamical calculations for helium-like atoms and, on the other, to make independent estimates of a number of physical constants, such as the fine structure constant α and the root-mean-square nuclear radii of the isotopes ^{4}He and ^{3}He. The possibility of measuring the fine structure intervals of helium for terms in the $1s3l$-configuration with an accuracy of 1 MHz has been considered[3] (laser cooling of atomic beams makes it possible to lower this value by roughly an order of magnitude) and this makes it possible, in principle, to investigate the previously unstudied spin–spin mixing effect for helium states with different orbital angular momenta of the same parity. For helium-like atoms with high nuclear charges Z (multiply charged ions), the contribution of the radiative corrections becomes comparable in order of magnitude to the fine structure intervals and an adequate description of the currently observed spectra of multiply charged ions[2] must include the combined correlation, relativistic, and quantum electrodynamical effects.

Thus, a rigorous theory of the spectra of helium-like atoms must account for higher-order effects, since their contribution to the observed spectral characteristics becomes an extremely important element in the analysis of precision observations. One such effect is the gauge dependence in relativistic calculations of the spectra of atoms and ions,[4] since, in a number of cases, its effect is comparable to the error in contemporary measurements of the fine-structure intervals in helium-like ions.[5] It is interesting to note in this regard, that the amplitude of the effect depends on the choice of basic computational scheme in a relativistic atomic theory, i.e., of quantum electrodynamical methods and methods based on the relativistic self-consistent field equations, and their refinements which take many-particle effects into account.[4]

The goal of this paper is a theoretical and numerical analysis of the gauge dependence in quantum electrodynamical calculations of the correlation energy of helium-like atoms for all terms of the $1s3l$-configuration, taking into account the spatial-spin symmetry of the vector model of the atom in a jj-coupling scheme for the angular momenta.

2. MATRIX ELEMENTS OF THE BREIT OPERATOR AND THEIR DEPENDENCE ON THE CHOICE OF GAUGE FOR THE PHOTON PROPAGATOR

The field theory methods applied to helium-like ions are generalizations of the quantum-electrodynamical approach to systems with a discrete spectrum and are based on an analysis of Feynman graphs for a bound electron corresponding to the lowest-order terms in the expansion of the S-matrix.

In the evolution-operator formalism the change $\Delta\varepsilon_n$ in the energy of an isolated nondegenerate state $|n\rangle$ is given by

$$\Delta\varepsilon_n=i\frac{\partial}{\partial t}\ln\langle n|U(t,t_0)|n\rangle, \tag{1}$$

where $U_0(t,t_0)$ is the evolution operator, which is introduced as the time displacement operator, i.e., $t\rangle=U(t,t_0)|t_0\rangle$, and allows us to obtain the state vector $|t\rangle$ at time t from a known state vector $|t_0\rangle$ at the initial time t_0. The limiting transition $\tau=t-t_0\infty$ is taken in the final state of the calculations. In calculating the correlation energy it is convenient to represent $U(t,t_0)$ in the form

$$U(t,t_0)=T_\psi\exp\left[-\frac{\alpha}{2}\int d^4x_1d^4x_2j^\mu(x_1)D(x_1,x_2)j_\mu(x_2)\right], \tag{2}$$

where T_ψ is the Wick chronological operator, which acts only on the operators of the electron-positron field, $j^\mu=(1/2)[\bar{\psi}\gamma^\mu,\psi]$ is the 4-current, $[a,b]$ is the commutator of operators a and b, and α is the fine structure constant. The photon Green's function $D(x_1,x_2)$ satisfies the equation

$$\langle\text{vac}|T\{A_\mu(x_1)A_\nu(x_2)\}|\text{vac}\rangle=D(x_1-x_2)g_{\mu\nu}, \tag{3}$$

where $|\text{vac}\rangle$ is the vacuum state, $g_{\mu\nu}$ is the metric tensor,[7] and $A_\mu(x)$ is the potential of the electromagnetic field. The function $D(x_1,x_2)$ defined in Eq. (3) depends only on the difference $x_1-x_2\equiv x$ of the 4-coordinates and has the form

$$D(x_1-x_2)=\frac{ic}{4\pi^3}\int\frac{d^4k\,\exp(-ikx)}{k^2+i0}$$
$$=\frac{ic}{4\pi^3}\int\frac{\exp(i\mathbf{k}\cdot\mathbf{r}-i\omega t)}{w^2/c^2-k^2+i0}d\omega\,dk, \tag{4}$$

where $k^\mu\equiv(\omega/c,\mathbf{k})$ and c is the speed of light in vacuum. Carrying out the integral with respect to $\mathbf{k}$ in Eq. (4), we obtain the following one-dimensional integral for $D(x)$

$$D(x)=-\frac{i}{2\pi r_{12}}\int\exp\left(-i\omega t+\frac{i|\omega|r_{12}}{c}\right)d\omega. \tag{5}$$

This last expression is convenient for use in analyzing the effect of the interelectronic interaction, since it can be used to go directly to the limit $c\rightarrow\infty$ corresponding to turning off the retardation effect. Equation (5) has been written in the Feynman gauge for the electromagnetic potentials. By changing the gauge, we can represent the right-hand side of Eq. (5) in the following form:

$$D(x_1-x_2)g_{\mu\nu}\leftrightarrow(g_{\mu\nu}+\lambda\partial_\mu\partial_\nu\Box^{-2})D(x_1-x_2), \tag{6}$$

where λ is an arbitrary parameter. In particular, $\lambda=-1$ corresponds to the transverse gauge (Landau gauge), while, for example, $\lambda=2$ corresponds to the Fried–Yennie gauge which has been in active use in recent years for calculating radiative corrections.[8] For carrying out relativistic calculations in a Coulomb gauge it is convenient to isolate the part $D^C(x)$ of the function $D(x)$ corresponding to the purely Coulomb interaction,

$$D^C(x)=-\frac{i}{r_{12}}\delta_{\mu,0}\delta_{\nu,0}\delta(t), \tag{7}$$

and the part $D^t_{lm}(x)$ (l and m are indices running from 0 to 3) corresponding to a transverse photon. The explicit expression for $D^t_{lm}(x)$ has the form[6]

$$D^t_{lm}(x)=g_{\mu\nu}D(x)-\int\nabla_{1l}\nabla_{2m}F(x,\omega)\frac{d\omega}{\omega^2}, \tag{8}$$

where $D(x)$ is defined above by Eq. (5), ∇_l denotes the lth component of the gradient, and the function $F(x,\omega)$ is given by

$$F(x,\omega)=-\frac{i\alpha}{2\pi r_{12}}\exp(i\omega t)\left[\exp\left(i\frac{|\omega|r_{12}}{c}\right)-1\right]. \tag{9}$$

The correction to the Coulomb interaction for the electrons, $V_C=1/r_{12}$, owing to exchange of a transverse photon, is usually referred to as the Breit interaction V_B. Using Eqs. (2) and (8) it is easy to show that V_B in the Coulomb gauge is given by the operator

$$V^C_B=-\frac{\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2\cos(\omega r_{12}/c)}{r_{12}}+(\boldsymbol{\alpha}_1\cdot\nabla_{r_{12}})$$
$$\times(\boldsymbol{\alpha}_2\cdot\nabla_{r_{12}})\frac{\cos(\omega r_{12}/c)-1}{\omega^2 r_{12}c^2}. \tag{10}$$

Here $\boldsymbol{\alpha}$ is the Dirac matrix.[7] In Eq. (10) the imaginary part corresponding to the contribution to the radiative width of the level has been omitted. As Eq. (10) implies, the operator V^C_B depends explicitly on the rate of exchange for transverse photons of frequency ω. The expression for V_B in the Feynman gauge has the form

$$V^F_B=\frac{1}{r_{12}}\left[\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2\cos\frac{\omega r_{12}}{c}+(1-r_{12})\cos\frac{\omega r_{12}}{c}\right]. \tag{11}$$

Despite the rather substantial external difference between these two representations for V_B, their use in relativistic calculations leads to identical results when basis wave functions which are solutions of the Dirac equation with a local potential are employed. This situation arises, for example, when perturbation theory in the parameter $1/Z$ is used (i.e., when the electron-electron interaction is small compared to the electron-nuclear interaction) or in the case where a local approach is applied to the electron-electron interactions in self-consistent field methods (the Dirac–Hartree–Fock–Slater method). In this case the equivalence of the representations (10) and (11) follows from the properties of the commutation relation

$$\left[H_1,\left[H_2,\frac{\exp(i\omega r_{12}/c)-1}{\omega^2 r_{12}}\right]\right], \tag{12}$$

used to write the second term in Eq. (10). In Eq. (12) H_i is the one-particle Dirac hamiltonian:

$$H_i=c\boldsymbol{\alpha}\cdot\mathbf{p}+\beta c^2-Z/r_i, \tag{13}$$

where $\mathbf{p}$ is the particle momentum. Using the formula for a double commutator containing an arbitrary function $s(r_{12})$,

$$[H_1,[H_2,s(r_{12})]]$$
$$=-(\boldsymbol{\alpha}_1\cdot\nabla_1)(\boldsymbol{\alpha}_2\cdot\nabla_2)s(r_{12})=\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2\frac{\partial}{\partial r_{12}}\frac{s(r_{12})}{r_{12}}$$
$$+\frac{(\boldsymbol{\alpha}_1\cdot\mathbf{r}_{12})(\boldsymbol{\alpha}_2\cdot\mathbf{r}_{12})}{r^3_{12}}\left[\frac{\partial^2}{\partial r^2_{12}}s(r_{12})-\frac{\partial}{\partial r_{12}}\frac{s(r_{12})}{r_{12}}\right]. \tag{14}$$

and applying it to Eq. (12), we obtain the following result:

$$-\frac{\exp(i\omega r_{12}/c)-1}{r_{12}} \tag{15}$$

Thus, Eqs. (10) and (11) are completely identical (in all orders with respect to the retardation parameter $i\omega r_{12}/c$).

When the basis functions are used with a nonlocal potential (e.g., in self-consistent field methods), the commutation relation (12) ceases to be valid and a gauge dependence begins to show up, even in the lowest orders of the expansions (10) and (11) in the retardation parameter $i\omega r_{12}/c$:

$$\Delta V_B = V_B^F - V_B^C = -\frac{\omega^2 r_{12}}{2} - \frac{\boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2}{2 r_{12}} + \frac{(\boldsymbol{\alpha}_1 \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}_2 \cdot \mathbf{r}_{12})}{2 r_{12}^3}. \tag{16}$$

For example, it has been shown[4] that the average value for ΔV_B (20 cm^{-1}) is of the same order of magnitude as the error in the measurement of the energy of the $2^3P_2 - 2^3S_1$-transition for helium-like argon (32 cm^{-1}). Note that when the wave functions are used with a local potential, applying Eq. (12) to the first term of Eq. (16) again yields $\Delta V_B = 0$.

A gauge dependence also appears in relativistic calculations of the nondiagonal matrix elements in the case where an intermediate scheme for coupling of the angular momenta is used to determine the state vector of an atom. For helium-like systems the simplest prototypes of these states are the two singly excited $1s2p$-states with total angular momentum $J=1$, since in the intermediate coupling scheme these states are written in terms of linear combinations of the $1s_{1/2}2p_{1/2}$ and $1s_{1/2}2p_{3/2}$ states. The energies of the $2p_{1/2}$ and $2p_{3/2}$ one-particle states are separated by the fine structure interval. Thus, the Breit operator in the forms (10) and (11) evidently cannot be used in relativistic calculations of the nondiagonal matrix elements since, according to Eq. (2), conservation of energy must hold for arbitrary initial and final states after integrating with respect to the time variable in Eq. (2). In order to eliminate this contradiction, a gauge dependent generalized Breit operator

$$\tilde{V}_B = \frac{1}{2}[V_B(\omega_{AC}) + V_B(\omega_{BD})], \tag{17}$$

has been introduced,[9] which corresponds to the scattering amplitude between arbitrary initial $|AB\rangle$ and final $|CD\rangle$ one-particle states in the two representations:

$$M^F_{CD,AB} = \langle CD | \frac{(1 - \boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2)}{r_{12}} G(r_{12}) | AB \rangle, \tag{18}$$

and

$$M^C_{CD,AB} = \langle CD | \frac{F(r_{12}) - \boldsymbol{\alpha}_1 \cdot \boldsymbol{\alpha}_2 G(r_{12})}{r_{12}} | AB \rangle. \tag{19}$$

The functions F and G are given in Ref. 10. By using the explicit forms of these functions, it is easy to show that for the diagonal matrix elements with a local potential, Eqs. (18) and (19) transform identically into one another, but that for the nondiagonal matrix elements, Eqs. (18) and (19) are no longer identical because of Eq. (16).

3. RESULTS AND DISCUSSION

In this section we present results of numerical calculations for the nondiagonal matrix elements corresponding to singlet–triplet mixing of the $1s3p\,^{1,3}P$ and $1s3d\,^{1,3}D$ states:

$$|E_1\rangle = \cos\frac{\theta}{2} |1s3l\,^3L_j\rangle + \sin\frac{\theta}{2} |1s3l\,^1L_j\rangle, \tag{20}$$

and

$$|E_2\rangle = -\sin\frac{\theta}{2} |1s3l\,^3L_j\rangle + \cos\frac{\theta}{2} |1s3l\,^1L_j\rangle. \tag{21}$$

TABLE I. Gauge dependence of the nondiagonal matrix elements.

Z	$Q^F(\alpha Z) - Q^C(\alpha Z)$	$P^F(\alpha Z) - P^C(\alpha Z)$
2	$0.52041 \cdot 10^{-17}$	$0.22889 \cdot 10^{-19}$
10	$0.83042 \cdot 10^{-13}$	$0.36621 \cdot 10^{-15}$
20	$0.52367 \cdot 10^{-11}$	$0.24643 \cdot 10^{-13}$
30	$0.58125 \cdot 10^{-10}$	$0.29979 \cdot 10^{-12}$
40	$0.31407 \cdot 10^{-9}$	$0.17912 \cdot 10^{-11}$
50	$0.11332 \cdot 10^{-8}$	$0.70964 \cdot 10^{-11}$
60	$0.31296 \cdot 10^{-8}$	$0.21102 \cdot 10^{-10}$
70	$0.70665 \cdot 10^{-8}$	$0.49802 \cdot 10^{-10}$
80	$0.13397 \cdot 10^{-7}$	$0.94893 \cdot 10^{-10}$
90	$0.21088 \cdot 10^{-7}$	$0.14264 \cdot 10^{-9}$
100	$0.25037 \cdot 10^{-7}$	$0.15055 \cdot 10^{-9}$

Here the E_λ ($\lambda = 1,2$) are the eigenvectors of the Hamiltonian of the atom and θ is the singlet-triplet mixing angle.[6,11] The nondiagonal matrix elements owing to the spin–spin interaction between the $1s3s\,^3S_1$ and $1s3d\,^3D_1$ states have been examined in detail in a recent paper.[11]

For the relativistic calculations of the nondiagonal matrix elements (18) and (19) we have used the basis Dirac wave functions in a j-j-coupling scheme for the angular momenta. The details of the calculations of the angular and radial integrals have been described elsewhere[11] and are omitted here for brevity. We note only that the use of analytic methods for calculating the radial integrals[11] makes it possible, in principle, to calculate the matrix elements (18) and (19) with arbitrary accuracy. The results of the calculations for the nondiagonal matrix elements are shown in Table I, which lists the differences of the functions $Q(\alpha Z)$ and $P(\alpha Z)$ (in the Coulomb and Feynman gauges). These functions determine the relativistic correlation energy to first in the interelectronic interaction according to the formulas[1)]

$$M^F_{3^3P_1 - 3^1P_1} = Z Q(\alpha Z), \tag{22}$$

and

$$M^C_{3^3D_2 - 3^1D_2} = Z P(\alpha Z). \tag{23}$$

The functions $Q(\alpha Z)$ and $P(\alpha Z)$ are dimensionless and can be written in the form of expansions in powers of the relativistic parameter $(\alpha Z)^2$

$$Q(\alpha Z) = q^{(0)} + q^{(2)}(\alpha Z)^2 + q^{(4)}(\alpha Z)^4 + \dots, \tag{24}$$

and

$$P(\alpha Z) = p^{(0)} + p^{(2)}(\alpha Z)^2 + p^{(4)}(\alpha Z)^4 + \dots \tag{25}$$

An analysis of the numerical data obtained in this paper yields the following conclusions:

1. In relativistic calculations of the correlation energy of helium-like atoms there is a first order dependence of the correlation energy on the choice of gauge for the Breit operator used to account for the electron–electron interaction effects. The contribution of the gauge dependence for the $3^3P_1 - 3^1P_1$ transition is 1.5×10^{-8} and $8 \times 10^{-6}\%$, respectively, for $Z=30$ and $Z=100$ (Fig. 1 and Table I). For the $3^3D_2 - 3^1D_2$ transition this contribution is 1.6×10^{-9} and $4 \times 10^{-7}\%$, respectively. For $Z>20$ the difference

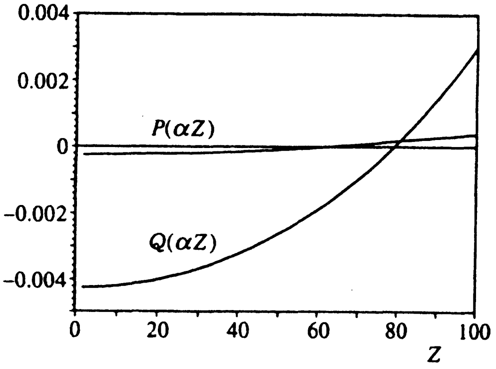

FIG. 1. The functions $Q(\alpha Z)$ and $P(\alpha Z)$ as functions of nuclear charge Z.

$Y_i = M_i^F - M_i^C$ of the amplitudes (18) and (19) is approximated, to fairly high accuracy, by the following simple formulas:

$$Y_{3^3P_1-3^1P_1} = Z^{5.548} \times 3.424 \times 10^{-19},$$

$$Y_{3^3D_2-3^1D_2} = Z^{5.723} \times 1.040 \times 10^{-21}.$$

2. The nondiagonal matrix elements, which contain the generalized Breit operator, depend on the nuclear charge Z and change sign at $Z>70$ for the $3^3P_1-3^1P_1$ transition and at $Z>60$ for the $3^3D_2-3^1D_2$ transition (see Fig. 1). The sign change is caused by a contribution from the retardation effect and by higher-order relativistic effects which are important for high nuclear charges Z.

3. The expansion coefficients in Eqs. (24) and (25) calculated with a Coulomb gauge are shown in Table II. The effects of the gauge dependence begin to show up only in coefficients of sixth and higher orders and, as an example, for the 3^3P-3^1P transition the differences in the values of $q^{(6)}$ and $q^{(8)}$ are equal to 0.55297×10^{-6} and $-0.56201 \cdot 10^{-5}$, respectively (for the coefficients $p^{(6)}$ and $p^{(8)}$ similar calculations yield 0.23165×10^{-8} and -0.41291×10^{-8}). These results are consistent with estimates[4] for singlet-triplet mixing of the 2^1P_1 and 2^3P_1 states of helium-like atoms.

TABLE II. Leading terms in the expansions of the functions P and Q in terms of the relativistic parameter $(\alpha Z)^2$.

Coefficients	Values	Coefficients	Values
$q^{(0)}$	$-0.42726 \cdot 10^{-2}$	$p^{(0)}$	$-0.24219 \cdot 10^{-3}$
$q^{(2)}$	$0.11676 \cdot 10^{-1}$	$p^{(2)}$	$0.11663 \cdot 10^{-2}$
$q^{(4)}$	$0.28273 \cdot 10^{-2}$	$p^{(4)}$	$0.18216 \cdot 10^{-3}$
$q^{(6)}$	$0.20279 \cdot 10^{-2}$	$p^{(6)}$	$-0.42390 \cdot 10^{-3}$
$q^{(8)}$	$-0.11513 \cdot 10^{-3}$	$p^{(8)}$	$-0.62353 \cdot 10^{-5}$

4. The contribution of the gauge dependence is extremely small numerically even for high Z (see Table I) and because of this it is impossible at present to make a comparative analysis with observational data, which is of fundamental interest. A similar conclusion also follows from relativistic calculations of the second order correlation energy.[12] This circumstance justifies a critical attitude toward self-consistent field methods in relativistic variants employing the exact Breit operator[4] (the Dirac–Hartree–Fock method). Contradictions of this sort do not arise when a local approach to the theory of the self-consistent field (the Dirac–Hartree–Fock–Slater method) is applied.

The authors thank the Russian Fund for Fundamental Research (Grant No. 95-02-05024) and the Scientific Foundation set up by Volkswagen AG (Grant No. 1/68770) for financial support of this work. One of the authors (V. G. P.) is grateful to the Technical University of Berlin for a warm reception and hospitality during his visit to Germany (September–December 1995). The authors are grateful to Prof. Paul Indelicato (Pierre and Marie Curie University, Paris) for stimulating discussions and interest in this work.

(1) Here and in what follows atomic units are used.

---

[1] F. S. Pavone, Phys. Scripta T **58**, 16 (1995).
[2] V. A. Boyko, V. G. Pal'chikov, I. Yu. Skobelev, and A. Ya. Faenov, *Spectra of Atoms with One and Two Electrons*, CRC Press USA, Boca Raton (1994).
[3] D. Kaiser and G. von Oppen, J. Phys. B **27**, 4835 (1994).
[4] Ol. Gorceix and P. Indelicato, Phys. Rev. A **37**, 1087 (1988).
[5] H. G. Beyer, F. Folkmann, and K. H. Schartner, Z. Phys. D **1**, 65 (1986).
[6] S. A. Zapryagaev, N. L. Manakov, and V. G. Pal'chikov, *Theory of Multiply Charged Ions with One and Two Electrons* [in Russian], Energoatomizdat, Moscow (1985).
[7] S. Schweber, *An Introduction to Relativistic Quantum Field Theory*, Row, Peterson and Co., New York (1961).
[8] K. Pachucki and H. Grotch, Phys. Rev. A **51**, 1854 (1995).
[9] M. Mittleman, Phys. Rev. A **4**, 897 (1971); **5**, 2395 (1972).
[10] J. Hata and I. P. Grant, J. Phys. B **17**, L107 (1984).
[11] V. G. Pal'chikov and G. von Oppen, Phys. Scripta **52**, 366 (1995).
[12] I. Lindgen, H. Persson, S. Salomonson, and L. Labzowsky, Phys. Rev. A **51**, 1167 (1995).

Translated by D. H. McNeill