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THE QUANTUM ELECTRODYNAMIC PROBLEM OF TWO ELECTRONS

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We solve the problem of the interaction of two quasimolecular electrons at an arbitrary distance from each other, i.e., near different atoms (nuclei). We regard the interaction as a second-order effect of the quantum electrodynamic perturbation theory in the coordinate representation. Taking the natural condition of the symmetry of the retardation factor, the electron spins, and the effects of retardation of the relativistic interaction of the two quasimolecular electrons located near different nuclei into account consistently, we obtain additional terms in the interelectron interaction operator compared with the standard Breit operator.

Keywords: interelectron interaction, retardation effects, Breit operator, quantum electrodynamics, quasimolecular electron

1. Introduction

Almost all two-electron processes with redistribution (two-electron recharging, recharging with simultaneous excitation or ionization, etc.), which accompany nonelastic collisions of multicharged ions with atoms, are necessarily related to the correlated electron transitions from the field of one atom remnant (or a bare nucleus) to the field of another. The leading contribution to the probability of such transitions comes from the configuration in which two active electrons of the target atom move to different nuclei, and the free-electron approximation holds for the zeroth approximation (see, e.g., [1] and the references therein). At low collision energies, quasiresonance processes with redistribution are characterized by cross sections that are large compared with the atomic radius and are therefore determined mainly by transitions at large internuclear distances R, which allows constructing a logically closed asymptotic theory of such processes (see [2]; see [1], [3], [4] for examples of more recent developments in this direction). Extending the asymptotic theory of processes with redistribution to the domain of relativistic coupling energies results in the need to consistently account for the correlation between two electrons localized near different nuclei located at large distances from each other compared with the characteristic wavelengths λ_0 in the spectrum of the interacting atoms. This domain of large interelectron distances $r_{12} = |\vec{r}_1 - \vec{r}_2|$, where $\vec{r}_1$ and $\vec{r}_2$ are the electron radius vectors, determines the probabilities of two-electron processes with redistribution in the asymptotic limit as $r_{12} \sim R \to \infty$; in what follows, we call the domain $r_{12} \sim R > \lambda_0$ the domain of far electron correlations.

Analyzing autoionization states of heavy multicharged quasimolecules with two excited electrons shows that the main correlation effect corresponds to configurations in which electrons are located far from each other, i.e., near different atoms [4], [5]. For studying the spectroscopy of autoionization states of such quasimolecules, realistic calculations must be based on a totally relativistic theory. In contrast to autoionization states of atomic systems, different physical aspects requiring a detailed study of rather general problems of

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the role of magnetic interactions and retardation effects in processes of the Auger ionization of atoms by slow highly charged ions prevail here.

But the formulation of the two-particle problem in relativistic quantum theory immediately encounters principal mathematical and logical obstacles. It can be reasonably said that a satisfactory relativistic theory of two-particle systems is still lacking. A direct generalization of the Dirac equation to two-electron systems is impossible because of the absence of a local Lorentz-invariant operator that takes the relativistic character of interelectron interaction (the retardation effects) into account.

Skipping a detailed discussion of the poorly investigated problem of relativistic two-particle interactions, we only note that a total relativistic Hamiltonian of a system could be given in the form of a series expansion in α^2 (where α is the fine structure constant). As early as 1929, Breit demonstrated [6] that such an expansion up to the first correction term provides a good approximation for the relativistic interaction between two electrons under the assumption that retardation effects in the spectrum of a helium-like atom are small. Breit obtained a relativistic operator of the interelectron interaction [6], [7]:

$$V(\vec{r}_{12}) = V_{\mathrm{C}}(r_{12}) + V_{\mathrm{B}}(\vec{r}_{12}) = \frac{e^2}{r_{12}} - \frac{e^2}{2r_{12}}\left[\vec{\alpha}_1\vec{\alpha}_2 + \frac{(\vec{\alpha}_1\vec{r}_{12})(\vec{\alpha}_2\vec{r}_{12})}{r_{12}^2}\right]. \tag{1}$$

Here, $\vec{\alpha}_1$ and $\vec{\alpha}_2$ are the commuting sets of Dirac matrices, $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$, and the subscripts 1 and 2 distinguish quantities related to the first and second electrons. The first term in (1) describes the electron electrostatic interaction, and the remaining Breit part $V_{\mathrm{B}}(\vec{r}_{12})$ takes the magnetic spin–spin interactions and retardation corrections due to the finite speed of the interaction propagation into account. Using quantum electrodynamics terminology, we can say that the retarded interaction is due to the exchange of virtual transversal photons between the electrons and the Coulomb interaction is due to the exchange by "longitudinal" and "scalar" photons [7].

But we must remember that Breit operator (1) ensures a good approximation describing the retarded interaction only while the interelectron distance r_{12} is small compared with $\lambda_0 = 2\pi c/\omega_0$, where ω_0 is the characteristic frequency in the spectrum of interacting electrons. This approximation fails in two-electron processes related to collisions of slow atoms because large interelectron distances r_{12}, in contrast, are essential in this case. Interest in the problem of two electrons belonging to two different neutral atoms located at an arbitrary distance from each other was therefore renewed at the beginning of the 1970s in relation to the intensive study of multiatomic systems in a radiation field. The decisive leap toward solving this problem was performed in [8]–[10], where the problem of the interaction of two electrons belonging to two different hydrogen-like atoms was studied by quantum electrodynamic methods in the general setting without imposing any restriction on the interatom distances. As a result, the generalized Breit operator of the interaction of two electrons via the field of virtual photons was obtained in [9], [10] as a second-order effect in the quantum electrodynamic perturbation theory. But a consistent treatment of relativistic effects was lacking in those papers. This can be seen, for instance, because the interaction operator constructed in [10] is nonsymmetric with respect to the pair of interacting particles. To take the effects of retardation of electron interaction completely into account, the natural condition of the symmetry of the "retardation factor" with respect to the interacting particles must be ensured. Here, we show that this results in the appearance of a new ("retarded") term in the relativistic two-electron interaction operator compared with the corresponding operator in [10].

Our studies are based on work by Gadomskii and collaborators [10], [11], who during last three decades extensively studied the problem of two-electron interaction in the third-order approximation in quantum electrodynamics, which includes the process of emitting (or absorbing) a real photon. This approach is important for the general setting of the problem and for solving several principal problems in classical, nonlinear, and quantum optics. In particular, it describes polarizing fields in a system of two hydrogen-like atoms in terms of which nonlocal equations for propagation of photons and electromagnetic waves in

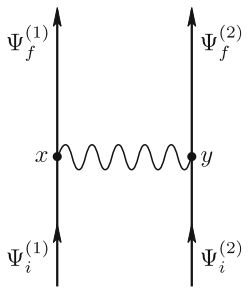

Fig. 1

various media were constructed depending on the types of quantum transitions and intermediate states in the spectra of interacting atoms. A certain completion of this circle of questions was found in [12].

The paper is organized as follows. In Sec. 2, we set the problem of the interaction of two quasimolecular electrons via the virtual photon field based on second-order effects in quantum electrodynamics. In Sec. 3, we derive the relativistic operator of interaction between two electrons located at an arbitrary distance from each other. A consistent accounting for the natural symmetry condition for the retardation factor with respect to the interacting particles results in an additional contribution to the relativistic two-electron interaction operator (32) compared with the generalized Breit operator in [10] (see formula (33)).

2. Effective energy of interaction of two electrons located at an arbitrary distance from each other

We regard the interaction of two electrons in an external electrostatic field as a second-order effect in quantum electrodynamics described by the Feynman diagram depicted in Fig. 1. The corresponding matrix element of the second-order scattering operator $S^{(2)}$ can be written in the form [13], [14]

$$S_{i\to f}^{(2)} \equiv \langle f|S^{(2)}|i\rangle = -i\int d^4x \int d^4y\, j_{fi}^{(2)\mu}(y) D_{\rm F}(y-x) j_{fi\mu}^{(1)}(x), \tag{2}$$

where $D_{\rm F}$ is the photon propagator and the transition current densities $j_{fi\mu}^{(1)}(x)$ and $j_{fi}^{(2)\mu}(y)$ are

$$j_{fi\mu}^{(1)}(x) = e\overline{\Psi}_f^{(1)}(x)\gamma_\mu^{(1)}\Psi_i^{(1)}(x), \qquad j_{fi}^{(2)\mu}(y) = e\overline{\Psi}_f^{(2)}(y)\gamma^{(2)\mu}\Psi_i^{(2)}(y). \tag{3}$$

Here, $e=-|e|$ is the electron charge, γ^μ are the Dirac matrices in the covariant representation, $\mu=0,1,2,3$, $\Psi_i^{(n)}$ and $\Psi_f^{(n)}$ are the wave functions of the respective initial and final states of the nth electron, $n=1,2$, $\overline{\Psi}_f^{(n)} = \Psi_f^{(n)+}\gamma^0$ is the Dirac-adjoint bispinor and $\Psi_f^{(n)+}$ is the Hermitian-adjoint bispinor. Everywhere below unless specifically indicated, we use the relativistic units $\hbar=c=1$, the notation $x^\mu=(t_1,\vec{r}_1)$ and $y^\mu=(t_2,\vec{r}_2)$ for the radius four-vectors and $d^4x = d^3x\,dt_1$ and $d^4y = d^3y\,dt_2$ for the four-volume elements. The superscripts (1) and (2) distinguish quantities related to different electrons. The subscripts i and f denote quantities pertaining to the initial and final states of the interacting electrons. In expressions (2) and (3), we use the representation for the Dirac matrices

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix},$$

where the matrix $\gamma^0=\beta$ is diagonal, the relations $\gamma^j=\beta\alpha_j$, $j=1,2,3$, are satisfied, $\vec{\sigma}$ are the known Pauli matrices, and I is the 2×2 unit matrix.

External electron legs of the diagram correspond to wave functions of stationary states,

$$\Psi^{(1)}_{i,f}(x) = \Psi^{(1)}_{i,f}(\vec{r}_1)e^{-iE^{(1)}_{i,f}t_1}, \qquad \Psi^{(2)}_{i,f}(y) = \Psi^{(2)}_{i,f}(\vec{r}_2)e^{-iE^{(2)}_{i,f}t_2}. \tag{4}$$

The quantities $E^{(1)}_i$ and $E^{(1)}_f$ and $E^{(2)}_i$ and $E^{(2)}_f$ are the initial and final energies of the first and second electrons. Taking formulas (4) into account, we segregate the explicit time dependence of the transition currents,

$$j^{(1)}_{fi\mu}(x) = j^{(1)}_{fi\mu}(\vec{r}_1)e^{i\omega^{(1)}_{fi}t_1}, \qquad j^{(2)\mu}_{fi}(x) = j^{(2)\mu}_{fi}(\vec{r}_2)e^{i\omega^{(2)}_{fi}t_2}, \tag{5}$$

where the transition frequency is $\omega^{(n)}_{fi} = E^{(n)}_f - E^{(n)}_i$, $n = 1, 2$.

We set the propagator

$$D_{\mathrm{F}}(y-x) = \int \frac{d^4k}{(2\pi)^4}\left(\frac{-4\pi e^{-ik(y-x)}}{k^2 + i\varepsilon}\right) \tag{6}$$

into correspondence with the internal photon line of the diagram. Here, $k = (\omega, \vec{k})$, $\vec{k}$ and ω are the respective wave vector and frequency of the quantum, and the infinitesimal imaginary addition in the denominator fixes the rules for bypassing poles in the complex plane. Substituting (5) and (6) in formula (2), we obtain the representation for the S-matrix:

$$S^{(2)}_{i\to f} = -i\int d^4x \int d^4y \int \frac{d^4k}{(2\pi)^4} j^{(2)\mu}_{fi}(\vec{r}_2)e^{i\omega^{(2)}_{fi}t_2}\left(\frac{-4\pi e^{-ik(y-x)}}{k^2+i\varepsilon}\right) j^{(1)}_{fi\mu}(\vec{r}_1)e^{i\omega^{(1)}_{fi}t_1}. \tag{7}$$

After integration over the time t_2, formula (7) becomes

$$S^{(2)}_{i\to f} = 4\pi i \int d^3x \int d^3y \int dt_1 \int d\omega\, \delta(\omega - \omega^{(2)}_{fi})e^{i(\omega^{(1)}_{fi}+\omega)t_1} \times$$

$$\times\, j^{(2)\mu}_{fi}(\vec{r}_2) j^{(1)}_{fi\mu}(\vec{r}_1) \int \frac{d^3k}{(2\pi)^3} \frac{e^{-i\vec{k}\vec{r}_{12}}}{\omega^2 - \vec{k}^2 + i\varepsilon}. \tag{8}$$

Then integrating over d^3k (using the rules for bypassing poles at the points $k = \pm(\omega + i\varepsilon' \operatorname{sgn}\omega)$), we obtain the representation

$$S^{(2)}_{i\to f} = -i\int d^3x \int d^3y \int dt_1 \int d\omega\, \delta(\omega - \omega^{(2)}_{fi}) \times$$

$$\times\, e^{i(\omega^{(1)}_{fi}+\omega)t_1} j^{(2)\mu}_{fi}(\vec{r}_2) \frac{e^{i|\omega|r_{12}}}{r_{12}} j^{(1)}_{fi\mu}(\vec{r}_1). \tag{9}$$

After integration over the time t_1 and the frequencies of virtual photons ω, the last expression becomes

$$S^{(2)}_{i\to f} = -2\pi i \delta(\omega^{(1)}_{fi} + \omega^{(2)}_{fi}) \int d^3x \int d^3y\, j^{(2)\mu}_{fi}(\vec{r}_2) \frac{e^{i|\omega^{(2)}_{fi}|r_{12}}}{r_{12}} j^{(1)}_{fi\mu}(\vec{r}_1). \tag{10}$$

We now pass from the scattering matrix $S^{(2)}_{i\to f}$ to the matrix $U^{(2)}_{i\to f}$ of the effective interaction energy of the system of two charges determined by the equality

$$S^{(2)}_{i\to f} = -2\pi i U^{(2)}_{i\to f} \delta(E^{(1)}_f - E^{(1)}_i + E^{(2)}_f - E^{(2)}_i). \tag{11}$$

Segregating the one-dimensional δ-function of the difference between the total electron energies in the initial and final states into a factor expresses the energy conservation law,

$$E^{(1)}_f + E^{(2)}_f = E^{(1)}_i + E^{(2)}_i, \tag{12}$$

which manifests the symmetry under the continuous time-shift operation. Because of conservation law (12), we conventionally write $|\omega_{fi}^{(1)}|$ and $|\omega_{fi}^{(2)}|$ in the simplified form $|\omega_{fi}|$ (implying $|\omega_{fi}| = |\omega_{fi}^{(1)}| = |\omega_{fi}^{(2)}|$). Then by (10) and (11), the matrix of the effective energy of interaction between two electrons is

$$U_{i\to f}^{(2)} = \int d^3x \int d^3y \, j_{fi}^{(2)\mu}(\vec{r}_2) \frac{e^{i|\omega_{fi}|r_{12}}}{r_{12}} \, j_{fi\mu}^{(1)}(\vec{r}_1). \tag{13}$$

All the formulas in this section pertain to matrix element (2). To obtain the complete expression for $S_{i\to f}^{(2)}$, the corresponding exchange matrix element expressing the indistinguishability of electrons must be added to matrix element (2).

3. The long-range interaction-type generalized Breit operator

Using definitions (3)–(5), we express the interaction currents in terms of wave functions in formula (13) for the matrix element of the effective interaction energy,

$$U_{i\to f}^{(2)} = e^2 \int d^3x \int d^3y \, \Psi_f^{(2)+}(\vec{r}_2)\Psi_f^{(1)+}(\vec{r}_1) \frac{1-\vec{\alpha}_1\vec{\alpha}_2}{r_{12}} e^{i|\omega_{fi}|r_{12}} \Psi_i^{(2)}(\vec{r}_2)\Psi_i^{(1)}(\vec{r}_1), \tag{14}$$

where $\vec{\alpha}_1$ and $\vec{\alpha}_2$ are the Dirac matrices acting on different one-electron wave functions: $\vec{\alpha}_1$ acts on $\Psi_i^{(1)}(\vec{r}_1)$ and $\vec{\alpha}_2$ acts on $\Psi_i^{(2)}(\vec{r}_2)$. Because the "retardation factor" $e^{i|\omega_{fi}|r_{12}}$, which depends explicitly on the initial and final energies of the system, enters this expression, in the general case, we cannot introduce a Hamiltonian of interaction between two electrons, i.e., an operator V for which the relation

$$U_{i\to f}^{(2)} = \langle f|V|i\rangle = \int d^3x \int d^3y \, \Psi_f^{(2)+}(\vec{r}_2)\Psi_f^{(1)+}(\vec{r}_1) V \Psi_i^{(2)}(\vec{r}_2)\Psi_i^{(1)}(\vec{r}_1) \tag{15}$$

is satisfied. Here, we assume that the operator of the effective potential energy V is a 16-component matrix in the spinor indices.

But in the approximation of low velocities ($v/c \ll 1$, where v is the speed of electrons in the atom and c is the speed of light in the vacuum), we can construct such an operator. Indeed, for atomic electrons, we have $|\omega_{fi}| \sim m(\alpha Z_{\text{eff}})^2$ in our units, where Z_{eff} is the effective nucleus charge action, which is equivalent to the action on a given electron of a nucleus screened by all the other electrons in the atom. We take into account that the characteristic interelectron distance in an atom is $r_{12} \sim (m\alpha Z_{\text{eff}})^{-1}$. Hence, the exponent $|\omega_{fi}|r_{12}$ in (14) is of the order of αZ_{eff}. In fact, for all the atomic electrons including the internal ones, the ratio v/c, being of the order of αZ_{eff}, is much smaller than unity, and we can therefore take the retardation and all other relativistic effects into account approximately by dropping terms of the order v^3/c^3 and higher in the v/c-expansion of matrix element (14). This approximation results in the known expression (1) for the Breit operator [6], [7], which now depends not only on the relative position $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$ of the pair of electrons but also on their spins. We claim that this expression well approximates the relativistic electron interaction only in the intra-atomic domain but becomes invalid in the domain of large interelectron distances ($r_{12} \gtrsim \lambda_0 = 2\pi c/\omega_0$). In this domain, which we call the domain of far electron correlations, retardation effects become more significant for the interelectron interaction.

We now consider a two-electron atom (or ion) $A^{(Z_a-2)+}$ and the bare nucleus B^{Z_b+} with empty shells located at an arbitrary distance R from the atom. Here, Z_a and Z_b are the charges of the atomic nuclei A^{Z_a+} and B^{Z_b+}, which we assume to be stable in the proposed two-center model. Let $\vec{r}_{na}$ and $\vec{r}_{nb}$ be the radius vectors of the nth electron with respect to the respective nuclei A^{Z_a+} and B^{Z_b+}, $n = 1, 2$. We now assume that one of the electrons of the atom $A^{(Z_a-2)+}$, for instance, the first electron tunnels to the closest proximity of the foreign nucleus B^{Z_b+}, while the second electron remains near its host nucleus A^{Z_a+}. If the

domains of spatial localizations of the electrons near the different nuclei (the first electron near B^{Z_b+} and the second electron near A^{Z_a+}) are sufficiently small (of the order of the atom size) and are well separated, then with the condition $\Delta r < R < \infty$ satisfied, we can expand the distance r_{12} between the electrons in a power series in the ratio $\Delta r/R$,

$$r_{12} = |\vec{r}_1 - \vec{r}_2| = R\left(1 + \frac{\vec{R}\Delta\vec{r}}{R^2} + \frac{M_1}{R}\right). \tag{16}$$

Here, $\Delta\vec{r} = \vec{r}_{1b} - \vec{r}_{2a}$, $\Delta r = |\Delta\vec{r}|$, $\vec{r}_{1b}$ and $\vec{r}_{2a}$ are the radius vectors of the first and the second electron with respect to the corresponding nuclei, and $M_1 = M_1(\Delta\vec{r}, \vec{R})$ are small corrections containing higher powers of the ratio $\Delta r/R$.

From the matrix of effective interaction energy (14), we segregate the factor

$$K(\vec{r}_1, \vec{r}_2; \omega_{fi}) = \frac{e^{i|\omega_{fi}|r_{12}/c}}{r_{12}}, \tag{17}$$

which is responsible for the virtual photon exchange between the two electrons. Here and hereafter, we use the system of units in which $c \neq 1$. It was previously assumed in [6], [7] when constructing the retardation factor that the only small parameter is the quantity $\omega_0 r_{12}/c \ll 1$ (or formally $1/c$). The expansion of the factor $K(\vec{r}_1, \vec{r}_2; \omega_{fi})$ thus obtained obviously holds while the interelectron distance r_{12} remains small compared with the characteristic wavelengths $\lambda_0 = 2\pi c/\omega_0$ in the spectrum of the interacting electrons. In what follows, we construct an asymptotic expansion for the factor K treating $1/c$ and $\Delta r/R$ simultaneously as natural small parameters. Such a selection of small parameters corresponds to the limit of noninteracting atoms ($R \to \infty$) [1]–[3], and this limit is realized in the two-center model, for instance, when electrons are located far from each other near different atoms (nuclei).

As in [10], we transform the retardation factor in (17) to the form

$$K(\vec{r}_1, \vec{r}_2; \omega_{fi}) = e^{i|\omega_{fi}|R/c}\frac{e^{i|\omega_{fi}|(r_{12}-R)/c}}{r_{12}}. \tag{18}$$

For electrons pertaining to different atoms, this transformation is convenient because it segregates the relativistic factor $e^{i|\omega_{fi}|R/c}$ of amplifying the effects of retardation of the interaction of charged particles at large mutual distances ($r_{12} \sim R \gtrsim \lambda_0$). Because the difference $r_{12} - R$ of relative distances between electrons r_{12} and nuclei R in the exponent of one of the rapidly oscillating exponential functions in retardation factor (18), the quantity $K(\vec{r}_1, \vec{r}_2; \omega_{fi})$ must be expanded not only in powers of $1/c$ but also in powers of the small parameter $\Delta r/R$. In what follows, we set

$$\frac{|\omega_{fi}|}{c}\,\frac{\Delta r}{R} \ll 1. \tag{19}$$

With this condition satisfied, the exponent $|\omega_{fi}|(r_{12} - R)/c$ in the right-hand side of (18) is a small quantity, and we can therefore expand the factor K in a power series in small parameter (19) and keep only the first three expansion terms,

$$K(\vec{r_1}, \vec{r_2}; \omega_{fi}) = e^{i|\omega_{fi}|R/c}\left\{f_0(r_{12}) + \frac{i}{c}|\omega_{fi}|f_1(r_{12}) - \frac{\omega_{fi}^2}{2c^2}f_2(r_{12})\right\}. \tag{20}$$

The coefficients

$$\begin{aligned} f_0(r_{12}) &= \frac{1}{g_0(r_{12})} = \frac{1}{r_{12}}, \\ f_1(r_{12}) &= \frac{g_1(r_{12})}{g_0(r_{12})} = \frac{r_{12} - R}{r_{12}}, \\ f_2(r_{12}) &= \frac{g_2(r_{12})}{g_0(r_{12})} = \frac{(r_{12} - R)^2}{r_{12}} \end{aligned} \tag{21}$$

of expansion (20) are in turn power series in $\Delta r/R$, which can be written directly using asymptotic representations of the functions g_0, g_1, and g_2 at small values of the parameter $\Delta r/R$:

$$g_0(\Delta\vec{r},\vec{R}) = R\left[1+\frac{\vec{R}\vec{\Delta r}}{R^2}+\frac{M_1}{R}\right],$$

$$g_1(\Delta\vec{r},\vec{R}) = \frac{\vec{R}\vec{\Delta r}}{R}+M_1, \qquad g_2(\Delta\vec{r},\vec{R}) = \left[\frac{\vec{R}\vec{\Delta r}}{R}+M_1\right]^2.$$

The obtained expansion (20) holds in the entire domain of the internucleus distance $\Delta r \le R < \infty$ of practical interest.

We eliminate frequencies from (20) using the Dirac equation

$$\widehat{H}^{(n)}(\vec{r}_n)\Psi_i^{(n)}(\vec{r}_n) = E_i^{(n)}\Psi_i^{(n)}(\vec{r}_n), \qquad \widehat{H}^{(n)}(\vec{r}_n)\Psi_f^{(n)}(\vec{r}_n) = E_f^{(n)}\Psi_f^{(n)}(\vec{r}_n). \tag{22}$$

Here, the index n takes the values 1 and 2, and the one-electron relativistic Hamiltonian $\widehat{H}^{(n)}(\vec{r}_n)$ acts in the space of Dirac wave functions $\Psi_{i,f}^{(n)}(\vec{r}_n)$ of the electron with the number n.

In formula (20), the expansion of the factor K has no symmetry under interchanging the interacting particles. To obtain the required symmetry in the last two terms of expansion (20), we use the relation $\omega_{fi}^{(1)} = -\omega_{fi}^{(2)}$, which expresses energy conservation law (12). Having the two possibilities $E_f^{(1)} > E_i^{(1)}$ or $E_f^{(1)} < E_i^{(1)}$, we consider the two cases $\omega_{fi}^{(1)} > 0$ and $\omega_{fi}^{(1)} < 0$ separately. If $E_f^{(1)} > E_i^{(1)}$ or $E_f^{(1)} < E_i^{(1)}$, then respectively $\omega_{fi}^{(1)} = -\omega_{fi}^{(2)} > 0$ or $\omega_{fi}^{(1)} = -\omega_{fi}^{(2)} < 0$ and $|\omega_{fi}^{(1)}| = \omega_{fi}^{(1)}$ or $|\omega_{fi}^{(1)}| = -\omega_{fi}^{(1)}$. Using these relations, we transform the second term in (20) to the symmetric form:

$$|\omega_{fi}|f_1(r_{12}) = |\omega_{fi}^{(1)}|f_1(r_{12}) = \pm\omega_{fi}^{(1)}f_1(r_{12}) = \pm\frac{1}{2}\,[E_f^{(1)} - E_i^{(1)} + E_i^{(2)} - E_f^{(2)}]f_1(r_{12}). \tag{23}$$

The plus sign in (23) corresponds to the case $E_f^{(1)} > E_i^{(1)}$ ($\omega_{fi}^{(1)} > 0$), and the minus sign corresponds to the case $E_f^{(1)} < E_i^{(1)}$ ($\omega_{fi}^{(1)} < 0$). When symmetrizing the quantity $|\omega_{fi}|f_1$, we could start with the equality $|\omega_{fi}|f_1 = |\omega_{fi}^{(2)}|f_1$ instead of the equality $|\omega_{fi}|f_1 = |\omega_{fi}^{(1)}|f_1$. It is easy to see that the representation for $|\omega_{fi}|f_1$ thus obtained is equivalent to representation (23). Because we multiply expression (20) by $\Psi_i^{(2)}(\vec{r}_2)\Psi_i^{(1)}(\vec{r}_1)$ from the right and by $\Psi_f^{(2)+}(\vec{r}_2)\Psi_f^{(1)+}(\vec{r}_1)$ from the left and subsequently integrate over $\vec{r}_1$ and $\vec{r}_2$, we can replace the energies $E_i^{(1)}$ and $E_i^{(2)}$ in (23) with the operators $\widehat{H}^{(1)}$ and $\widehat{H}^{(2)}$ to the right of the factor $f_1(r_{12})$ and replace the energies $E_f^{(1)}$ and $E_f^{(2)}$ with the operators $\widehat{H}^{(1)}$ and $\widehat{H}^{(2)}$ to the left of the factor $f_1(r_{12})$,

$$|\omega_{fi}|f_1(r_{12}) \to \pm\frac{1}{2}\{\widehat{H}^{(1)}f_1(r_{12}) - f_1(r_{12})\widehat{H}^{(1)} + f_1(r_{12})\widehat{H}^{(2)} - \widehat{H}^{(2)}f_1(r_{12})\} =$$

$$= \pm\frac{1}{2}\{[\widehat{H}^{(1)}, f_1(r_{12})] + [f_1(r_{12}), \widehat{H}^{(2)}]\}. \tag{24}$$

Here and hereafter, the square brackets denote the commutators of the corresponding quantities.

Similarly (using the relation $\omega_{fi}^{(1)} = -\omega_{fi}^{(2)}$), we eliminate frequencies from the third term in expansion (20):

$$-\omega_{fi}^2 f_2(r_{12}) = (E_f^{(1)} - E_i^{(1)})(E_f^{(2)} - E_i^{(2)})f_2(r_{12}) \to$$

$$\to f_2(r_{12})\widehat{H}^{(1)}\widehat{H}^{(2)} - \widehat{H}^{(1)}f_2(r_{12})\widehat{H}^{(2)} - \widehat{H}^{(2)}f_2(r_{12})\widehat{H}^{(1)} + \widehat{H}^{(1)}\widehat{H}^{(2)}f_2(r_{12}) =$$

$$= \left[\widehat{H}^{(1)}, [\widehat{H}^{(2)}, f_2(r_{12})]\right]. \tag{25}$$

Substituting operator expressions (24) and (25) in the right-hand side of (20), we obtain the transformation of the factor K:

$$K(\vec{r}_1,\vec{r}_2;\omega_{fi}) \to e^{i|\omega_{fi}|R/c}\left\{f_0(r_{12}) \pm \frac{i}{2c}\big([\widehat{H}^{(1)}, f_1(r_{12})] + [f_1(r_{12}), \widehat{H}^{(2)}]\big) + \frac{1}{2c^2}\big[\widehat{H}^{(1)}, [\widehat{H}^{(2)}, f_2(r_{12})]\big]\right\}, \quad (26)$$

where $|\omega_{fi}| = |\omega_{fi}^{(1)}| = |\omega_{fi}^{(2)}|$ and the functions f_0, f_1, and f_2 are still given by equalities (21).

Double expansion (20) therefore gives K-factor (17) in powers of $1/c$ and $\Delta r/R$. In the expansion in $1/c$, we then retain only the first three terms, imposing no restrictions on the expansion in the small parameter $\Delta r/R$; the function M_1 contains all higher correction terms. In what follows, we therefore take interactions of two quasimolecular electrons of arbitrary multipolarity into account.

The motion of separate electrons in a two-center system $A^{(Z_a-2)+} + B^{Z_b+}$ is described by the Dirac one-electron Hamiltonian for the problem of two Coulomb centers at the distance R from each other,

$$\widehat{H}^{(n)} = c\vec{\alpha}_n\hat{\vec{p}}_n + \beta_n mc^2 + V(\vec{r}_n), \quad n = 1,2, \quad (27)$$

where

$$V(\vec{r}_n) = -\left(\frac{Z_a e^2}{r_{na}} + \frac{Z_b e^2}{r_{nb}}\right), \qquad r_{na,nb} = \left|\vec{r}_n \pm \frac{\vec{R}}{2}\right|. \quad (28)$$

Here and hereafter, $\hbar \neq 1$, $\hat{\vec{p}}_n = -i\hbar\vec{\nabla}_n$ is the momentum operator, $\vec{\nabla}_n$ is the three-dimensional gradient with respect to the coordinates $\vec{r}_n$ of the electron with the number n, and the index n on the matrices $\vec{\alpha}_n$ and β_n indicates that these matrices act on the function $\Psi_i^{(n)}(\vec{r}_n)$. We can obviously introduce other terms into Hamiltonian (27), for instance, taking a finite size and the spin of the nucleus, screening of the nucleus field by the electron shell of the atomic core, etc., into account.

We calculate the commutators in (26). We first note that the only term in $\widehat{H}^{(n)}$ that does not commute with $f_1(r_{12})$ and $f_2(r_{12})$ is $c\vec{\alpha}_n\hat{\vec{p}}_n$. When substituting the operators $\widehat{H}^{(1)}$ and $\widehat{H}^{(2)}$ given by expression (27) in the commutator in (26), we can therefore disregard all terms not containing the matrices $\vec{\alpha}_n$,

$$\begin{aligned} &[\widehat{H}^{(1)}, f_1] = c[\vec{\alpha}_1\hat{\vec{p}}_1, f_1], \qquad [f_1, \widehat{H}^{(2)}] = c[f_1, \vec{\alpha}_2\hat{\vec{p}}_2], \\ &\big[\widehat{H}^{(1)}, [\widehat{H}^{(2)}, f_2]\big] = c^2\big[\vec{\alpha}_1\hat{\vec{p}}_1, [\vec{\alpha}_2\hat{\vec{p}}_2, f_2]\big]. \end{aligned} \quad (29)$$

Using these relations together with the obvious auxiliary formula

$$[\vec{\alpha}_n\hat{\vec{p}}_n, f_{1,2}] = -i\hbar(\vec{\alpha}_n\vec{\nabla}_n)f_{1,2},$$

we easily find that the contributions of the second and third terms in expansion (26) are determined by the operator equalities

$$\pm\frac{i}{2c}([\widehat{H}^{(1)}, f_1] + [f_1, \widehat{H}^{(2)}]) = \pm\hbar R\,\frac{\vec{\alpha}_1\vec{n} + \vec{\alpha}_2\vec{n}}{2r_{1,2}^2}, \quad (30)$$

$$\frac{1}{2c^2}\big[\widehat{H}^{(1)}, [\widehat{H}^{(2)}, f_2]\big] = -\frac{\hbar^2}{2}(\vec{\alpha}_1\vec{\nabla}_1)(\vec{\alpha}_2\vec{\nabla}_2)r_{12} - \frac{\hbar^2R^2}{2}(\vec{\alpha}_1\vec{\nabla}_1)(\vec{\alpha}_2\vec{\nabla}_2)\frac{1}{r_{12}}, \quad (31)$$

where $\vec{n} = (\vec{r}_1 - \vec{r}_2)/|\vec{r}_1 - \vec{r}_2|$. The quantity $\langle f|V|i\rangle$ can therefore indeed be represented in form (15), where the operator V describing the virtual photon exchange between particles is (here again $\hbar = 1$)

$$\begin{aligned} V^{(\pm)}(\vec{r}_1,\vec{r}_2;R) = e^2\cdot\exp\left(\frac{i|\omega_{fi}|R}{c}\right)\Bigg\{&\frac{1}{r_{12}} - \frac{\vec{\alpha}_1\vec{\alpha}_2 + (\vec{\alpha}_1\vec{n})(\vec{\alpha}_2\vec{n})}{2r_{12}} \pm \\ &\pm R\frac{\vec{\alpha}_1\vec{n} + \vec{\alpha}_2\vec{n}}{2r_{12}^2} - R^2\frac{\vec{\alpha}_1\vec{\alpha}_2 - 3(\vec{\alpha}_1\vec{n})(\vec{\alpha}_2\vec{n})}{2r_{12}^3}\Bigg\}. \end{aligned} \quad (32)$$

In this equality, the plus sign of the term containing the factor R corresponds to the case $E_f^{(1)} > E_i^{(1)}$, and the minus sign corresponds to the case $E_f^{(1)} < E_i^{(1)}$. We calculate matrix element (15) of this operator with the four-component wave functions $\Psi_i^{(n)}(\vec{r}_n)$ and $\Psi_f^{(n)}(\vec{r}_n)$. The first term in (32) is the energy of the instant (Coulomb) interaction between electrons, and the remaining terms take corrections due to the retardation of relativistic interaction and due to the presence of electron spins into account.

In the limit of a unified atom ($R \to 0$), operator (32) becomes relativistic Breit operator (1) of the interaction of two atomic electrons in helium-like systems. We can therefore consider operator (32) a direct generalization of the Breit operator [6], [7] to the domain of arbitrarily large interelectron distances, where the relativistic nature of the interaction of moving charges is manifested most clearly. Such a generalization is nontrivial because expression (32) (in contrast to Breit expression (1)) contains retarded terms proportional to R and R^2. This additional contribution to $V^{(\pm)}$ is essentially relativistic and appears because of the additional retardation of the relativistic interaction between two electrons located at an arbitrarily large distance compared with $\lambda_0 = 2\pi c/\omega_0$.

Because we generalize the Breit operator here, we can call expression (32) the generalized Breit operator of long-range type (to stress the possibility of using it to solve two-electron problems in the physics of slow atomic collisions [1]–[3], in the theory of quasimolecular Auger spectroscopy [4], [5], and in several important problems in nonlinear and quantum optics [8]–[12]).

To analyze the symmetry properties of operator (32), we introduce the notation P_{12} for the operator of permutation of the pair of interacting particles 1 and 2. Acting with the operator P_{12} on $V^{(\pm)}(\vec{r}_1, \vec{r}_2; R)$, we obtain

$$P_{12} V^{(\pm)}(\vec{r}_1, \vec{r}_2; R) = V^{(\mp)}(\vec{r}_1, \vec{r}_2; R).$$

We here take into account that $\vec{\alpha}_1\vec{n}$ and $\vec{\alpha}_2\vec{n}$ change their sign when particles 1 and 2 are interchanged, and their product is therefore unchanged. But the third term in (32) is not symmetric: it is antisymmetric under interchanging the particles. We also stress that the obtained expression for operator (32) is explicitly symmetric with respect to the interacting particles. This is not surprising, because we symmetrize each separate term of expansion (20) by formulas (23)–(25) and the functions f_0, f_1, and f_2 in the right-hand side of (26) depend only on the distance between the particles. Therefore, the symmetry of formula (21) under interchanging the vectors $\vec{r}_1 \leftrightarrows \vec{r}_2$ is obvious.

In [9]–[12], which initiated the contemporary studies of the two-electron problem, the result

$$\widehat{U}^{(2)}(\vec{r}_1, \vec{r}_2; R) = e^2 \cdot \exp\left(\frac{i|\omega_{fi}|R}{c}\right)\left\{\frac{1}{r_{12}} - \frac{\vec{\alpha}_1\vec{\alpha}_2 + (\vec{\alpha}_1\vec{n})(\vec{\alpha}_2\vec{n})}{2r_{12}} + \right.$$
$$\left. + R\frac{\vec{\alpha}_2\vec{n}}{r_{12}^2} - R^2\frac{\vec{\alpha}_1\vec{\alpha}_2 - 3(\vec{\alpha}_1\vec{n})(\vec{\alpha}_2\vec{n})}{2r_{12}^3}\right\} \tag{33}$$

was obtained for the relativistic operator of two-electron interaction. A principal drawback of this operator is the absence of symmetry in the description of the pair of interacting particles. As mentioned above, in our construction of operator (32), we obtain the equality in the particle description by the proper symmetrization of the last two terms in the expansion of retardation factor (26). As a result, final expression (32) for the operator $V^{(\pm)}(\vec{r}_1, \vec{r}_2; R)$, in addition to the terms represented in (33), contains the new term $\pm R(\vec{\alpha}_1\vec{n})/2r_{12}^2$, which is due to the additional retardation in the electron interaction. This was lacking in [9]–[12] and resulted in the incorrect result (33) for the operator of the relativistic interaction of two electrons.

4. Conclusion

We have used the quantum electrodynamic approach to solve the problem of the interaction of two quasimolecular electrons located at an arbitrary distance from each other near different atoms (nuclei). We

regarded the interaction as a second-order effect in the quantum electrodynamic perturbation theory with the Feynman diagram in Fig. 1. We now indicate the main properties of this interaction.

We have two domains of the configuration space where the generalized Breit operator $V^{(\pm)}(\vec{r}_1, \vec{r}_2; R)$ behaves differently when the distance r_{12} between the two electrons changes. For instance, as $R \to 0$, formula (32) for $V^{(\pm)}(\vec{r}_1, \vec{r}_2; R)$ becomes limit expression (1), which correctly describes the retardation effects of the relativistic interaction only at a small interparticle distance r_{12}. In particular, the applicability domain for Breit formula (1) is restricted by the condition on the coordinate variables

$$\frac{\omega_0 r_{12}}{c} \ll 1, \tag{34}$$

where ω_0 is the characteristic frequency of the spectrum of the interacting electrons. We let Ω_{I} denote the corresponding domain in the configuration space, which we call the domain of close electron correlations. But in the domain Ω_{II}, where the electrons belong to different nuclei and condition (19) is satisfied for all $\Delta r \le R < \infty$, Breit operator (1) fails to describe the relativistic interaction of two electrons even on the qualitative level. At the same time, the relativistic operator $V^{(\pm)}(\vec{r}_1, \vec{r}_2; R)$, constructed here and called the generalized Breit operator of the long-range interaction type, allows describing the retarded interaction of two electrons uniformly in the domain Ω_{I} of close electron correlations and in the domain Ω_{II} of far electron correlations. This operator can therefore be used to solve many two-electron problems in atomic and molecular spectroscopy, astrophysics, the theory of slow atomic collisions, etc.

For each domain of distances r_{12}, we have the corresponding time scale of interaction transfer and the corresponding calculation approximations in which we segregate small parameters and take different types of interaction into account. We thus again confirm that we can use the generalized Breit operator $V^{(\pm)}(\vec{r}_1, \vec{r}_2; R)$ to solve multielectron two-center problems and that the quantum electrodynamic pattern of two-electron interaction based on standard Breit operator (1) is incomplete.

As shown in the preceding section, in the derivation of Breit operator (1), the standard assumption is [7] that the only small parameter in which the retardation factor must be expanded is quantity (34). This means that in addition to the characteristic (mean) transition time $T_0 = 2\pi/\omega_0$, we also use the unified time scale $T_{\mathrm{T}} = r_{12}/c$ corresponding to the domain Ω_{I}. We can interpret this time as the interaction transfer time. We must then satisfy the condition $2\pi T_{\mathrm{T}} \ll T_0$, i.e., that a substantial change in the electron density in a system of two interacting electrons occurs during the interaction transfer time.

At large interelectron distances (in the domain Ω_{II}), where the interaction transfer time $T_{\mathrm{T}} = R/c$ is much larger than the mean electron transition time $T_0 = 2\pi/\omega_0$, the natural small parameter is quantity (19). Exchange by virtual photons at such a distance results in an interelectron interaction (cf. (32)) that in addition to the Coulomb and Breit interactions (1), contains additional terms due to increasing retardation effects in the spin–orbit and spin–spin interactions of the two electrons. The parameter that determines the increase in the influence of the retardation effects on the electron interaction effects is the ratio T_{B}/T_0 or R/λ_0, where $\lambda_0 = 2\pi c/\omega_0$.

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