The generalized Breit operator of the interaction between two quasimolecular electrons in the framework of the third-order effects of quantum electrodynamics

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Abstract
The problem of the interaction of two quasimolecular electrons located at an
arbitrary distance from each other and near different atoms (nuclei) is solved.
Effects of the third order of quantum electrodynamics, which include the
exchange of a virtual photon between the electrons and emission (absorption)
of a real photon, are considered. The general expression for the matrix elements
of the operator of the effective interaction energy of the two quasimolecular
electrons with the external radiation field, which allows us to calculate the
probabilities of inelastic processes with rearrangement in slow collisions of
multiply-charged ions with relativistic atoms, is obtained. Carrying out
consistently the procedure of symmetrization of the retardation factor with
respect to both the electrons results in the appearance of additional terms in
the relativistic operator of the interaction of two quasimolecular electrons in
comparison with both the standard and generalized Breit operators known
previously.

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1. Introduction

Inelastic collisions of atomic particles, especially multielectron ones, are accompanied by
many processes of modification of their charge and electronic states. The simplest examples,
which are studied quite well, are one-electron ion–atom processes with rearrangement (for
example, the resonance and quasi-resonance charge exchange), in which only one electron
changes the state and the other one can be considered frozen. Such processes have high
efficiency and play an important role in formation of the inverse population of ionic levels
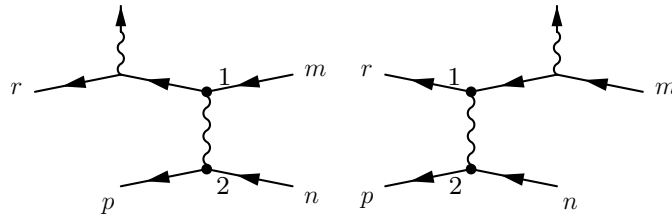
Figure 1. The Feynman diagrams of the third-order effects of QED for the interaction of the two quasimolecular electrons with emission or absorption of the real photon.

in solar coronal plasma and new thermonuclear facilities [1, 2]. However, the two-electron processes with rearrangement have either the same or larger probabilities when compared with the one-electron processes [3–7] at thermal energies of collisions. Various Auger processes studied by Kishinevsky and Parilis [7], the two-electron capture [3–6] and the two-electron capture with simultaneous excitation of an ion [4] occupy an important place among the two-electron processes. Large values of total cross-sections and velocity constants allow us to assume that the specified processes with rearrangement are determined by electron transitions when the distance R between colliding particles is rather large. The presence of a small parameter $1/R$ gives a chance to elaborate a consistent asymptotic theory of such processes. No wonder that the framework of the asymptotic approach [3, 4, 6, 8, 9] has solely allowed many approved results to be obtained in the theory of multielectron ion–atom processes.

Additionally, in the last few decades considerable attention was given to study the influence of intensive electromagnetic radiation on characteristics of the inelastic processes accompanying collisions of highly charged ions with heavy atoms. Interest in this range of problems is caused by the possibility of inducing (by means of laser radiation) various processes occurring in ion–atom collisions, which involve electrons of outer and inner shells. In the majority of theoretical and experimental papers, the two-electron processes with rearrangement (see, e.g., [2, 6, 10–14] and references therein), which happen at large internuclear distances and are accompanied by absorption (emission) of photons, has been considered. The specified processes contain the strongly correlated electron transitions, which recently were intensively studied both experimentally [2, 12] and theoretically [10, 13]. Clarification of the basic features and basic mechanisms of radiative collisional processes with rearrangement is crucial for this field.

Since the future interest in similar investigations will doubtlessly increase, it is worthwhile to consider in detail the course of quantum processes corresponding to the Feynman diagrams presented in figure 1. To do that, it is necessary to take into account the fact that the followed exchange mechanism is typical for all two-electron processes with rearrangement: one of the active electrons of atom (ion) $A^{(Z_a-2)+}$ tunnels to a 'foreign' ion B^{Z_b+} with the following dipole–multipole simultaneous transition of two electrons located near different nuclei. Therefore, we assume in the present paper that the exchange matrix element corresponding to the course of two-electron processes with rearrangement is determined by the configuration when the active electrons are far apart—near different atoms (nuclei). In the case when under favourable conditions, the mechanisms of nonadiabatic coupling cause multielectronic transitions by involving the electrons of inner shells; the realistic calculations of parameters of the interaction of heavy (relativistic) atomic particles in the course of the collision should be based on the completely relativistic theory. However, even the formulation of the two-particle problem in the relativistic quantum theory encounters principal mathematical and logical obstacles. This

is mainly caused by the absence of the local Lorentz-invariant operator that takes into account the relativistic nature of the interelectron interaction (the effects of retardation). The modern quantum field theory of electromagnetic interactions (quantum electrodynamics), based on the *S*-matrix formalism and Feynman diagram technique, gives only the recipe of construction of such an operator in the form of a series in powers of α^2 (where $\alpha \approx 1/137$ is the fine structure constant). As early as 1929, Breit demonstrated [15] that accounting for the first (non-zero) term of such an expansion is a good approximation for the relativistic interaction between the two electrons under the condition of smallness of the retardation effects in the spectrum of He-like atoms. The expression for the relativistic operator of the interaction of two electrons obtained by Breit is of the form [15]

$$V(\vec{r}_{12}) = V_C(r_{12}) + V_B(\vec{r}_{12}) = \frac{e^2}{r_{12}} - \frac{e^2}{2r_{12}} \left[\vec{\alpha}_1 \vec{\alpha}_2 + \frac{(\vec{\alpha}_1 \vec{r}_{12})(\vec{\alpha}_2 \vec{r}_{12})}{r_{12}^2} \right], \qquad (1)$$

where $\vec{\alpha}_1$ and $\vec{\alpha}_2$ are the two commuting sets of the Dirac matrices, $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$, and the lower indices 1 and 2 distinguish the quantities relating to the first and second electron, respectively.

To date, expression (1) for the operator of the interelectron interaction is the base of most applications of the quasi-relativistic Dirac–Breit equation to multielectron problems of atomic physics and astrophysics. In particular, the quantum electrodynamic corrections of the Breit type V_B are often included in the perturbative calculations of atomic structures [16], but have not been taken into account in calculations of the electron structure of heavy multiply charged quasimolecules until now. However, the applicability of the Breit operator (1) is restricted by the requirement of smallness of the time $T_{\text{int}} = r_{12}/c$ of interaction transmission when compared with the average time $T_0 = 2\pi/\omega_0$ of electronic transitions, where ω_0 is the characteristic frequency of a spectrum of interacting electrons. It is obvious that this requirement is certainly satisfied when the distances between electrons are not too large, e.g. the interatomic distances of He-like atoms.

In view of this, in our previous paper [17], we have given the arguments that cast doubt on the possibility of using the Breit operator (1) for determination of the asymptotics of the exchange interaction, corresponding to simultaneous capture of two electrons in slow collisions of multiply-charged ions with atoms [3, 4]. In essence, these arguments pertain equally to other two-electron processes with rearrangement, including radiative collisional ones, if the basic contribution to the transition probability comes from the configuration when the electrons are located near different nuclei and the approximation of independent electrons is valid as a zero approximation. In fact, we meet here a new quantum electrodynamic problem of interaction of two quasimolecular electrons with emission (absorption) of a real photon that has no satisfactory solution until now. As far back as in the early seventies of the last century, the interest in the given problem arose in the connection with the intensive study of multiatomic systems placed into a field of radiation. The credit for the realization and development of new ideas in this direction goes to the authors of papers [18–21], where the problem of interaction of two bound electrons belonging to two hydrogen-like atoms was considered by using methods of quantum electrodynamics without any restrictions on interatomic distances. However, the generalized Breit operator constructed in the above quoted papers does not manifest the symmetry with respect to the interacting particles and therefore, cannot be utilized in the consistent relativistic quantum theory. It is precisely this circumstance that motivated us to return to the problem of two quasimolecular electrons anew.

The structure of the paper is as follows. In section 2, the general expression for the matrix element of the operator of the effective energy of interaction of the system of two quasimolecular electrons with the external field of radiation is given. In section 3, the

relativistic operator of interaction of two quasimolecular electrons via the field of virtual photons with emission (absorption) of the real photon is constructed. This operator is the generalization of the well-known Breit operator (1).

2. The matrix of effective energy of the interaction of two quasimolecular electrons at an arbitrary distance from each other

Describing a quasimolecule $(AB)^{(Z_a+Z_b-2)+}$ by methods of quantum electrodynamics, we consider it as a system of two electrons that interact via quantized electromagnetic field and move in an external (electric) field of two fixed nuclei A^{Z_a+} and B^{Z_b+} with charges Z_a and Z_b located at distance R from each other. Hereinafter, the nuclei are assumed to be infinitely heavy, point-like and structureless.

The simplest systems of this type are two-electron heteronuclear quasimolecules HeH^+, $HeBe^{4+}$, HeC^{6+}, etc. Such quasimolecules are produced in atmospheres of stars and experiments with thermonuclear plasma and atomic (or ionic) beams. These systems are as important as a helium atom in the theory of multielectron atoms. The results obtained here and developed theoretical methods can be used further for the investigation of more complicated quasimolecular systems.

The quantum electrodynamic perturbation theory based on the *S*-matrix formalism and Feynman diagram technique is a natural ground for the field-theoretic consideration of quantum mechanical problems. Here all interesting physical quantities, including the interaction potentials (exchange and long-range) of particles in the course of collision of the two-electron atom $A^{(Z_a-2)+}$ with the slow multiply-charged ion B^{Z_b+}, can be expressed in terms of the *S*-matrix, for which calculation we can use the standard Feynman rules formulated in quantum electrodynamics. In its standard quantum mechanical form (see, e.g., [3, 4, 8]), the matrix element of the two-electron exchange interaction of the atom $A^{(Z_a-2)+}$ with the ion B^{Z_b+} is determined as a non-diagonal matrix element of the operator of interelectron interaction calculated between (adiabatic) electron wavefunctions of the quasimolecule $(AB)^{(Z_a+Z_b-2)+}$, which correspond to the cases of various localizations of active electrons in the initial and final states. In the quantum electrodynamic approach used below, this matrix element is a constituent of a more general matrix element of the operator of effective energy of interaction of the system of two quasimolecular electrons with an external field of radiation. In this case, the third-order effects of quantum electrodynamics, which include the exchange of virtual photons between the electrons and emission (absorption) of a real photon, are considered. The Feynman diagrams of these effects are presented in figure 1; two parts of the interaction, each of which takes into account the intermediate states in the quasimolecular spectrum with either positive or negative frequency, are separated.

In order to reach the solution of the formulated problem, we shall consider processes of interaction of two quasimolecular electrons located near different nuclei that are accompanied by emission or absorption of real photons. To achieve this aim, we shall not follow previous papers [15, 22, 23] in assuming that the interelectron distance r_{12} is small in comparison with the corresponding wavelength $\lambda_0 = 2\pi c/\omega_0$ in the spectrum of the interacting electrons. All the equations obtained below are valid for arbitrary interelectron distances including arbitrarily large ones. One can meet the latter case (see review [4]) when seeking asymptotics $(R \rightarrow \infty)$ of the exchange interaction corresponding to the course of various multielectron processes with rearrangement in slow collisions of atoms with multiply-charged ions. The typical example of a process with rearrangement, occurring due to the direct interaction of two electrons located near different nuclei, is the quasiresonant two-electron charge exchange of atoms $A^{(Z_a-2)+}$ (e.g. helium) on multiply-charged ions B^{Z_b+} (N^{5+} [24], Ar^{6+} [25], C^{4+} [3–5]).

When the collision velocities are smaller than the orbital velocities of the bound electrons, the two-electron capture happens at large distances between the colliding atomic particles: $R \sim r_{12} \gg 1$. In the operating (i.e. asymptotic) domain of internuclear distances, the process occurs basically as an overlap of two inelastic transitions for each electron separately: the electron from an outer (inner) orbit of the atom $A^{(Z_a-2)+}$ transfers to an inner (outer) orbit of the atom $B^{(Z_b-2)+}$. Inelastic transitions are possible only as a result of the interaction of the electrons with each other via a field of virtual photons. The specified 'crossing' transitions of the electrons [3, 4] cause filling the intermediate excited states of the multiply charged projectile ion with following emission of photons in the short-wave ultra-violet and long-wave x-ray ranges of the spectrum.

In recent years, the cross-sections of radiation emission for some transitions in excited multiply-charged ions, created in the course of capture of the electrons by ions with charges $Z_b = 3 \div 8$ ($Z_b = 10, 18, 36$) from atoms of helium (argon) and from hydrogen molecules, have been determined by the methods of optical spectroscopy (see, e.g., [26]). In particular, the existence of the radiative two-electron charge exchange has been confirmed in experiments [24] in collisions of ions N^{5+} with atoms of helium at energies 0.357–4.28 keV per charge unit, where radiation of the line 76.5 nm (the transition $2s^2\,^1S$–$2s2p\,^1P$ in N^{3+}) was observed.

We shall now calculate the *S*-matrix of the third-order quantum electrodynamic effects, defined by the Feynman diagrams shown in figure 1. Let the coefficients *m* and *n* (*p* and *r*) denote sets of quantum numbers of the initial (final) states of the electrons. According to the general rules formulated, e.g. in [22], we obtain the matrix element

$$S^{(3)}_{i \to f} = S^{(3)}_{mn,pr} - S^{(3)}_{nm,pr}, \tag{2}$$

where

$$S^{(3)}_{mn,pr} = -\mathrm{i}e^3 \int \overline{\Psi}_r(x_1') \overline{\Psi}_p(x_2''') \mathcal{K}^{(3)}_{12}(1,2;3) \Psi_m(x_1'') \Psi_n(x_2''') \, \mathrm{d}^4 x_1' \, \mathrm{d}^4 x_1'' \, \mathrm{d}^4 x_2''', \tag{3}$$

and $S^{(3)}_{nm,pr}$ differs from $S^{(3)}_{mn,pr}$ by the permutation of indices *m* and *n*. Hereinafter, we use units $\hbar = c = 1$ and the following notations: $e = -|e|$ is the electron charge, $\Psi_{m(n)}$ are the solutions of the Dirac equation with the potential of two Coulomb centres for the given initial electronic states $m(n)$, $\overline{\Psi}_{r(p)} \equiv \Psi^+ \gamma_4$, Ψ^+ is the Hermitian conjugate two-Coulomb-centre wavefunction of the final electronic states $r(p)$, $x \equiv (\vec{r}, \mathrm{i}t)$ is a four-dimensional vector and $\vec{r}$ is a usual three-dimensional position vector of the electron relative to the nucleus A^{Z_a+} or B^{Z_b+}. Indices 1 and 2 are used to denote the quantities corresponding to the different electrons.

Using the standard rules of correspondence [22], it is easy to verify that the operator $\mathcal{K}^{(3)}_{12}(1,2,3)$ in (3) has the following analytic structure:

$$\mathcal{K}^{(3)}_{12}(1,2;3) = \widehat{A}(x_1') S(x_1', x_1'') \gamma''_{\mu_1} D(x_1'' - x_2''') \gamma'''_{\mu_2} + \gamma'_{\mu_1} S(x_1', x_1'') \widehat{A}(x_1'') \gamma'''_{\mu_2} D(x_1' - x_2'''). \tag{4}$$

Here, $\gamma_\mu \equiv (\vec{\gamma}, \gamma_4)$ is the covariant form of the Dirac matrices, $\vec{\gamma} = -\mathrm{i}\beta\vec{\alpha}$, $\gamma_4 = \beta$,

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

$\vec{\sigma}$ are the Pauli matrices, 0 and *I* are, respectively, 2×2 zero and unit matrices. The symbol $\widehat{A}$ denotes the convolution of the components of the 4-vector A_μ ($\mu = 1, 2, 3, 4$) with the Dirac matrices γ_μ: $\widehat{A} = \sum_\mu \gamma_\mu A_\mu$. In the representation of the secondary quantization, we write the operator of the four-dimensional potential of the electromagnetic field in the form

$$A_\mu(x_1') = \sum_{\vec{k},\lambda} g_{\vec{k}} e^\lambda_{\mu \vec{k}} \big(\widehat{C}_{\vec{k}\lambda} \mathrm{e}^{\mathrm{i}k x_1'} + \widehat{C}^+_{\vec{k}\lambda} \mathrm{e}^{-\mathrm{i}k x_1'} \big), \tag{5}$$

where $kx_1' = \vec{k}\vec{r}_1' - \omega_{\vec{k}}t_1'$ is the scalar product of the four-dimensional vector $x_1' = (\vec{r}_1', it_1')$ and the four-dimensional wave vector $k = (\vec{k}, i\omega_{\vec{k}})$ satisfying the condition $k^2 = \vec{k}^2 - \omega_{\vec{k}}^2 = 0$, $\omega_{\vec{k}} \equiv \omega$ is the frequency of real photons, $e_{\mu\vec{k}}^\lambda$ are the unit vectors of polarization of real photons (indices $\lambda = 1, 2$ correspond to the transverse polarization); $\widehat{C}_{\vec{k}\lambda}^+$ and $\widehat{C}_{\vec{k}\lambda}$ are the operators of creation and annihilation of real photons in the states with the polarisation $\lambda = 1, 2$, momentum $\vec{k}$ and energy ω. The coupling constants $g_{\vec{k}} = (2\pi/\omega\Omega)^{1/2}$ contain the normalization volume Ω, and since the final expressions does not contain Ω, we shall assume that $\Omega = 1$ henceforth.

In the Furry pattern [22], the electron propagator,

$$S(x_1', x_1'') = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega'' \, e^{i\omega''(t_1' - t_1'')} \sum_{l_\pm} \frac{\Psi_l(\vec{r}_1')\overline{\Psi}_l(\vec{r}_1'')}{\omega_l(1 - i0) + \omega''}, \tag{6}$$

corresponds to the internal electron lines in the diagrams of figure 1. The summation in (6) is carried out over all the intermediate electronic states with both positive ($l = l_+$) and negative ($l = l_-$) frequencies. In the Feynman gauge, the propagator

$$D(x_1'' - x_2''') = \frac{4\pi}{i(2\pi)^4} \int \frac{\exp\{i[k'(\vec{r}_1'' - \vec{r}_2''') - \omega'(t_1'' - t_2''')]\}}{\vec{k}'^2 - \omega'^2 - i0} d\vec{k}' \, d\omega' \tag{7}$$

corresponds to the internal photon lines, where $\vec{k}'$ denotes the wave vector of the virtual photons with the frequency ω'.

The primed indices of four-dimensional vectors $x = (\vec{r}, it)$ and the γ-matrices in the operator (4) and in the wavefunctions indicate that they belong to the domains of integration over the spacetime coordinates of the interacting particles in the S-matrix (3). The Dirac matrices γ_μ with different primed indices are mutually commuting.

The matrix element $S_{mn,pr}^{(3)}$ can be represented in the form that is convenient for applications and allows for a simple physical interpretation. For this purpose, let us separate the time factors

$$\Psi_m(x_1'') = \Psi_m(\vec{r}_1'') \, e^{-i\omega_m t_1''} \tag{8}$$

in the wavefunctions from (3) (similarly for Ψ_n, Ψ_r and Ψ_p). Consider instead of the S-matrix, the matrix of effective energy of interaction $U_{mn,pr}^{(3)}$ of a system of two bound electrons that is defined by the relation

$$S_{mn,pr}^{(3)} = -2\pi i U_{mn,pr}^{(3)} \delta(\omega + \omega_p - \omega_m + \omega_r - \omega_n). \tag{9}$$

Here, ω_m, ω_n are frequencies of the initial states of the electrons and ω_r, ω_p are frequencies of the final states. The sign of the frequency of an optical photon ω indicates that the positive-frequency part, which is proportionate to the creation operator of the photon in the given mode $\vec{k}\lambda$, is separated in the operator of the vector potential (5). The factorized one-dimensional δ-function usually expresses the law of conservation of energy

$$E_p - E_m + E_r - E_n + \hbar\omega = 0, \tag{10}$$

which is general for all the considered effects of the third-order (interaction of the electrons via the field of virtual photons + emission (absorption) of a real photon). The dependence on the Planck constant $\hbar$ in equation (10) is recovered in the explicit form. Equations (9) and (10) are written for the processes involving emission of a real photon; one has to flip the sign of the frequency ω in (9) and (10) to obtain the corresponding relations for absorption.

Having substituted the explicit expressions (6)–(8) for the propagators and the wavefunctions into the matrix operator (3) and carried out the integration over the times

t'_1, t''_1, t'''_2, the frequencies and the wave vectors in the matrix $S^{(3)}_{mn,pr}$, we obtain the following matrix of the effective energy of interaction ($\hbar = c = 1$):

$$
U^{(3)}_{mn,pr} = e^3 \int d\vec{r}\,' \, d\vec{r}\,'' \, d\vec{r}\,''' \left\{ -\frac{1}{|\vec{r}\,'' - \vec{r}\,'''|} \sum_{l_\pm} \frac{\exp\{i|\omega_p - \omega_n||\vec{r}\,'' - \vec{r}\,'''|\}}{\omega_l(1 - i0) - \omega - \omega_r} \overline{\Psi}_r(\vec{r}\,') \hat{A}(\vec{r}\,') \right.
$$

$$
\times \Psi_l(\vec{r}\,') \overline{\Psi}_l(\vec{r}\,'') \gamma''_\mu \Psi_m(\vec{r}\,'') \overline{\Psi}_p(\vec{r}\,''') \gamma'''_\mu \Psi_n(\vec{r}\,''')
$$

$$
-\frac{1}{|\vec{r}\,' - \vec{r}\,'''|} \sum_{l_\pm} \frac{\exp\{i|\omega_p - \omega_n||\vec{r}\,' - \vec{r}\,'''|\}}{\omega_l(1 - i0) + \omega - \omega_m}
$$

$$
\left. \times \overline{\Psi}_r(\vec{r}\,') \gamma'_\mu \Psi_l(\vec{r}\,') \overline{\Psi}_l(\vec{r}\,'') \hat{A}(\vec{r}\,'') \Psi_m(\vec{r}\,'') \overline{\Psi}_p(\vec{r}\,''') \gamma'''_\mu \Psi_n(\vec{r}\,''') \right\}, \tag{11}
$$

where $\Psi_{m(n)}, \Psi_{r(p)}$ and Ψ_l are the coordinate wavefunctions of the electrons (without the time factors), and $\vec{r}\,'$ and $\vec{r}\,''$ are the position vectors of the first electron, and $\vec{r}\,'''$ is the position vector of the second electron. Matrix (2) corresponds to one of the eight processes that occur due to the interaction of the active electrons via the field of virtual photons and are accompanied by emission (absorption) of a real photon. Other processes can be taken into account by the corresponding change of notation of the wavefunctions.

3. The generalized Breit operator

Following the previous section, one can represent the general expression for the matrix of the effective energy of interaction of the two bound quasimolecular electrons with the external field of radiation in the form

$$
U^{(3)}_{i \to f} = U^{(3)}_{mn,pr} - U^{(3)}_{nm,pr}. \tag{12}
$$

According to (11), the matrix element $U^{(3)}_{mn,pr}$ reads

$$
U^{(3)}_{mn,pr} = e^3 \int \Psi^+_r(\vec{r}\,') \Psi^+_p(\vec{r}\,''') \sum_{l\pm} \left\{ \gamma'_4 \gamma'_\delta A'_\delta \frac{\Psi_l(\vec{r}\,') \Psi^+_l(\vec{r}\,'')}{\omega_l(1 - i0) - \omega - \omega_r} \right.
$$

$$
\times \frac{1 - \vec{\alpha}''\vec{\alpha}'''}{|\vec{r}\,'' - \vec{r}\,'''|} \exp\{i|\omega_p - \omega_n||\vec{r}\,'' - \vec{r}\,'''|\}
$$

$$
+ \frac{1 - \vec{\alpha}'\vec{\alpha}'''}{|\vec{r}\,' - \vec{r}\,'''|} \exp\{i|\omega_p - \omega_n||\vec{r}\,' - \vec{r}\,'''|\}
$$

$$
\left. \times \frac{\Psi_l(\vec{r}\,') \Psi^+_l(\vec{r}\,'')}{\omega_l(1 - i0) + \omega - \omega_m} \gamma''_4 \gamma''_\delta A''_\delta \right\} \Psi_m(\vec{r}\,'') \Psi_n(\vec{r}\,''') \, d\vec{r}\,' \, d\vec{r}\,'' \, d\vec{r}\,'''. \tag{13}
$$

Here $\vec{\alpha}', \vec{\alpha}'', \vec{\alpha}'''$ are the Dirac matrices, the operator $\vec{\alpha}''(\vec{\alpha}')$ acts on the function $\Psi_m(\vec{r}\,'')$ $(\Psi_l(\vec{r}\,'))$ and the operator $\vec{\alpha}'''$ acts on the function $\Psi_n(\vec{r}\,''')$; A_δ are the components of the vector potential without the time factors, the index δ covers the values of 1, 2, 3 and the summation over the twice repeated index δ is carried out from $\delta = 1$ to $\delta = 3$.

Let us consider the first term in (13), and inside it, we separate the factor

$$
K(\vec{r}\,'', \vec{r}\,'''; \omega_{pn}) = \frac{1 - \vec{\alpha}''\vec{\alpha}'''}{|\vec{r}\,'' - \vec{r}\,'''|} \exp\left\{ \frac{i}{c}|\omega_{pn}||\vec{r}\,'' - \vec{r}\,'''| \right\}, \tag{14}
$$

corresponding to the exchange of virtual photons between the two electrons. Here, $\omega_{pn} = \omega_p - \omega_n$, and we use the system of units where $c \neq 1$. Because the retardation factor $\exp\left\{ \frac{i}{c}|\omega_{pn}||\vec{r}\,'' - \vec{r}\,'''| \right\}$, which depends explicitly on the initial and final energies of the system, appears in this expression, in the general case we cannot introduce the operator of

the interaction between the two electrons $B_{1l}(\vec{r}\,'', \vec{r}\,''')$, whose matrix element would be equal to $U^{(3)}_{mn,pr}$. However, we can construct such an operator within the approximation of small velocities ($v/c \ll 1$, where v is the velocity of the electron in the atom and c is the velocity of light in the vacuum).

Since expression (13) is valid in the united-atom limit ($R \to 0$, $Z = Z_a + Z_b$), it is worthwhile to use the simple example of two interacting electrons in a He-like atom in order to trace the procedure of replacement of the retardation factor in (14) by the corresponding operator. In this case, the estimate $|\omega_{pn}| \sim m(\alpha Z)^2$ takes place for the characteristic value of ω_{pn}, where $Z = Z_a + Z_b$ is the total charge of the nuclei A^{Z_a+} and B^{Z_b+}. Furthermore, we take into account that the characteristic value of the interelectron distance is defined by atomic sizes: $|\vec{r}\,'' - \vec{r}\,'''| \sim (m\alpha Z)^{-1}$. Hence, under the condition $\alpha Z \ll 1$, the exponent in (14) is a small quantity of the order of αZ, so one can expand the exponential factor in powers of $1/c$ to within terms $O(c^{-3})$. The transition from the specified expansion to its operator form in the c^{-2}-approximation is carried out by an appropriate symmetrization of all terms retained in the c^{-1}-expansion of the retardation factor (14) and by the subsequent replacement of the frequencies (by means of the Dirac equation) by the corresponding Hamiltonians of the separate electrons. As a result, we arrive at the known expression (1) for the Breit operator [15, 22, 23], which depends not only on the relative position of the pair of the electrons, but also on their spin variables.

Now we can say that the Breit expression (1) is a good approximation for the relativistic interaction between the two electrons as long as interelectron distances of interest are smaller than the corresponding wavelengths $\lambda_0 = 2\pi c/\omega_0$ in the spectrum of the interacting electrons. However, the results will be invalid, if we use expression (1) in the two-electron problems related to slow atomic collisions because interelectron distances are large.

In the case of interaction of the two quasimolecular electrons located at an arbitrary distance from each other near different nuclei, we meet with a radically opposite situation. Here, the situation becomes complicated because the absolute value of the exponents in $U^{(3)}_{mn,pr}$-matrix (13) becomes larger than a unit and the exponential factors become rapidly oscillating functions in the (asymptotic) domain of interelectron distances of interest. The specified circumstance renders the impossibility of direct usage of the several first terms of the c^{-1}-expansion of the retardation factor to construct the relativistic operator of interaction of the two bound electrons at arbitrary distances between them (including arbitrarily large ones). At the same time, this far domain of interelectron distances determines the probabilities of processes with rearrangement in the asymptotic limit ($R \to \infty$) in many two-electron problems of the theory of slow atomic collisions (e.g. the problem of quasiresonant two-electron charge exchange in the reaction $He + N^{5+} \to He^{2+} + N^{3+}$). In this domain, which we shall call *the domain of far electron correlations*, the effects of retardation of interaction of charged particles are amplified essentially.

As mentioned in the introduction, the fundamental possibility of generalization of the Breit operator to the case of quasimolecular electrons has been established in papers [19, 20] in the example of the problem of interaction of two bound electrons belonging to two hydrogen-like atoms, located at an arbitrary distance from each other. However, referring to these papers, we have discovered [17] that the generalized Breit operator obtained therein does not manifest the symmetry with respect to the interacting particles and, therefore, cannot be utilized in the consistent relativistic quantum theory. As mentioned in [17], the essential deficiency of the procedure of passing from the retardation factor to the corresponding operator, which was accepted in papers [19, 20], consists in an unequal treatment of the pair of interacting particles. The problem of two quasimolecular electrons with emission (absorption) of a real photon demands a further careful investigation for this very reason.

The method, which we shall use to solve this important quantum electrodynamic problem, represents a further development of the method applied in papers [17, 19] to solving the problem of the interaction of two atomic electrons in the framework of the second-order effects of quantum electrodynamics. As shown below, consistent application of the procedure of symmetrization of the retardation factor with respect to both the particles leads to the appearance of additional terms in the relativistic operator of the interaction of the two electrons when compared to both the standard (1) and generalized [20] Breit operators.

As known [3, 4, 27], the exponential dependence of one-electron two-centre wavefunctions on coordinates results in the fact that at large internuclear distances R, the integration over $\vec{r}\,''$ or $\vec{r}\,'$ in expression (13) is localized in the vicinity of the nucleus B^{Z_b+}. In (13), the integration over $\vec{r}\,'''$ is basically localized in the vicinity of A^{Z_a+}. Thus, two spherical domains of coordinates $|\vec{r}\,' - \vec{R}|$ $(|\vec{r}\,'' - \vec{R}|) \lesssim (m\alpha Z_b)^{-1}$ and $|\vec{r}\,'''| \lesssim (m\alpha Z_a)^{-1}$, which physically correspond to the localization of the electrons near the different centres, are the most essential for rather large R in the corresponding integrals of matrix (13). For the specified domains of electron coordinates, it is necessary to construct the operator $B_{1l}(\vec{r}\,'', \vec{r}\,''')$, describing the exchange of virtual photons in terms of matrix (13).

After these preliminary remarks, we shall immediately deduce the relativistic operator of interaction of the two quasimolecular electrons located at an arbitrary distance from each other. The initial object for us is the two-electron atom $A^{(Z_a-2)+}$ located at an arbitrary distance R from the nucleus B^{Z_b+}. Consider now the typical situation (for processes with rearrangement) when one of the active electrons of the atom $A^{(Z_a-2)+}$, say the first electron, has tunnelled into the vicinity of the 'foreign' nucleus B^{Z_b+} and the second electron has remained near the 'host' nucleus A^{Z_a+}. If the domains of spatial localization of the electrons near the different nuclei (of the first electron near the nucleus B^{Z_b+} and of the second one near A^{Z_a+}) are rather small (of the order of atomic sizes) and rather far apart, then the relative distance between the electrons can be expanded in powers of the ratio $\Delta r/R$ under the condition $\Delta r < R < \infty$,

$$|\vec{r}\,'' - \vec{r}\,'''| = R\left(1 + \frac{\vec{R}\Delta\vec{r}}{R^2} + \frac{M}{R}\right). \tag{15}$$

Here, $\Delta\vec{r} = \vec{r}_{1b} - \vec{r}_{2a}$, $\Delta r = |\Delta\vec{r}|$, $\vec{r}_{1b}$ $(\vec{r}_{2a})$ is the position vector of the first (second) electron with respect to the nucleus B^{Z_b+} (A^{Z_a+}), $M = M(\Delta\vec{r}, \vec{R})$ are small corrections containing higher powers of $\Delta r/R$. Therewith, the smallness of the parameter $\Delta r/R$ means that the electrons are located close to the different atoms (nuclei).

In previous papers [15, 22, 23], when constructing the expansion of the retardation factor, it was assumed that is the quantity $\omega_0 r/c \ll 1$ (or formally $1/c$) is a unique small parameter, where r is the distance between the electrons. It is obvious that this requirement is satisfied for not too large distances between the electrons, for instance, for interatomic distances of helium-like atoms. The asymptotic expansion of the K-factor (14) is constructed below for the case when both $1/c$ and $\Delta r/R$ are natural small parameters. Such a selection of small parameters differs from the limiting case of the one (united) He-like atom $(R = 0)$, studied by Drake [23], and is realized within the used quasimolecular model, for instance, when the electrons are far apart and near the different centres.

To assign the exact meaning to the K-factor (14), we transform it as follows:

$$K(\vec{r}\,'', \vec{r}\,'''; \omega_{pn}) = \frac{1 - \vec{\alpha}\,''\vec{\alpha}\,'''}{|\vec{r}\,'' - \vec{r}\,'''|}\, e^{\frac{i}{c}|\omega_{pn}|R}\, e^{\frac{i}{c}|\omega_{pn}|(|\vec{r}\,'' - \vec{r}\,'''| - R)}. \tag{16}$$

For the quasimolecular electrons located near the different nuclei, the performed transformation is convenient due to the factorization of the R-dependent relativistic factor $\exp\left\{\frac{i}{c}|\omega_{pn}|R\right\}$ of the amplification of the effects of dynamic retardation of the interaction,

which are encoded in the dependence of this factor on the initial and final energies of the system: $\omega_{pn} = E_p - E_n$. However, a basic advantage of such a transformation is the fact that the problem of the expansion of the retardation factor (14) is reduced to the expansion of the specialized (for the considered quasimolecular model with the two electrons near the different centres) exponential multiplier $\exp\left\{\frac{i}{c}|\omega_{pn}|(|\vec{r}\,'' - \vec{r}\,'''| - R)\right\}$ by means of this transformation. The presence of the difference $|\vec{r}\,'' - \vec{r}\,'''| - R$ in the last exponent indicates that such an expansion should be carried out not only in the powers of $1/c$, but also in the powers of the small parameter $\Delta r/R$.

Henceforth, we shall assume that the requirement

$$\frac{1}{c}|\omega_{pn}|\frac{\vec{R}\Delta\vec{r}}{R} \ll 1 \tag{17}$$

is satisfied. The distance R between the nuclei can vary in the range $\Delta r \leqslant R < \infty$ and has a dynamical meaning in our problem, i.e. it appears in the expression for the energy spectrum.

The analysis given above demonstrates that under condition (17), the exponential factor $\exp\left\{\frac{i}{c}|\omega_{pn}|(|\vec{r}\,''-\vec{r}\,'''|-R)\right\}$ on the right-hand side of (16) is small, compared to an unity. This fact allows us to formally expand the K-factor (16) in powers of $1/c$. We have the expansion up to the terms of the order of c^{-2} inclusively:

$$K(\vec{r}\,'', \vec{r}\,'''; \omega_{pn}) = (1 - \vec{\alpha}''\vec{\alpha}''')\exp\left\{\frac{i}{c}|\omega_{pn}|R\right\}$$
$$\times \left\{f_0(\vec{r}\,'', \vec{r}\,''') + \frac{i}{c}|\omega_{pn}|f_1(\vec{r}\,'', \vec{r}\,''') - \frac{1}{2c^2}\omega_{pn}^2 f_2(\vec{r}\,'', \vec{r}\,''')\right\}. \tag{18}$$

We provide the explicit form of the coefficient functions f_0, f_1 and f_2, finally determining the dependence of the required relativistic operator $B_{1l}(\vec{r}\,'', \vec{r}\,''')$ on the spatial positions of the electrons:

$$
\begin{aligned}
f_0(\vec{r}\,'', \vec{r}\,''') &= \frac{1}{g_0(\vec{r}\,'', \vec{r}\,''')} = \frac{1}{|\vec{r}\,'' - \vec{r}\,'''|}, \\
f_1(\vec{r}\,'', \vec{r}\,''') &= \frac{g_1(\vec{r}\,'', \vec{r}\,''')}{g_0(\vec{r}\,'', \vec{r}\,''')} = \frac{|\vec{r}\,'' - \vec{r}\,'''| - R}{|\vec{r}\,'' - \vec{r}\,'''|}, \\
f_2(\vec{r}\,'', \vec{r}\,''') &= \frac{g_2(\vec{r}\,'', \vec{r}\,''')}{g_0(\vec{r}\,'', \vec{r}\,''')} = \frac{(|\vec{r}\,'' - \vec{r}\,'''| - R)^2}{|\vec{r}\,'' - \vec{r}\,'''|}.
\end{aligned}
\tag{19}
$$

Now let us use the fact that the considered problem contains (in addition to $1/c$) one more small parameter $\Delta r/R$ and expand the functions g_0, g_1, g_2 appearing on the right-hand side of equalities (19) in powers of $\Delta r/R$:

$$
\begin{aligned}
g_0(\Delta\vec{r}, \vec{R}) &= R\left[1 + \frac{\vec{R}\Delta\vec{r}}{R^2} + \frac{M}{R}\right], \\
g_1(\Delta\vec{r}, \vec{R}) &= \frac{\vec{R}\Delta\vec{r}}{R} + M, \qquad g_2(\Delta\vec{r}, \vec{R}) = \left[\frac{\vec{R}\Delta\vec{r}}{R} + M\right]^2.
\end{aligned}
\tag{20}
$$

Note that in this case, given formulae (15), (20) are heuristic in character because only the leading terms of the asymptotic expansions are written in an explicit form here.

From the form of expressions (15) and (20), it formally follows that the parameter of expansion (18) is actually not $1/c$, but the small dimensionless quantity (17), and it is obvious that the expansion coefficients (18) in turn are power series in $\Delta r/R$. Actually, it means that if the distance between the electrons is comparable with the distance between the nuclei, then one can use formulae (20) and expand the functions f_0, f_1, f_2 (18) into power series with

respect to $\Delta r / R$. If such expansion is not performed, then one can take into account (within the c^{-2}-approximation of interest) the interaction of the quasimolecular electrons of all the multipolarities in the closed form.

We eliminate the frequencies in expression (18) by using the Dirac equations:

$$\widehat{H}''\Psi_m(\vec{r}\,'') = \omega_m \Psi_m(\vec{r}\,''), \qquad \widehat{H}'''\Psi_n(\vec{r}\,''') = \omega_n \Psi_n(\vec{r}\,'''). \tag{21}$$

Evidently, in order to take into account completely the retardation effects of interaction of the electrons, we should transform the expansion of the K-factor (18) such that it takes the form that is symmetric with respect to both the electrons. We shall carry out such symmetrization below and simultaneously represent the required relativistic operator $B_{1l}(\vec{r}\,'', \vec{r}\,''')$ in the form that is convenient for perturbative calculations.

In order to move from frequencies to operators, we shall first transform the second term (on the right-hand side of (18)) into a slightly different equivalent form. Namely, by means of the easily checkable relation $\omega_n - \omega_p = R_{1l}(\omega_l - \omega_m)$, we divide this term into two groups of terms:

$$|\omega_{pn}| f_1(\vec{r}\,'', \vec{r}\,''') \equiv \pm \tfrac{1}{2}[R_{1l}(\omega_l - \omega_m) + (\omega_n - \omega_p)] f_1(\vec{r}\,'', \vec{r}\,'''). \tag{22}$$

Here, $R_{1l} = (\omega_n - \omega_p)/(\omega_l - \omega_m)$, the plus sign in (22) corresponds to the case $\omega_p < \omega_n$, and the minus sign corresponds to the case $\omega_p > \omega_n$. Because in the calculations of the matrix elements (13), the quantity $K(\vec{r}\,'', \vec{r}\,'''; \omega_{pn})$ is always multiplied by $\Psi_l^+(\vec{r}\,'')\Psi_p^+(\vec{r}\,''')$ from the left and by $\Psi_m(\vec{r}\,'')\Psi_n(\vec{r}\,''')$ from the right and subsequently integrated over $\vec{r}\,''$ and $\vec{r}\,'''$, one can replace the frequencies ω_m and ω_n in the last expression by the operators $\widehat{H}''$ and $\widehat{H}'''$ to the right of the factor $f_1(\vec{r}\,'', \vec{r}\,''')$ and replace the frequencies ω_l and ω_p with the operators $\widehat{H}''$ and $\widehat{H}'''$ to the left of the factor $f_1(\vec{r}\,'', \vec{r}\,''')$. After such transformations, the expression on the right-hand side of (22) takes the following form:

$$|\omega_{pn}| f_1(\vec{r}\,'', \vec{r}\,''') \to \pm \tfrac{1}{2}\{R_{1l}[\widehat{H}'' f_1(\vec{r}\,'', \vec{r}\,''') - f_1(\vec{r}\,'', \vec{r}\,''')\widehat{H}''] + f_1(\vec{r}\,'', \vec{r}\,''')\widehat{H}'''$$

$$- \widehat{H}''' f_1(\vec{r}\,'', \vec{r}\,''')\} = \pm \tfrac{1}{2}\{R_{1l}[\widehat{H}'', f_1(\vec{r}\,'', \vec{r}\,''')] + [f_1(\vec{r}\,'', \vec{r}\,'''), \widehat{H}''']\}. \tag{23}$$

Hereinafter, the square brackets denote the commutators of corresponding quantities.

Taking into account the relation $\omega_n - \omega_p = R_{1l}(\omega_l - \omega_m)$, we transform the third term in expansion (18) to the symmetric form

$$- \omega_{pn}^2 f_2(\vec{r}\,'', \vec{r}\,''') = R_{1l}(\omega_l - \omega_m)(\omega_p - \omega_n) f_2(\vec{r}\,'', \vec{r}\,'''). \tag{24}$$

Replace the frequencies in (24) by operators analogously to what has been done in (23). Then, we have the following transformation:

$$-\omega_{pn}^2 f_2(\vec{r}\,'', \vec{r}\,''') \to R_{1l}\{f_2(\vec{r}\,'', \vec{r}\,''')\widehat{H}''\widehat{H}''' - \widehat{H}'' f_2(\vec{r}\,'', \vec{r}\,''')\widehat{H}''' - \widehat{H}''' f_2(\vec{r}\,'', \vec{r}\,''')\widehat{H}''$$

$$+ \widehat{H}''\widehat{H}''' f_2(\vec{r}\,'', \vec{r}\,''')\} = R_{1l}[\widehat{H}'', [\widehat{H}''', f_2(\vec{r}\,'', \vec{r}\,''')]]. \tag{25}$$

Having substituted the operator expressions (23) and (25) into the right-hand side of (18), we arrive at the following transformation of the K-factor:

$$K(\vec{r}\,'', \vec{r}\,'''; \omega_{pn}) \to (1 - \vec{\alpha}''\vec{\alpha}''')\, e^{\frac{i}{c}|\omega_{pn}|R}\left\{ f_0(\vec{r}\,'', \vec{r}\,''') \pm \frac{i}{2c}(R_{1l}[\widehat{H}'', f_1(\vec{r}\,'', \vec{r}\,''')] \right.$$

$$\left. + [f_1(\vec{r}\,'', \vec{r}\,'''), \widehat{H}''']) + \frac{R_{1l}}{2c^2}[\widehat{H}'', [\widehat{H}''', f_2(\vec{r}\,'', \vec{r}\,''')]] \right\}. \tag{26}$$

The functions f_0, f_1 and f_2 appearing here are still given by equalities (19). Note that the thus found representation (26) for the K-factor ensures the equality in the description of the pair of interacting particles.

In our consideration, the double expansion (18), (20) therefore represents the *K*-factor (14) in powers of $1/c$ and $\Delta r/R$. Moreover, we retain only the first three terms in the expansion in $1/c$, imposing no restrictions on the expansion in the small parameter $\Delta r/R$ because the function *M* contains all the higher order terms. In what follows, we therefore take into account the interactions of the two quasimolecular electrons of an arbitrary multipolarity.

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

$$
\begin{aligned}
\widehat{H}'' &= c\vec{\alpha}''\hat{\vec{p}}'' + \beta''mc^2 - \frac{Z_a e^2}{|\vec{r}\,'' - \vec{R}_a|} - \frac{Z_b e^2}{|\vec{r}\,'' - \vec{R}_b|}, \\
\widehat{H}''' &= c\vec{\alpha}'''\hat{\vec{p}}''' + \beta'''mc^2 - \frac{Z_a e^2}{|\vec{r}\,''' - \vec{R}_a|} - \frac{Z_b e^2}{|\vec{r}\,''' - \vec{R}_b|}.
\end{aligned}
\tag{27}
$$

Here, we keep $\hbar \neq 1$ explicitly, $Z_a e$ and $Z_b e$ are the charges of the point nuclei, $\hat{\vec{p}}'' = -i\hbar\vec{\nabla}''$ and $\hat{\vec{p}}''' = -i\hbar\vec{\nabla}'''$ denote the operators of momentum of the electrons. All the position vectors in (27) are measured from the origin of the laboratory system of coordinates, $\vec{R}_a$ and $\vec{R}_b$ are the position vectors of nuclei A^{Z_a+} and B^{Z_b+}, respectively; the internuclear distance can be expressed as $R = |\vec{R}_b - \vec{R}_a|$.

Analyzing the performed calculations, it is easy to understand that result (26) can be readily generalized. For this purpose it is necessary to introduce additional terms into the Hamiltonians (27), for instance, to take into account a finite size and spin of the nucleus, screening of the nucleus field by the electronic shell of the atomic core, etc. However, we must remember that the eigenvalue problem (21) for such a Hamiltonian cannot be solved in an explicit form except for limiting cases (e.g. the case of large internuclear distances [27]).

Let us now calculate the commutators appearing on the right-hand side of (26). First, note that only one term in $\widehat{H}''(\widehat{H}''')$, namely $c\vec{\alpha}''\hat{\vec{p}}''(c\vec{\alpha}'''\hat{\vec{p}}''')$, is noncommuting with $f_1(\vec{r}\,'', \vec{r}\,''')$ and $f_2(\vec{r}\,'', \vec{r}\,''')\, c\vec{\alpha}''\hat{\vec{p}}''(c\vec{\alpha}'''\hat{\vec{p}}''')$. For this reason, having substituted the expressions (27) for the operators $\widehat{H}''$ and $\widehat{H}'''$, we can disregard all the terms not containing the matrices $\vec{\alpha}''$, $\vec{\alpha}'''$ simultaneously:

$$
\begin{aligned}
&[\widehat{H}'', f_1] = c[\vec{\alpha}''\hat{\vec{p}}'', f_1], \quad [f_1, \widehat{H}'''] = c[f_1, \vec{\alpha}'''\hat{\vec{p}}'''], \\
&[\widehat{H}'', [\widehat{H}''', f_2]] = c^2[\vec{\alpha}''\hat{\vec{p}}'', [\vec{\alpha}'''\hat{\vec{p}}''', f_2]].
\end{aligned}
\tag{28}
$$

Having calculated the commutators (28) by means of the easily verifiable equations $[\vec{\alpha}''\hat{\vec{p}}'', f_{1,2}] = \vec{\alpha}''\hat{\vec{p}}'' f_{1,2}, [\vec{\alpha}'''\hat{\vec{p}}''', f_{1,2}] = \vec{\alpha}'''\hat{\vec{p}}''' f_{1,2}$, we find that the contributions of the second and third terms into expansion (26) are determined by the operator expressions:

$$
\pm\frac{i}{2c}(R_{1l}[\widehat{H}'', f_1] + [f_1, \widehat{H}''']) = \pm\hbar R \frac{R_{1l}\vec{\alpha}''\vec{n} + \vec{\alpha}'''\vec{n}}{2|\vec{r}\,'' - \vec{r}\,'''|^2},
\tag{29}
$$

$$
\begin{aligned}
\frac{1}{2c^2} R_{1l}[\widehat{H}'', [\widehat{H}''', f_2]] = -\frac{\hbar^2}{2} R_{1l}\bigg[(\vec{\alpha}''\vec{\nabla}'')(\vec{\alpha}'''\vec{\nabla}''')|\vec{r}\,'' - \vec{r}\,'''| \\
+ R^2(\vec{\alpha}''\vec{\nabla}'')(\vec{\alpha}'''\vec{\nabla}''')\frac{1}{|\vec{r}\,'' - \vec{r}\,'''|} \bigg],
\end{aligned}
\tag{30}
$$

where $\vec{n} = (\vec{r}\,'' - \vec{r}\,''')/|\vec{r}\,'' - \vec{r}\,'''|$. Thus, the operator, which describes (in the $U^{(3)}_{mn,pr}$-matrix (13)) the interaction of the two electrons via the field of virtual photons, is of the form

$$
\begin{aligned}
B_{1l}(\vec{r}\,'', \vec{r}\,''') = e^2 \exp\left\{\frac{i}{c}|\omega_{pn}|R\right\} \bigg\{ \frac{1 - \vec{\alpha}''\vec{\alpha}'''}{|\vec{r}\,'' - \vec{r}\,'''|} \pm R\frac{R_{1l}\vec{\alpha}''\vec{n} + \vec{\alpha}'''\vec{n}}{2|\vec{r}\,'' - \vec{r}\,'''|^2} \\
+ \frac{R_{1l}}{2}\left(\frac{\vec{\alpha}''\vec{\alpha}''' - (\vec{\alpha}''\vec{n})(\vec{\alpha}'''\vec{n})}{|\vec{r}\,'' - \vec{r}\,'''|} - R^2\frac{\vec{\alpha}''\vec{\alpha}''' - 3(\vec{\alpha}''\vec{n})(\vec{\alpha}'''\vec{n})}{|\vec{r}\,'' - \vec{r}\,'''|^3} \right) \bigg\}.
\end{aligned}
\tag{31}
$$

Here, the plus sign in front of the term containing the factor R corresponds to the case $\omega_p < \omega_n$, and the minus sign corresponds to the case $\omega_p > \omega_n$. The first term in (31) represents the energy of the instantaneous (Coulomb) interaction of the electrons, and other ones take into account the corrections due to the retardation of relativistic interaction and the presence of the electron spins.

Similarly, we consider the exchange of virtual photons in the second term of matrix (13) (see the second diagram in figure 1). After necessary transformations of the corresponding retardation factor, we arrive at the operator $B_{2l}(\vec{r}\,', \vec{r}\,''')$, which can be obtain from (31) after replacing the coefficient R_{1l} by $R_{2l} = (\omega_n - \omega_p)/(\omega_r - \omega_l)$.

In the special case of the resonance exchange of photons, we have $R_{1l} = 1$, and the operator (31) is transformed into the generalized Breit operator [17] for the interaction of the two quasimolecular electrons without emission or absorption of real photons. The condition $R_{1l} = 1$ implies that the transition of the system of the two particles into the intermediate state should be carried out according to the law of conservation of energy: $E_n - E_p = E_l - E_m$. As it is expected, the operator (31) is transformed into the known Breit operator (1) for the interaction of the two atomic electrons in He-like atoms at $R_{1l} = 1$ and $R \to 0$ (the united-atom limit). Thereby, one can consider the operator (31) as a natural generalization of the Breit operator [15, 22] to the case of arbitrarily large interelectron distances where influence of the effect of dynamic retardation on the spin interactions of the electrons is amplified. The nontrivial moment of such a generalization is the presence of additional (compared to the Breit expression (1)) retardation terms depending on both the dimensional parameter R and the spin operators of the electrons in expression (31) for $B_{1l}(\vec{r}\,'', \vec{r}\,''')$. Furthermore, note that this additional contribution to $B_{1l}(\vec{r}\,'', \vec{r}\,''')$ has essentially a relativistic character and appears due to an additional retardation of the relativistic interaction between the two quasimolecular electrons located at large distances from each other, compared to $\lambda_0 = 2\pi c/\omega_0$.

According to the improvement of the Breit operator made in the present paper, it is justifiable to call expression (31) *the generalized radiative Breit operator of the long-range type* (to stress the possibility of using it to solve a wide range of two-electron problems in physics of radiative atom–molecule collisions [2, 6, 10–14], in the theory of quasimolecular Auger spectroscopy [7], and in several important problems of nonlinear and quantum optics [17–21, 23]).

Note that the obtained expression (31) for the operator $B_{1l}(\vec{r}\,'', \vec{r}\,''')$ is symmetrical with respect to both the electrons. This is the result of the appropriate symmetrization of all the terms in expansion (18) of the K-factor with respect to both the electrons. The symmetrical representation for the relativistic operator of interaction of the two quasimolecular electrons has been originally obtained in paper [17] on the basis of a consistent consideration of the second-order effects of quantum electrodynamics that take into account the virtual exchange of photons of all the polarizations.

In the series of papers [18–21] that actually led to the present stage of the investigations of the problem of two electrons, the following expression has been obtained for the relativistic operator of interaction of the two atomic electrons at an arbitrary distance from each other within that of the third-order effects of quantum electrodynamics:

$$\widetilde{B}_{1l}(\vec{r}\,'', \vec{r}\,''') = e^2 \exp\left\{\frac{\mathrm{i}}{c}|\omega_{pn}|R\right\} \left\{\frac{1 - \vec{\alpha}''\vec{\alpha}'''}{|\vec{r}\,'' - \vec{r}\,'''|} + R\frac{\vec{\alpha}'''\vec{n}}{|\vec{r}\,'' - \vec{r}\,'''|^2}\right.$$

$$\left. + \frac{R_{1l}}{2}\left(\frac{\vec{\alpha}''\vec{\alpha}''' - (\vec{\alpha}''\vec{n})(\vec{\alpha}'''\vec{n})}{|\vec{r}\,'' - \vec{r}\,'''|} - R^2\frac{\vec{\alpha}''\vec{\alpha}''' - 3(\vec{\alpha}''\vec{n})(\vec{\alpha}'''\vec{n})}{|\vec{r}\,'' - \vec{r}\,'''|^3}\right)\right\}. \tag{32}$$

As can be readily seen from the structure of the second term of (32), which is proportional to R, the principal drawback of this operator is the absence of the symmetry in the description of the pair of interacting particles.

An important remark, which follows from the comparison of formulae (31) and (32), is that a consistent application of the procedure of symmetrization of the two last terms in the expansion of the retardation factor (18) leads to the appearance of a new term $\pm R_{1l} R(\vec{\alpha}''\vec{n})/2|\vec{r}'' - \vec{r}'''|^2$ in the final expression (31) for the operator $B_{1l}(\vec{r}'', \vec{r}''')$ in comparison with representation (32). This term is due to an additional retardation in the interaction of the electrons located at arbitrarily large distances from each other. Therefore, one can expect that some results of references [18–21] might be erroneous because of employing the operator (32) in the calculations.

4. Conclusion

The problem of interaction of two quasimolecular electrons via a field of virtual photons that is accompanied by emission or absorption of a real photon is solved in the current paper. Such an interaction is considered as a third-order effect of quantum electrodynamics described by the Feynman diagrams in figure 1. We now shall list main properties of this interaction.

We have two domains of the configuration space where the generalized Breit operator of the long-range interaction type (31) behaves differently if the relative distance $r_{12} = |\vec{r}'' - \vec{r}'''|$ between the two electrons changes. For instance, in the united-atom limit ($R \to 0$), formula (31) for the operator $B_{1l}(\vec{r}'', \vec{r}''')$ becomes the limiting (Breit) expression (1), which correctly describes the retardation effects of the relativistic interaction only at a small interparticle distance r_{12}. More precisely, we can conclude that the domain of applicability of the Breit formula (1) is given by

$$\omega_0 r_{12}/c \ll 1, \tag{33}$$

where ω_0 is a characteristic frequency of the spectrum of the interacting electrons. Let Ω_{cl} denote such a domain of the configuration space, which we call the domain of close electron correlations. However, in the domain Ω_f, where the electrons belong to the different nuclei and inequality (17) is satisfied for all $\Delta r \leqslant R < \infty$, the Breit operator (1) fails to describe even qualitatively the relativistic interaction of the two electrons. At the same time, the relativistic operator B_{1l} (31) constructed herein describes the retarded interaction of the two quasimolecular electrons in the domain Ω_{cl} of close electron correlations as well as in the domain Ω_f of far electron correlations. Therefore, this operator can be used to solve many two-electron problems in atomic and molecular spectroscopy, astrophysics, theory of slow atomic collisions, etc. Moreover, it is necessary to employ the relativistic operator of interaction of the two electrons (31) in mathematical modelling of atomic clusters [28], investigation of optical properties of various nanostructural systems in intense optical fields [29, 30] and solving some important problems of recording, reading and transmission of quantum information from one two-level atom (qubit) to another [31, 32].

For each of the domains Ω_{cl} and Ω_f of the interelectron distances r_{12}, we have the corresponding time scales of interaction transfer and the corresponding approximated calculations, in which we separate small parameters and take into account the different types of intermediate states and interactions. Thus, we reiterate not only that we can use the generalized Breit operator $B_{1l}(\vec{r}'', \vec{r}''')$ to solve the multielectron two-centre problems, but also the quantum electrodynamic treatment of two-electron interaction based on the standard Breit operator (1) is incomplete.

As shown in the preceding section, the standard assumption in the derivation of the Breit operator (1) is that the only small parameter, with respect to which the retardation factor must be expanded, is quantity (33) [22]. This means that in addition to the characteristic (mean) transition time $T_e = 2\pi/\omega_0$, we also use the unified time scale $T_{\text{int}} = r_{12}/c$, corresponding to the domain Ω_{cl}. We can interpret this time as an interaction transfer time. Then, the condition $2\pi T_{\text{int}} \ll T_e$, that a substantial change in the electron density of the system of the two interacting electrons occurs during the interaction transfer time, must be satisfied.

At rather large interelectron distances (in the domain Ω_f), where the interaction transfer time $T_{\text{int}} = R/c$ is much larger than the mean electron transition time T_e, the natural small parameter for expansion is the dimensionless quantity (17). Exchange by virtual photons at such distances results in the interelectron interaction (31) that, in addition to the Coulomb and Breit interactions (1), contains additional relativistic terms depending on the electron spin operators and internuclear distance R. These terms appear due to an additional retardation of the interaction of the two quasimolecular electrons located at an arbitrary distance from each other. Thereby, expression (31) for the relativistic operator $B_{1l}(\vec{r}'', \vec{r}''')$ differs from the similar result (32) of papers [18–21] not only by the additional factor $\pm 1/2$ in the second term of expression (31), but also by the additional term $\pm R R_{1l}(\vec{\alpha}''\vec{n})/2|\vec{r}'' - \vec{r}'''|^2$, which takes into account the additional retardation of the interaction of the two quasimolecular electrons.

References

[1] Gillaspy J D 2001 *J. Phys. B: At. Mol. Opt. Phys.* **34** R93
[2] Verma P *et al* 2005 *Nucl. Instrum. Methods Phys. Res.* B **235** 309
[3] Karbovanets M I, Lazur V Yu and Chibisov M I 1984 *Zh. Eksp. Teor. Fiz.* **86** 84
    Karbovanets M I, Lazur V Yu and Chibisov M I 1984 *Sov. Phys.—JETP* **59** 47 (Engl. Transl.)
[4] Chibisov M I and Janev R K 1988 *Phys. Rep.* **166** 1
[5] Grozdanov T P, Janev R K and Lazur V Yu 1985 *Phys. Scr.* **32** 64
[6] Barat M and Roncin P 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 2205
[7] Parilis E S, Kishinevskii L M, Matveev V I and Krakov B G 1989 *Auger Processes at Atomic Collisions* (Tashkent: PhAN) (in Russian)
[8] Nikitin E E and Smirnov B M 1990 *Slow Atomic Collisions* (Moscow: Energoatomizdat) (in Russian)
[9] Smirnov B M 2001 *Usp. Fiz. Nauk* **171** 233
    Smirnov B M 2001 *Phys. Usp.* **44** 221 (Engl. Transl.)
[10] Eichler J and Meyerhof W E 1995 *Relativistic Atomic Collisions* (New York: Academic)
[11] Agre M Ya and Rapoport L P 1979 *Zh. Eksp. Teor. Fiz.* **77** 74
     Agre M Ya and Rapoport L P 1979 *Sov. Phys.—JETP* **50** 37 (Engl. Transl.)
[12] Beiersdorfer P *et al* 1999 *Phys. Scr.* **T80A** 121
[13] Tökési K *et al* 1999 *Phys. Scr.* **T80** 408
[14] Lankin A V, Morozov I V, Norman G E and Skobelev I Yu 2008 *Zh. Eksp. Teor. Fiz.* **133** 701
     Lankin A V, Morozov I V, Norman G E and Skobelev I Yu 2008 *JETP* **106** 608
[15] Breit G 1929 *Phys. Rev.* **34** 553
[16] Grant I P 2007 *Relativistic Quantum Theory of Atoms and Molecules: Theory and Computation* (New York: Springer)
[17] Lazur V Yu, Migalina S I and Reitii A K 2009 *Teor. Mat. Fiz.* **158** 391
     Lazur V Yu, Migalina S I and Reitii A K 2009 *Theor. Math. Phys.* **158** 333 (Engl. Transl.)
[18] Gadomskii O N, Nagibarov V R and Solovarov N K 1972 *Zh. Eksp. Teor. Fiz.* **63** 813
     Gadomskii O N, Nagibarov V R and Solovarov N K 1973 *Sov. Phys.—JETP* **36** 390 (Engl. Transl.)
[19] Gadomskii O N, Nagibarov V R and Solovarov N K 1976 *Zh. Eksp. Teor. Fiz.* **70** 435
     Gadomskii O N, Nagibarov V R and Solovarov N K 1976 *Sov. Phys.—JETP* **43** 225 (Engl. Transl.)
[20] Gadomsky O N and Altunin K K 1998 *Zh. Eksp. Teor. Fiz.* **113** 471
     Gadomsky O N and Altunin K K 1998 *JETP* **87** 842 (Engl. Transl.)
[21] Gadomskii O N 2000 *Usp. Fiz. Nauk* **170** 1554
     Gadomskii O N 2000 *Phys. Usp.* **43** 1071 (Engl. Transl.)
[22] Akhiezer A I and Berestetskiy V B 1969 *Quantum Electrodynamics* (Moscow: Nauka) (in Russian)
     Akhiezer A I and Berestetskiy V B 1965 (New York: Wiley) (English Transl. prev. ed.)

[23] Drake G W F 1972 *Phys. Rev.* A **5** 1979
[24] Bouchama T, Desesquelles J, Druetta M, Farison M and Martin S 1987 *J. Phys. B: At. Mol. Phys.* **20** L457
[25] Afrosimov V V, Basalaev A A, Panov M N and Samoilov A V 1986 *Zh. Eksp. Teor. Fiz.* **91** 465
     Afrosimov V V, Basalaev A A, Panov M N and Samoilov A V 1986 *Sov. Phys.—JETP* **64** 273 (Engl. Transl.)
[26] Gordeev Yu S, Dijkkamp D, Drentje A G and Heer F J 1983 *Abstracts of Papers of XIII ICPEAC* (Amsterdam:
     North-Holland) p 541
     Tawara H, Takács E, Suta T, Makónyi K, Ratliff L P and Gillaspy J D 2006 *Phys. Rev.* A **73** 012704
[27] Gorvat P P, Lazur V Yu, Migalina S I, Shuba I M and Yanev R K 1996 *Teor. Mat. Fiz.* **109** 232
     Gorvat P P, Lazur V Yu, Migalina S I, Shuba I M and Yanev R K 1996 *Theor. Math. Phys.* **109** 1423
[28] Yamamoto Y *et al* 2004 *Phys. Rev. Lett.* **93** 011801
[29] Malyshev V and Moreno P 1966 *Phys. Rev.* A **53** 416
[30] Gadomsky O N and Glukhov A G 2006 *Zh. Eksp. Teor. Fiz.* **130** 31
     Gadomsky O N and Glukhov A G 2006 *JETP* **103** 23
[31] Gadomsky O N and Voronov Yu Yu 2002 *Zh. Eksp. Teor. Fiz.* **121** 1028
     Gadomsky O N and Voronov Yu Yu 2002 *JETP* **94** 882
[32] Gadomskii O N and Kharitonov Yu Ya 2004 *Kvantovaya Elektron.* **34** 249
     Gadomskii O N and Kharitonov Yu Ya 2004 *Quantum Electron.* **34** 249