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# Interaction of two quasimolecular electrons via the field of virtual photons as a second-order effect of quantum electrodynamics

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The problem of interaction of two quasimolecular electrons located at an arbitrary distance from each other and near different atoms (nuclei) is solved. The interaction is considered as a second-order effect of quantum electrodynamics in the coordinate representation. It is shown that consistent account of the natural condition of the interaction symmetry with respect to both electrons leads to the additional contribution to the relativistic interaction of the two quasimolecular electrons compared with both the standard Breit operator and the generalized Breit operator obtained previously [O. N. Gadomskii, Usp. Fiz. Nauk **170**, 1145 (2000) [Phys. Usp. **43**, 1071 (2000)]]. The generalized Breit-Pauli operator for interaction of two quasimolecular electrons located at an arbitrary distance from each other is obtained.

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## I. INTRODUCTION

Superheavy quasimolecules [1,2] or quasiatoms with the total charge $Z_a + Z_b > 137$ of nuclei whose binding energies can be larger than the rest energy of an electron are created in collisions of heavy ions. In order to study the electron structure of such quasimolecules, totally relativistic consideration is necessary. Relativistic effects are essential also when calculating terms of the multiply charged light quasimolecules [2]. In the specified cases it is necessary to consider the multielectron effects within the method of self-consistent field [3] as well. Note that the problem of accounting for relativistic effects arises in a number of traditional problems of the theory of ion-atom collisions. We are on the threshold of investigating the phenomena caused by slow highly charged ions—completely stripped nuclei of krypton, xenon, and even uranium with energies below 100 eV per unit charge have already been obtained [4]. The interaction of such ions with atoms of matter has not been studied yet and should be essentially quasimolecular. Consistent theory regarding this interaction must be based on the relativistic wave equations.

The study of multiparticle quasimolecular effects and multielectron processes with rearrangement (for example, such as two-electron charge exchange, charge exchange with simultaneous excitation or ionization, etc.) in slow collisions of highly charged ions with heavy (relativistic) atoms is next. In the case when under favorable conditions the mechanisms of nonadiabatic coupling result in strongly correlated electron transitions involving electrons of internal (nonoptical) shells, the relativistic effects become essential, and a consistent accounting of them demands the generalization of the adiabatic asymptotic theory of multielectron processes with rearrangement [5,6] to the range of relativistic binding energies. It is necessary to stress here that the followed exchange mechanism is typical for all specified two-electron processes with rearrangement (see [5,6] and the references therein): one of the active electrons of atom (ion) $\mathrm{A}^{(Z_a-2)+}$ tunnels to a "foreign" ion (or bare nucleus) $\mathrm{B}^{Z_b+}$, followed by the strongly correlated simultaneous transition of two electrons belonging to different nuclei. For such transitions, relativistic effects are manifested not only in the modification of one-electron wave functions which are solutions of the Dirac equation for the two-Coulomb-center problem [7,8], but also in distinction of interelectron interaction from the purely Coulomb one due to the retardation, for example. Therefore, rather general problems of the role of magnetic interactions and retardation effects in immediate interaction between the two active electrons located at arbitrary distances from each other near different centers require special investigation. Moreover, one can even say that without such study it is impossible to understand the dynamics of strongly correlated motion of particles during the collision process.

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

Skipping a detailed discussion of the poorly investigated problems of relativistic multiparticle interactions, we only note that the modern quantum field theory of electromagnetic interactions [quantum electrodynamics (or QED)], based on the $S$-matrix formalism and Feynman diagram technique, gives only the recipe of construction of such an operator in the form of expansion in powers of the fine structure constant $\alpha$. As early as 1929, Breit demonstrated [9] that up to the first correction term such an expansion provides a good approximation for the relativistic interaction between two electrons under the assumption that retardation effects in the spectrum of a heliumlike atom are small. Breit has obtained the following relativistic operator of the interelectron

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interaction [9]:

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

where $\vec{\alpha}_1$ and $\vec{\alpha}_2$ are the commuting sets of the Dirac matrices, $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$, $r_{12} = |\vec{r}_{12}|$, and the subscripts 1 and 2 distinguish the quantities relating to the first and second electrons, respectively. We have to remember that the applicability of the Breit operator (1) is limited by the condition that interelectron distance $r_{12}$ must be smaller than the characteristic wavelength $\lambda_0$ in the spectrum of interacting electrons. This approximation fails in two-electron problems related to slow atomic collisions because large interelectron distances $r_{12}$, in contrast, are operating in this case [6]. Therefore, interest in the problem of two electrons belonging to two hydrogenlike atoms located at an arbitrary distance from each other was renewed at the beginning of the 1970s as a result of the intensive study of multiatomic systems in a radiation field. The credit for the realization and development of new ideas in this direction goes to the authors of Refs. [10–13], where the problem of the interaction of two bound electrons belonging to two hydrogenlike atoms was studied using quantum electrodynamic methods in the general formulation without imposing any restriction on the interatom distances. However, by turning to these works we discovered [14] that the generalized Breit operator constructed there does not manifest the symmetry with respect to the interacting particles and, therefore, cannot be utilized in the consistent relativistic quantum theory. The correct account of a natural condition of symmetry of the retardation factor with respect to both electrons gives (as is shown in the current article) the additional contribution to the relativistic operator of interaction between two quasimolecular electrons when compared with the corresponding operator from Refs. [10–13].

The article is organized as follows. In Sec. II, the formulation of the problem of interaction of two quasimolecular electrons via the field of virtual photons in the framework of the second-order effects of quantum electrodynamics is described. The relativistic operator of interaction of two bound electrons, which is a generalization of the Breit operator (1) to the range of arbitrarily large interelectron distances, is obtained in the next section. In Sec. IV, as a result of conversion from the relativistic Dirac bispinors to nonrelativistic Pauli spinors in a matrix of the effective energy of interaction, the explicit form of the generalized Breit-Pauli operator for interaction of two quasimolecular electrons located at an arbitrary distance from each other is found. In the last section, the final results are discussed and compared with corresponding results of the previous papers devoted to the problem of two electrons.

## II. MATRIX OF THE EFFECTIVE ENERGY OF INTERACTION OF TWO QUASIMOLECULAR ELECTRONS

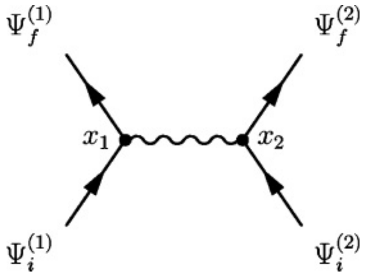

FIG. 1. Feynman diagram of the second-order effects of QED for interaction of two quasimolecular electrons.

We consider the interaction of two electrons in an external electrostatic field as a second-order effect of quantum electrodynamics defined by the Feynman diagram shown in Fig. 1. The corresponding matrix element of the second-order scattering operator $S^{(2)}$ can be represented in the form [15,16]

$$S^{(2)}_{i\to f} \equiv \langle f|S^{(2)}|i\rangle = -i\int d^4x_1\int d^4x_2\, j^{(2)\mu}_{fi}(x_2) \times D_F(x_2 - x_1)\, j^{(1)}_{fi\mu}(x_1), \quad (2)$$

where $D_F$ is the photon propagator and the transition current densities $j^{(1)}_{fi\mu}(x_1)$ and $j^{(2)\mu}_{fi}(x_2)$ are defined by

$$\begin{aligned} j^{(1)}_{fi\mu}(x_1) &= e\overline{\Psi}^{(1)}_f(x_1)\gamma^{(1)}_\mu\Psi^{(1)}_i(x_1), \\ j^{(2)\mu}_{fi}(x_2) &= e\overline{\Psi}^{(2)}_f(x_2)\gamma^{(2)\mu}\Psi^{(2)}_i(x_2). \end{aligned} \quad (3)$$

Here, $e = -|e|$ is the electronic charge; $\gamma^\mu$ ($\mu = 0,1,2,3$) are the Dirac matrices in the covariant representation; $\Psi^{(n)}_i$ and $\Psi^{(n)}_f$ are wave functions of the respective initial and final states of the $n$th electron, $n = 1,2$; $\overline{\Psi}^{(n)}_f = \Psi^{(n)+}_f\gamma^0$ is the Dirac-adjoint bispinor; and $\Psi^{(n)+}_f$ is the Hermitian-adjoint bispinor. In expression (2), we use the relativistic units $\hbar = c = 1$, the notation $x^\mu_1 = (t_1,\vec{r}_1)$ and $x^\mu_2 = (t_2,\vec{r}_2)$ for the radius four vectors, and $d^4x_1 = d^3x_1dt_1$ and $d^4x_2 = d^3x_2dt_2$ 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 following representation for the Dirac matrices:

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

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 0 and $I$ are, respectively, $2\times 2$ zero and unit matrices.

The wave functions of stationary states

$$\begin{aligned} \Psi^{(1)}_{i,f}(x_1) &= \Psi^{(1)}_{i,f}(\vec{r}_1)e^{-iE^{(1)}_{i,f}t_1}, \\ \Psi^{(2)}_{i,f}(x_2) &= \Psi^{(2)}_{i,f}(\vec{r}_2)e^{-iE^{(2)}_{i,f}t_2} \end{aligned} \quad (4)$$

correspond to the external electron lines of the diagram. The quantities $E^{(1)}_i$ [$E^{(1)}_f$] and $E^{(2)}_i$ [$E^{(2)}_f$] are the initial [final] energies of the first and second electrons, respectively. Taking into account formulas (4), we factorize the time factors in the transition currents:

$$j^{(1)}_{fi\mu}(x_1) = j^{(1)}_{fi\mu}(\vec{r}_1)e^{i\omega^{(1)}_{fi}t_1}, \quad j^{(2)\mu}_{fi}(x_1) = j^{(2)\mu}_{fi}(\vec{r}_2)e^{i\omega^{(2)}_{fi}t_2}, \quad (5)$$

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

Having integrated in the $S$ matrix with respect to times, frequencies, and wave vectors of the virtual photons, we arrive at an expression for the matrix of the effective energy of two atomic electrons ($\hbar = c = 1$):

$$U^{(2)}_{i\to f} = \int d^3x_1 \int d^3x_2\, j^{(2)\mu}_{fi}(\vec r_2)\frac{e^{i|\omega_{fi}||\vec r_1-\vec r_2|}}{|\vec r_1-\vec r_2|}\, j^{(1)}_{fi\mu}(\vec r_1). \tag{6}$$

Hereafter $|\omega_{fi}| = |\omega^{(1)}_{fi}| = |\omega^{(2)}_{fi}|$. Proceeding 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 is performed using the relation

$$S^{(2)}_{i\to f} = -2\pi i U^{(2)}_{i\to f}\,\delta\big(E^{(1)}_f - E^{(1)}_i + E^{(2)}_f - E^{(2)}_i\big). \tag{7}$$

The factorization of one-dimensional $\delta$ function, depending on the difference between final and initial total energies of the electrons, expresses the energy conservation law

$$E^{(1)}_f + E^{(2)}_f = E^{(1)}_i + E^{(2)}_i, \tag{8}$$

which is the manifestation of symmetry under the continuous time-shift operation.

All the equations displayed in this section pertain to the matrix element (2). In order to obtain the complete expression for $S^{(2)}_{i\to f}$, the corresponding exchange matrix element expressing the indistinguishability of electrons must be added to the matrix element (2).

## III. THE GENERALIZED BREIT OPERATOR OF LONG-RANGE TYPE

Using definitions (3)–(5) we express the interaction currents in terms of wave functions in formula (6) for the matrix element of the effective interaction energy,

$$\begin{aligned} U^{(2)}_{i\to f} &= e^2 \int d^3x_1 \int d^3x_2 \Psi^{(2)+}_f(\vec r_2)\Psi^{(1)+}_f(\vec r_1) \\ &\quad\times \frac{1-\vec\alpha_1\vec\alpha_2}{|\vec r_1-\vec r_2|} e^{i|\omega_{fi}||\vec r_1-\vec r_2|}\Psi^{(2)}_i(\vec r_2)\Psi^{(1)}_i(\vec r_1), \end{aligned} \tag{9}$$

where $\vec\alpha_1$ and $\vec\alpha_2$ are the Dirac matrices acting on different one-electron wave functions: $\vec\alpha_1$ acts on $\Psi^{(1)}_i(\vec r_1)$ and $\vec\alpha_2$ acts on $\Psi^{(2)}_i(\vec r_2)$. Since the "retardation factor" $\exp\{i|\omega_{fi}|r_{12}\}$, which depends explicitly on the initial and final energies of the system, enters into this expression, in the general case we cannot introduce a Hamiltonian of interaction between two electrons, that is, an operator $V$ for which the relation

$$\begin{aligned} U^{(2)}_{i\to f} &= \langle f|V|i\rangle \\ &= \int d^3x_1 \int d^3x_2 \Psi^{(2)+}_f(\vec r_2)\Psi^{(1)+}_f(\vec r_1) \\ &\quad\times V\Psi^{(2)}_i(\vec r_2)\Psi^{(1)}_i(\vec r_1) \end{aligned} \tag{10}$$

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

However, such an operator can be constructed in the approximation of small velocities ($v/c \ll 1$, where $v$ is the velocity of electrons in the atom and $c$ is the velocity of light in the vacuum). For this purpose let us consider a two-electron atom (or ion) $\mathrm{A}^{(Z_a-2)+}$ and the bare nucleus $\mathrm{B}^{Z_b+}$ located at an arbitrary distance $R$ from the atom. Here $Z_a$ and $Z_b$ are the charges of the atomic nuclei $\mathrm{A}^{Z_a+}$ and $\mathrm{B}^{Z_b+}$, which are assumed to be stable in the proposed two-center model. Let $\vec r_{na}$ and $\vec r_{nb}$ be the position vectors of the $n$th electron with respect to the nuclei $\mathrm{A}^{Z_a+}$ and $\mathrm{B}^{Z_b+}$, $n = 1,2$. We now assume that one of the electrons of the atom $\mathrm{A}^{(Z_a-2)+}$, the first electron, for instance, tunnels into the vicinity of the foreign nucleus $\mathrm{B}^{Z_b+}$, while the second electron is located near its host nucleus $\mathrm{A}^{Z_a+}$. If the domains of spatial localizations of the electrons near the different nuclei (the first electron near $\mathrm{B}^{Z_b+}$ and the second one near $\mathrm{A}^{Z_a+}$) are rather small (of the order of the atom size) and rather far from each other, then under the condition $\Delta r < R < \infty$ the relative distance $r_{12}$ between the electrons can be represented in the form of the expansion in powers of the ratio $\Delta r/R$:

$$|\vec r_1 - \vec r_2| = R\left(1 + \frac{\vec R\Delta\vec r}{R^2} + \frac{M}{R}\right). \tag{11}$$

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

In the matrix of effective interaction energy (9), let us consider the factor

$$K(\vec r_1,\vec r_2;\omega_{fi}) = \frac{e^{i|\omega_{fi}|r_{12}/c}}{r_{12}}, \tag{12}$$

which is responsible for the virtual photon exchange between the two electrons. Hereinafter, we use the system of units in which $c \neq 1$. In the previous articles [9,17], only the quantity $\omega_0 r_{12}/c \ll 1$ (or formally $1/c$) was assumed to be a small parameter when constructing the expansion of the retardation factor. This condition is obviously satisfied for not-too-large interelectron distances, for example, for intra-atomic distances in He-like atoms. An asymptotic expansion of the $K$-factor (12) is constructed below for the case when simultaneously $1/c$ and $\Delta r/R$ are natural small parameters. Such a selection of small parameters differs from the limiting case of a single (united) He-like atom ($R = 0$) studied in [9,17], and is realized within the used model when the electrons are located rather far from each other near different centers, for instance.

Further, we transform the $K$-factor (12) as follows:

$$K(\vec r_1,\vec r_2;\omega_{fi}) = e^{i|\omega_{fi}|R/c}\frac{e^{i|\omega_{fi}|(r_{12}-R)/c}}{r_{12}}. \tag{13}$$

For electrons belonging to different atoms, this transformation is convenient due to the factorization of the relativistic factor $\exp\{i|\omega_{fi}|R/c\}$ of the amplification of the effects of interaction retardation, which are encoded in the dependence of this factor on both the internuclear distance $R$ and difference of energies of one-particle states: $|\omega_{fi}| = |\omega^{(n)}_{fi}| = |E^{(n)}_f - E^{(n)}_i|, n = 1,2$.

Let us now assume that

$$\frac{|\omega_{fi}|}{c}\frac{\vec R\Delta\vec r}{R} \ll 1. \tag{14}$$

Internuclear distance therewith can vary over the wide range $\Delta r \leqslant R < \infty$. When condition (14) is satisfied, the exponent $|\omega_{fi}|(r_{12} - R)/c$ in the right-hand side of (13) is a small quantity and we can expand the $K$-factor (12) in powers of

$1/c$. So we obtain the expansion to within the terms $\sim c^{-2}$:

$$K(\vec{r}_1,\vec{r}_2;\omega_{fi}) = e^{i|\omega_{fi}|R/c}\left\{ f_0(r_{12}) + \frac{i}{c}|\omega_{fi}|f_1(r_{12}) - \frac{\omega_{fi}^2}{2c^2}f_2(r_{12})\right\}. \quad (15)$$

The coefficients

$$f_0(r_{12}) = \frac{1}{r_{12}}, \quad f_1(r_{12}) = \frac{r_{12}-R}{r_{12}}, \quad f_2(r_{12}) = \frac{(r_{12}-R)^2}{r_{12}} \quad (16)$$

of expansion (15) are in turn power series in $\Delta r/R$. Actually, it means that if the domains of space localization of electrons near different centers are rather far from each other, then one can expand the functions $f_0$, $f_1$, and $f_2$ from (15) in powers of $\Delta r/R$. If one does not do such a expansion, then one can take into account (in $c^{-2}$ approximation) the interaction of quasimolecular electrons of all multipolarities in the closed form.

Let us eliminate frequencies in expression (15) by using the Dirac equations:

$$\begin{aligned}\hat{H}^{(n)}(\vec{r}_n)\Psi_i^{(n)}(\vec{r}_n) &= E_i^{(n)}\Psi_i^{(n)}(\vec{r}_n),\\ \hat{H}^{(n)}(\vec{r}_n)\Psi_f^{(n)}(\vec{r}_n) &= E_f^{(n)}\Psi_f^{(n)}(\vec{r}_n).\end{aligned} \quad (17)$$

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

The expansion of the $K$-factor in the form (15) has no symmetry under interchanging the interacting particles. In order to obtain the required symmetry in the last two terms of expansion (15), we use the relation $\omega_{fi}^{(1)} = -\omega_{fi}^{(2)}$, which expresses the energy conservation law (8). If $E_f^{(1)} > E_i^{(1)}$ $[E_f^{(1)} < E_i^{(1)}]$, then $\omega_{fi}^{(1)} = -\omega_{fi}^{(2)} > 0$ $[\omega_{fi}^{(1)} = -\omega_{fi}^{(2)} < 0]$ and $|\omega_{fi}^{(1)}| = \omega_{fi}^{(1)}$ $[|\omega_{fi}^{(1)}| = -\omega_{fi}^{(1)}]$. Using these relations, one can transform the second term in (15) to the symmetric form:

$$\begin{aligned}|\omega_{fi}|f_1(r_{12}) &= \left|\omega_{fi}^{(1)}\right|f_1(r_{12}) = \pm\omega_{fi}^{(1)}f_1(r_{12})\\ &= \pm\tfrac{1}{2}\left[E_f^{(1)} - E_i^{(1)} + E_i^{(2)} - E_f^{(2)}\right]f_1(r_{12}).\end{aligned} \quad (18)$$

The plus sign in (18) corresponds to the case $E_f^{(1)} > E_i^{(1)}$ $[\omega_{fi}^{(1)} > 0]$, and the minus sign corresponds to the case $E_f^{(1)} < E_i^{(1)}$ $[\omega_{fi}^{(1)} < 0]$.

Since we multiply expression (15) 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 (18) with the operators $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$ to the right of the factor $f_1(r_{12})$ and replace the energies $E_f^{(1)}$ and $E_f^{(2)}$ with the operators $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$ to the left of the factor $f_1(r_{12})$:

$$\begin{aligned}|\omega_{fi}|f_1(r_{12}) &\to \pm\tfrac{1}{2}\{\hat{H}^{(1)}f_1(r_{12}) - f_1(r_{12})\hat{H}^{(1)}\\ &\quad + f_1(r_{12})\hat{H}^{(2)} - \hat{H}^{(2)}f_1(r_{12})\}\\ &= \pm\tfrac{1}{2}\{[\hat{H}^{(1)},f_1(r_{12})] + [f_1(r_{12}),\hat{H}^{(2)}]\}.\end{aligned} \quad (19)$$

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

Using the relation $\omega_{fi}^{(1)} = -\omega_{fi}^{(2)}$, we transform the third term in the expansion (15) to the symmetric form:

$$\begin{aligned}-\omega_{fi}^2 f_2(r_{12}) &= \left(E_f^{(1)} - E_i^{(1)}\right)\left(E_f^{(2)} - E_i^{(2)}\right)f_2(r_{12})\\ &\to f_2(r_{12})\hat{H}^{(1)}\hat{H}^{(2)} - \hat{H}^{(1)}f_2(r_{12})\hat{H}^{(2)}\\ &\quad - \hat{H}^{(2)}f_2(r_{12})\hat{H}^{(1)} + \hat{H}^{(1)}\hat{H}^{(2)}f_2(r_{12})\\ &= \boldsymbol{[}\hat{H}^{(1)},[\hat{H}^{(2)},f_2(r_{12})]\boldsymbol{]}.\end{aligned} \quad (20)$$

Substituting operator expressions (19) and (20) into the right-hand side of (15), we obtain the transformation of the $K$-factor:

$$\begin{aligned}K(\vec{r}_1,\vec{r}_2;\omega_{fi}) \to e^{i|\omega_{fi}|R/c}\Big\{ & f_0(r_{12}) \pm \frac{i}{2c}([\hat{H}^{(1)},f_1(r_{12})]\\ & + [f_1(r_{12}),\hat{H}^{(2)}])\\ & + \frac{1}{2c^2}\boldsymbol{[}\hat{H}^{(1)},[\hat{H}^{(2)},f_2(r_{12})]\boldsymbol{]}\Big\}.\end{aligned} \quad (21)$$

Therefore, the $K$-factor (12) is represented by means of the double expansion (15) in powers of $1/c$ and $\Delta r/R$. In the expansion in terms of $1/c$ we retain only the first three terms, imposing no restrictions on the expansion in the small parameter $\Delta r/R$ because the function $M$ contains all the higher correction terms. For this reason, we take into account interaction of two quasimolecular electrons of arbitrary multipolarity.

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

$$\hat{H}^{(n)} = c\vec{\alpha}_n\hat{\vec{p}}_n + \beta_n mc^2 + V(\vec{r}_n), \quad n = 1,2, \quad (22)$$

$$V(\vec{r}_n) = -\left(\frac{Z_a e^2}{r_{na}} + \frac{Z_b e^2}{r_{nb}}\right), \quad r_{na,nb} = |\vec{r}_n \pm \vec{R}/2|. \quad (23)$$

Hereafter, $\hbar \neq 1$, $\hat{\vec{p}}_n = -i\hbar\vec{\nabla}_n$ is the momentum operator of the $n$th electron, $\vec{\nabla}_n$ 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 $\vec{\alpha}_n$ and $\beta_n$ indicates that these matrices act on the function $\Psi_i^{(n)}(\vec{r}_n)$.

With the performed calculations in mind it is easy to understand that the result (21) can be obviously generalized by the means of introduction of the additional terms into the Hamiltonians (22), for instance, taking into account a finite size and the spin of the nucleus, screening of the nucleus field by the electron shell of the atomic core, etc. However, we have to remember that except for limiting cases (for example, large internuclear distances [7,8]) the eigenvalue problem (17) for such a Hamiltonian cannot be solved in an explicit form.

Let us now calculate the commutators appearing in (21). First of all, note that only one term in $\hat{H}^{(n)}$, namely $c\vec{\alpha}_n\hat{\vec{p}}_n$, is noncommuting with $f_1(r_{12})$ and $f_2(r_{12})$. For this reason we can disregard all terms not containing the matrices $\vec{\alpha}_n$ in expressions (22) for operators $\hat{H}^{(1)}$, $\hat{H}^{(2)}$ when they are substituted into the commutators in (21). Then we find that the contributions of the second and third terms into the expansion (21) are determined by the following operator expressions:

$$\pm\frac{i}{2c}([\hat{H}^{(1)},f_1] + [f_1,\hat{H}^{(2)}]) = \pm\hbar R\frac{\vec{\alpha}_1\vec{n} + \vec{\alpha}_2\vec{n}}{2r_{12}^2}, \quad (24)$$

$$\frac{1}{2c^2}[\hat{H}^{(1)},[\hat{H}^{(2)},f_2]] = -\frac{\hbar^2}{2}(\vec{\alpha}_1\vec{\nabla}_1)(\vec{\alpha}_2\vec{\nabla}_2)r_{12} - \frac{\hbar^2R^2}{2}(\vec{\alpha}_1\vec{\nabla}_1)(\vec{\alpha}_2\vec{\nabla}_2)\frac{1}{r_{12}}, \qquad (25)$$

where $\vec{n} = \vec{r}_{12}/r_{12}$.

Therefore, the quantity $\langle f|V|i\rangle$ can indeed be represented in the form (10), where the operator $V$ describing the virtual photon exchange between particles in the matrix $U^{(2)}_{i\to f}$ is (here again $\hbar = 1$):

$$V^{(\pm)}(\vec{r}_1,\vec{r}_2;R) = e^2\exp\left(\frac{i}{c}|\omega_{fi}|R\right)\left\{\frac{1}{r_{12}} - \frac{\vec{\alpha}_1\vec{\alpha}_2 + (\vec{\alpha}_1\vec{n})(\vec{\alpha}_2\vec{n})}{2r_{12}} \pm R\frac{\vec{\alpha}_1\vec{n} + \vec{\alpha}_2\vec{n}}{2r_{12}^2} - R^2\frac{\vec{\alpha}_1\vec{\alpha}_2 - 3(\vec{\alpha}_1\vec{n})(\vec{\alpha}_2\vec{n})}{2r_{12}^3}\right\}. \qquad (26)$$

In this equality, the plus sign of the term containing the factor $R$ corresponds to the case $E^{(1)}_f > E^{(1)}_i$ and the minus sign corresponds to the case $E^{(1)}_f < E^{(1)}_i$. The first term in (26) is the energy of the instant (Coulomb) interaction between electrons, and the remaining terms take into account corrections due to the retardation of relativistic interaction and the presence of electron spins.

In the limiting case of a unified atom ($R \to 0$), the operator (26) transforms into the relativistic Breit operator (1) of the interaction of two atomic electrons in heliumlike systems. Therefore, we can consider the operator (26) as a direct generalization of the Breit operator [9,17] to the domain of arbitrarily large interelectron distances. Such a generalization is nontrivial because expression (26), in contrast to Breit expression (1), contains retarded terms which depend on both $R$ and spin operators of the electrons. This additional contribution to $V^{(\pm)}$ has essentially a relativistic character and appears due to an additional retardation of the relativistic interaction between the two electrons located at an arbitrary distance apart.

According to the improvement of the Breit operator made in the present article, it is worthwhile to call expression (26) *the generalized Breit operator of long-range type* (in order to stress the possibility of using it to solve two-electron problems in the physics of slow atomic collisions [6,18,19], in the theory of quasimolecular Auger spectroscopy [20,21], and in several important problems of nonlinear and quantum optics [10–13,22]).

Also, let us call our attention to the fact that the obtained operator (26) is symmetric with respect to both interacting particles. This is due to the appropriate symmetrization of $c^{-1}$ expansion (15) of the $K$-factor with respect to both electrons.

In the series of articles [10,11] that actually initiated the present stage of investigations of the problem of two electrons, the following result has been obtained for the relativistic operator of interaction of two atomic electrons via the field of virtual photons without emission (absorption) of real photons at an arbitrary distance from each other within the effects of the third order of quantum electrodynamics:

$$\hat{U}^{(2)}(\vec{r}_1,\vec{r}_2;R) = e^2\exp\left(\frac{i}{c}|\omega_{fi}|R\right)\left\{\frac{1}{r_{12}} - \frac{\vec{\alpha}_1\vec{\alpha}_2 + (\vec{\alpha}_1\vec{n})(\vec{\alpha}_2\vec{n})}{2r_{12}} + R\frac{\vec{\alpha}_2\vec{n}}{r_{12}^2} - R^2\frac{\vec{\alpha}_1\vec{\alpha}_2 - 3(\vec{\alpha}_1\vec{n})(\vec{\alpha}_2\vec{n})}{2r_{12}^3}\right\}. \qquad (27)$$

A principal drawback of this operator is the absence of symmetry in the description of the pair of interacting particles.

An important remark, which follows from comparison of formulas (26) and (26), consists of the fact that consistent application of the procedure of symmetrization of the $K$-factor [see (21)] with respect to both electrons leads to the appearance of a new term $\pm R(\vec{\alpha}_1\vec{n})/2r_{12}^2$ in the final expression (26) for the operator $V^{(\pm)}(\vec{r}_1,\vec{r}_2;R)$ when compared with terms of the representation (27). This term is caused by the additional retardation in the interaction of electrons located at arbitrarily large distances from each other. Therefore, one can expect an occurrence of erroneous results by using the operator (27) from [10–13] in calculations.

## IV. CONVERSION TO TWO-COMPONENT PAULI SPINORS

### A. Generalized two-particle Breit-Pauli operator

The conversion to approximative two-component wave functions $\Phi^{(n)}_i$ and $\Phi^{(n)}_f$ in the matrix $U^{(2)}_{i\to f}$ [see (10)] is done by the following transformations [17]:

$$\Psi^{(n)}_{i,f}(\vec{r}_n) = \begin{pmatrix} \varphi^{(n)}_{i,f}(\vec{r}_n) \\ \frac{\hat{\vec{\sigma}}_n\hat{\vec{p}}_n}{2mc}\varphi^{(n)}_{i,f}(\vec{r}_n) \end{pmatrix}, \qquad \varphi^{(n)}_{i,f}(\vec{r}_n) = \left(1 - \frac{\hat{\vec{p}}_n^{\,2}}{8m^2c^2}\right)\Phi^{(n)}_{i,f}(\vec{r}_n). \qquad (28)$$

Let us transform the matrix element

$$\langle f|V^{(\pm)}|i\rangle = \langle\Psi^{(1)*}_f(\vec{r}_1)\Psi^{(2)*}_f(\vec{r}_2) \times |V^{(\pm)}(\vec{r}_1,\vec{r}_2;R)|\Psi^{(1)}_i(\vec{r}_1)\Psi^{(2)}_i(\vec{r}_2)\rangle \qquad (29)$$

by means of functions (28) so that it takes the form

$$\langle\Phi^*_f(1,2)|V^{(\pm)}_{BP}|\Phi_i(1,2)\rangle = \int d^3x_1\int d^3x_2\Phi^{(1)*}_f(\vec{r}_1)\Phi^{(2)*}_f(\vec{r}_2) \times V^{(\pm)}_{BP}(\vec{r}_1,\vec{r}_2;R)\Phi^{(1)}_i(\vec{r}_1)\Phi^{(2)}_i(\vec{r}_2), \qquad (30)$$

where $V^{(\pm)}_{BP}(\vec{r}_1,\vec{r}_2;R)$ can be considered as the operator of interaction energy of two quasimolecular electrons at an arbitrary distance from each other. The wave functions $\Phi_i(1,2) = \Phi^{(1)}_i(\vec{r}_1)\Phi^{(2)}_i(\vec{r}_2)$ and $\Phi_f(1,2) = \Phi^{(1)}_f(\vec{r}_1)\Phi^{(2)}_f(\vec{r}_2)$ in (30) are the nonsymmetrized products of two-component normalized wave functions (28) of separate electrons in initial and final state, respectively. The electron coordinates in functions $\Psi^{(2)}_{if}(\vec{r}_2)$ and $\Psi^{(1)}_{i,f}(\vec{r}_1)$ are measured from nuclei $A^{Z_a+}$ and $B^{Z_b+}$, respectively.

At first, let us consider the problem of transformation of the matrix element (29) of the operator of the Coulomb electron interaction $e^2/r_{12}$ into the form (30). By substituting the functions (28) into (29) and using necessary transformations, we obtain the following expression to within terms $O(1/c^2)$:

$$
\begin{aligned}
&e^2 \exp\left(\frac{i}{c}|\omega_{fi}|R\right) \langle f|\frac{1}{r_{12}}|i\rangle \\
&\quad = e^2 \exp\left(\frac{i}{c}|\omega_{fi}|R\right) \int \bigg\{ \Phi_f^{(1)*}(\vec{r}_1)\Phi_f^{(2)*}(\vec{r}_2)\Phi_i^{(1)}(\vec{r}_1)\Phi_i^{(2)}(\vec{r}_2) - \frac{1}{8m^2c^2}\Phi_f^{(1)*}(\vec{r}_1)\Phi_f^{(2)*}(\vec{r}_2)\Phi_i^{(1)}(\vec{r}_1)\big[\hat{\vec{p}}_2^{\,2}\Phi_i^{(2)}(\vec{r}_2)\big] \\
&\qquad - \frac{1}{8m^2c^2}\Phi_f^{(1)*}(\vec{r}_1)\Phi_f^{(2)*}(\vec{r}_2)\big[\hat{\vec{p}}_1^{\,2}\Phi_i^{(1)}(\vec{r}_1)\big]\Phi_i^{(2)}(\vec{r}_2) - \frac{1}{8m^2c^2}\Phi_f^{(1)*}(\vec{r}_1)\big[\hat{\vec{p}}_2^{\,2}\Phi_f^{(2)}(\vec{r}_2)\big]^*\Phi_i^{(1)}(\vec{r}_1)\Phi_i^{(2)}(\vec{r}_2) \\
&\qquad - \frac{1}{8m^2c^2}\big[\hat{\vec{p}}_1^{\,2}\Phi_f^{(1)}(\vec{r}_1)\big]^*\Phi_f^{(2)*}(\vec{r}_2)\Phi_i^{(1)}(\vec{r}_1)\Phi_i^{(2)}(\vec{r}_2) + \frac{1}{4m^2c^2}\big[\vec{\sigma}_1\hat{\vec{p}}_1\Phi_f^{(1)}(\vec{r}_1)\big]^*\big[\vec{\sigma}_1\hat{\vec{p}}_1\Phi_i^{(1)}(\vec{r}_1)\big]\Phi_f^{(2)*}(\vec{r}_2)\Phi_i^{(2)}(\vec{r}_2) \\
&\qquad + \frac{1}{4m^2c^2}\Phi_f^{(1)*}(\vec{r}_1)\Phi_i^{(1)}(\vec{r}_1)\big[\vec{\sigma}_2\hat{\vec{p}}_2\Phi_f^{(2)*}(\vec{r}_2)\big]^*\big[\vec{\sigma}_2\hat{\vec{p}}_2\Phi_i^{(2)}(\vec{r}_2)\big]\bigg\}\frac{d^3x_1d^3x_2}{r_{12}}. \qquad (31)
\end{aligned}
$$

Expression (31) can be transformed into the form

$$
\begin{aligned}
\langle\Phi_f^*(1,2)|V_1|\Phi_i(1,2)\rangle &= \int d^3x_1 \int d^3x_2 \Phi_f^{(1)*}(\vec{r}_1)\Phi_f^{(2)*}(\vec{r}_2) \\
&\quad \times V_1\Phi_i^{(1)}(\vec{r}_1)\Phi_i^{(2)}(\vec{r}_2). \qquad (32)
\end{aligned}
$$

For this purpose, first of all, it is necessary to carry out the integration by parts. We take into account that for the considered quasimolecular model of two electrons near different centers, the higher powers of quantity $1/r_{12}$ do not become infinity when the internuclear distance $R$ varies over the interval $\Delta r < R < \infty$. However, there is a situation when taking into account the higher powers of quantity $1/r_{12}$ results in nontrivial $\delta$-functional contributions into the operator of electrostatic energy of two electrons. Obviously, it takes place in the limiting case of the united atom, that is, when $R \to 0$. Really, as $R$ decreases, the field in which electrons move increasingly resembles the field in the united heliumlike atom with the total nuclear charge $Z = Z_a + Z_b$. It actually means that on the interval $0 \leqslant R < \Delta r$, where the overlap of wave functions from different centers is essential, the electrons perceive both nuclei as a single Coulomb center. Over this interval the replacement of exact quasimolecular wave functions by simpler wave functions of united atom is physically justified. In this case all electronic coordinates should be measured from a single point, where for the sake of convenience we arrange the origin of the coordinate system. As the integrand in (31) contains the higher powers of the quantity $1/r_{12}$, first of all it is necessary to separate out the specified point ($\vec{r}_1 = \vec{r}_2$), that is, the origin of coordinates. At $\vec{r}_1 \to \vec{r}_2$ the integral over the sphere around the origin of coordinates gives a finite quantity. As this quantity depends only on the integrand at $\vec{r}_1 = \vec{r}_2$, it can also be represented in the form of a volume integral of the expression containing a three-dimensional Dirac $\delta$ function $\delta(\vec{r}_1 - \vec{r}_2)$. Taking into account these remarks we obtain the following operator:

$$
\begin{aligned}
V_1 &= e^2 \exp\left(\frac{i}{c}|\omega_{fi}|R\right)\bigg\{\frac{1}{r_{12}} - \frac{\pi}{m^2c^2}\delta(\vec{r}_{12}) \\
&\quad + \frac{1}{4m^2c^2}\frac{\vec{\sigma}_2[\vec{n}\times\hat{\vec{p}}_2] - \vec{\sigma}_1[\vec{n}\times\hat{\vec{p}}_1]}{r_{12}^2}\bigg\}. \qquad (33)
\end{aligned}
$$

In the united-atom limit ($R \to 0$) the first term

$$
V_{1C} = e^2 \exp\left(\frac{i}{c}|\omega_{fi}|R\right)\frac{1}{r_{12}} \qquad (34)
$$

on the right-hand side of (33) tends to the Coulomb electron interaction $V_C(r_{12}) = e^2/r_{12}$. Thus, it is reasonable enough that the operator $V_{1C}$ (34) is an analog of the Coulomb interaction of electrons at an arbitrary distance from each other but, unlike $V_C(r_{12})$, depends on initial and final energies of system explicitly: $|\omega_{fi}| = |\omega_{fi}^{(n)}| = |E_f^{(n)} - E_i^{(n)}|$, $n = 1,2$. First and foremost, it reflects pure relativistic effects of retardation of interaction of charged particles at arbitrary distances from each other, including arbitrarily large ones.

We return to detailed interpretation of other terms of the operator $V_1$ (33) later in this article. Here we only point out the key property of the operator $V_{1C}$ (34), namely, its periodic dependence on internuclear distance $R$.

Let us transform the matrix element (29) of the remaining terms of the operator $V^{(\pm)}$ (26) by means of the wave functions (28). Note that for transformation of the retarded terms containing $\vec{\alpha}$-matrices [see (26)], it is sufficient to replace $\varphi_{i,f}^{(n)}(\vec{r}_n)$ with $\Phi_{i,f}^{(n)}(\vec{r}_n)$ because the functions $\Phi_{i,f}^{(n)}(\vec{r}_n)$ already contain the factor $1/c^2$.

We carry out the transformations in the same way that we have used when obtaining the explicit expression (33) for the operator $V_1$. However, as the integrand contains the strong singularity at the origin of coordinates in the limiting case $R \to 0$, the mathematical treatment for atomic ($0 \leqslant R < \Delta r$) and quasimolecular ($\Delta r < R < \infty$) domains slightly differs.

At large internuclear distances ($\Delta r < R < \infty$) the domains of configuration space, which are responsible for localization of electrons near different centers, can be considered as being nonoverlapped. Actually, it means that, unlike in the case of single heliumlike atom ($R \to 0$) considered in [17], higher powers of the quantities

$$
(\vec{a}\vec{n})(\vec{b}\vec{n})/r_{12}, \quad R(\vec{a}\vec{n})/r_{12}^2, \quad R^2(\vec{a}\vec{n})(\vec{b}\vec{n})/r_{12}^3, \qquad (35)
$$

where $\vec{a}$ and $\vec{b}$ are arbitrary vectors, do not become infinite when $R$ varies over the quasimolecular domain $\Delta r < R <$

$\infty$. In this domain, even within the roughest approximation it is necessary to take into account the distinction between localizations of nuclei (unlike the interval $0 \leqslant R < \Delta r$) and to consider the interaction between electrons and fixed nuclei.

Carrying out the transformations described previously, we repeatedly encounter the operator expressions of the form

$$(\hat{\vec{p}}_1\vec{a})(\hat{\vec{p}}_2\vec{b})\frac{1}{r_{12}} = -\frac{1}{r_{12}^3}\left\{\vec{a}\vec{b} - \frac{3(\vec{a}\vec{r}_{12})(\vec{b}\vec{r}_{12})}{r_{12}^2}\right\} + \frac{4\pi}{3}(\vec{a}\vec{b})\delta(\vec{r}_{12}), \qquad (36)$$

containing the constant vectors $\vec{a}$, $\vec{b}$. The last formula is valid also in the case when the wave functions in the matrix elements (29) and (30) are spherically symmetric.

The structure of other singularities, arising from transformations described earlier, can be obtained by means of similar considerations, which have led us to representation (36). There is the specific delicacy which consists of the fact that all higher powers of quantities (35), which contain $R$ (or $R^2$) in the coefficients, give zero contributions in the limit $R \to 0$ due to the factor $R$ (or $R^2$). Certainly, nontrivial $\delta$-functional singularities will arise at $R \to 0$ only from those higher degrees of quantities (35) which do not contain $R$ or $R^2$ as a factor.

Combining the expressions coming from both the Coulomb term and the retarded terms in (26), we write at once the final result for the operator of the electrostatic energy of two quasimolecular electrons to within the terms $\sim 1/c^2$ inclusive:

$$V_{BP}^{(\pm)} = V_{1C} + \widetilde{V}_{BP}^{(\pm)} = V_{1C} + V_D + V_{LL}^{(\pm)} + V_{SS} + V_{SL}. \qquad (37)$$

Here, the following notations are used:

$$V_D = -\pi\left(\frac{e\hbar}{mc}\right)^2 \exp\left(\frac{i}{c}|\omega_{fi}|R\right)\delta(\vec{r}_{12}), \qquad (38)$$

$$\begin{aligned} V_{LL}^{(\pm)} = &-\frac{e^2}{2m^2c^2}\exp\left(\frac{i}{c}|\omega_{fi}|R\right)\left\{\frac{\hat{\vec{p}}_1\hat{\vec{p}}_2 + \vec{n}(\vec{n}\hat{\vec{p}}_1)\hat{\vec{p}}_2}{r_{12}}\right. \\ &\left. + \frac{R^2}{r_{12}^3}[\hat{\vec{p}}_1\hat{\vec{p}}_2 - 3\vec{n}(\vec{n}\hat{\vec{p}}_1)\hat{\vec{p}}_2]\right\} \\ &\pm \frac{e^2}{2mc}\exp\left(\frac{i}{c}|\omega_{fi}|R\right)\frac{R}{r_{12}^2}[\vec{n}\hat{\vec{p}}_1 + \vec{n}\hat{\vec{p}}_2], \end{aligned} \qquad (39)$$

$$\begin{aligned} V_{SS} = &\left(\frac{e\hbar}{2mc}\right)^2 \exp\left(\frac{i}{c}|\omega_{fi}|R\right)\left\{\frac{1}{r_{12}^3}[\vec{\sigma}_1\vec{\sigma}_2 - 3(\vec{\sigma}_1\vec{n})(\vec{\sigma}_2\vec{n})]\right. \\ &\left. + \frac{R^2}{r_{12}^5}[15(\vec{\sigma}_1\vec{n})(\vec{\sigma}_2\vec{n}) - 9\vec{\sigma}_1\vec{\sigma}_2] - \frac{8\pi}{3}(\vec{\sigma}_1\vec{\sigma}_2)\delta(\vec{r}_{12})\right\}, \end{aligned} \qquad (40)$$

$$\begin{aligned} V_{SL} = &\frac{e^2\hbar}{4m^2c^2}\exp\left(\frac{i}{c}|\omega_{fi}|R\right)\left\{\frac{1}{r_{12}^2}[-(\vec{\sigma}_1 + 2\vec{\sigma}_2)[\vec{n}\times\hat{\vec{p}}_1]\right. \\ &+ (\vec{\sigma}_2 + 2\vec{\sigma}_1)[\vec{n}\times\hat{\vec{p}}_2]] \\ &\left. + \frac{3R^2}{r_{12}^4}[\vec{\sigma}_1[\vec{n}\times\hat{\vec{p}}_1] - \vec{\sigma}_2[\vec{n}\times\hat{\vec{p}}_2]]\right\}. \end{aligned} \qquad (41)$$

All terms of the operator $V_{BP}^{(\pm)}$ (37) have a clear physical interpretation and describe the well-known physical effects arising in a system of the two interacting quasimolecular electrons; so the operators $V_D$ (38) and $V_{LL}^{(\pm)}$ (39) have a clear orbital origin. Therefore, the physical meaning of the operator $V_D$ (38) is easily seen from its $\delta$-like structure: In the limit $R \to 0$, $V_D$ is transformed into the two-particle singular part $-\pi(e\hbar/mc)^2\delta(\vec{r}_{12})$ of the known Darwin (contact) interaction of electrons with nuclei and with each other [9,17]. From the $\delta$-functional structure of (38) it also follows that the operator $V_D$ should be taken into account only in the atomic domain $0 \leqslant R < \Delta r$.

Let us discuss the physical meaning of the operator $V_{LL}^{(\pm)}$ (39). When $R$ tends to zero it turns into the usual operator of the retarded interaction between two electrons in the united He-like atom [17]. Therefore, it is reasonable to consider the operator $V_{LL}^{(\pm)}$ (39) as an operator of the retarded interaction of two quasimolecular electrons at an arbitrary distance from each other.

Let us give the expression for the operator of retarded interaction of two quasimolecular electrons that was found in Refs. [10–13]. In our notation it is of the form

$$\begin{aligned} V_{LL} = &-\frac{e^2}{2m^2c^2}\exp\left(\frac{i}{c}|\omega_{fi}|R\right)\left\{\frac{\hat{\vec{p}}_1\hat{\vec{p}}_2 + \vec{n}(\vec{n}\hat{\vec{p}}_1)\hat{\vec{p}}_2}{r_{12}}\right. \\ &\left. + \frac{R^2}{r_{12}^3}[\hat{\vec{p}}_1\hat{\vec{p}}_2 - 3\vec{n}(\vec{n}\hat{\vec{p}}_1)\hat{\vec{p}}_2]\right\} \\ &+ \frac{e^2}{mc}\exp\left(\frac{i}{c}|\omega_{fi}|R\right)\frac{R}{r_{12}^2}\vec{n}\hat{\vec{p}}_1. \end{aligned} \qquad (42)$$

This expression does not possess the property of symmetry with respect to the interacting particles and therefore cannot be applied in the consistent relativistic quantum theory.

The comparison of formulas (39) and (42) shows that the operator $V_{LL}^{(\pm)}$ differs from the operator $V_{LL}$ not only by the additional factor $\pm 1/2$ in the last term of (39), but also by the additional retarded term

$$\pm\frac{e^2}{2mc}\exp\left(\frac{i}{c}|\omega_{fi}|R\right)\frac{R}{r_{12}^2}\vec{n}\hat{\vec{p}}_2,$$

which is proportional to $R$. Thus, expression (39) gives the more complete description of the retardation effects in the interaction of electrons than expression (42) found in the previous articles [10–13].

Let us now discuss the physical meaning of the operator $V_{SS}$ (40). First of all, note that in the limiting case $R \to 0$ it is transformed into the usual operator of the spin-spin interaction of electrons in a He-like atom [17]. Thus, the operator $V_{SS}$ (40) is a natural generalization of the operator of the spin-spin interaction to the case of two quasimolecular electrons located at an arbitrary distance from each other.

It must be emphasized that expression (40) is in agreement with the corresponding result of Refs. [10–13] only in the quasimolecular domain $\Delta r < R < \infty$. Note, however, that the singularities of the integrand of (29) in the atomic domain $0 \leqslant R < \Delta r$ were not studied in these articles. As is known (see [15,17]), the singular part of the operator $V_{SS}$ (40) is a manifestation of the so-called spin-contact interaction between electrons (Fermi interaction) and is related to the $\delta$-functional singularity of expression (36) in the origin of coordinates. As well as in the case of the operator $V_D$ (38), the $\delta$-functional term $[\sim(\vec{\sigma}_1\vec{\sigma}_2)\delta(\vec{r}_{12})]$ entering into (40) gives the nontrivial contribution to the matrix element (30) only at $R \to 0$. In the other cases, when the overlap of wave functions from various centers can be neglected, this term disappears at $\Delta r \leqslant R < \infty$.

Finally, let us clarify the physical meaning of the operator $V_{SL}$ (41). In the limiting case $R \to 0$ it becomes the corresponding spin-orbit term in the Breit-Pauli operator [15,17], which describes the interaction between spin and orbital magnetic moments of electrons in a He-like atom. Thus, the last term $V_{SL}$ in (37) is nothing but the operator of spin-orbit retardation of two quasimolecular electrons at an arbitrary distance from each other.

Also, let us call attention to the fact that the second term $-3R^2(\vec{\sigma}_2[\vec{n} \times \hat{\vec{p}}_2])/r_{12}^4$, entering into the last square brackets of expression (41), has been lost in Refs. [11,12]. It is absent in the review [13] as well [see formula (3.8)]. As is seen from (41), the operator $V_{SL}$ is symmetric with respect to both electrons and, therefore, takes into account the spin-orbit retardation of two quasimolecular electrons more completely than the corresponding operator of [12,13].

The following remark needs to be made as to the expression obtained for the generalized Breit-Pauli operator $V_{BP}^{(\pm)}$. Although we are mainly interested in the quasimolecular domain ($\Delta r < R < \infty$), formulas (37)–(41) are written in the form valid in all interval of variation of $R$ ($0 \leqslant R < \infty$). When $R$ tends to zero, the operator $V_{BP}^{(\pm)}$ (37) becomes the corresponding two-particle part of the known Breit-Pauli operator in the coordinate space [15,17]. Therewith, it turns out that, regardless of the coupling constant smallness, the terms containing $\delta$ functions become the "operating" ones in the limiting expression. Thus, the role of these $\delta$-functional terms in the generalized Breit-Pauli operator (37)–(41) is reduced to providing the mathematical correctness of the limiting transition to the case of single heliumlike atom ($R \to 0$) investigated in [17].

Finally, we emphasize that one should not assign any meaning (of presence of especially strong coupling, for example) to the formal transformation of singular parts of operators $V_D$ (38) and $V_{SS}^{(\pm)}$ (40) into infinity (at $R = 0$ and $\vec{r}_1 = \vec{r}_2$). The integral values of all correction terms $\widetilde{V}_{BP}^{(\pm)}$ in the operator of interaction $V_{BP}^{(\pm)}$ are identical and, from the standpoint of performed expansion, all of them should be considered as small corrections in comparison with the first term $V_{1C}$ (34), which is an analog of the Coulomb interaction.

### B. Electric dipole-dipole interaction of two quasimolecular electrons

The role of various terms in the interaction operator (37) is determined by the type of quantum transition in the spectrum of the quasimolecule $(\mathrm{AB})^{(Z_a+Z_b-2)+}$. Here, we shall consider the interaction of two electrons located near different nuclei taking into account only the orbital degrees of freedom. The operator $V_{1C} + V_{LL}^{(\pm)}$, corresponding to this part of interelectron interaction, has purely orbital origin. Further, we shall consider the case $\omega_0 R/c \sim 1$ when distances between nuclei are comparable with the characteristic wavelength in the spectrum of interacting electrons. At large $R$ one can expand the functions $1/r_{12}$, $1/r_{12}^2$, and $1/r_{12}^3$, entering into the operator $V_{1C} + V_{LL}^{(\pm)}$, in multipoles and restrict oneself to several first terms of the expansion. The convenient form of multipolar expansion for the operator $1/r_{12}$ has been obtained in [23] (see also [24]).

In practical calculations, one usually has to deal with the dipole-dipole and quadrupole-quadrupole interactions. Here we shall restrict ourselves by considerating only the electric dipole transitions for which the corresponding operator is of the form

$$\begin{aligned} V_{1C,\mathrm{dip}} + V_{LL,\mathrm{dip}}^{(\pm)} = \exp\left(\frac{i}{c}|\omega_{fi}|R\right) & \\ \times \Bigg\{ & \frac{\vec{d}_{1b}\vec{d}_{2a} - 3(\vec{n}_R\vec{d}_{1b})(\vec{n}_R\vec{d}_{2a})}{R^3} \\ & \pm \frac{e}{2mc}\left[\frac{\vec{d}_{1b}\hat{\vec{p}}_2 - 3(\vec{n}_R\vec{d}_{1b})(\vec{n}_R\hat{\vec{p}}_2)}{R^2}\right. \\ & \left. - \frac{\vec{d}_{2a}\hat{\vec{p}}_1 - 3(\vec{n}_R\vec{d}_{2a})(\vec{n}_R\hat{\vec{p}}_1)}{R^2}\right] \\ & - \frac{e^2}{m^2c^2}\frac{\hat{\vec{p}}_1\hat{\vec{p}}_2 - (\vec{n}_R\hat{\vec{p}}_1)(\vec{n}_R\hat{\vec{p}}_2)}{R}\Bigg\}, \end{aligned} \qquad (43)$$

where $\vec{d}_{1b} = e\vec{r}_{1b}$, $\vec{d}_{2a} = e\vec{r}_{2a}$ are the operators of the electric dipole moments of separate electrons, $\vec{n}_R$ is the unit vector oriented in the direction of $\vec{R}$, and $\vec{r}_{2a}$ of electrons 1 and 2 are measured from nuclei $\mathrm{B}^{Z_b+}$ and $\mathrm{A}^{Z_a+}$, respectively. The operator (43) is the operator of electric dipole-dipole interaction of two electrons located at an arbitrarily large distance from each other, near different nuclei. The difference of this operator from the corresponding operator [12; see formula (3.9)] consists of the fact that expression (43) contains the additional retarded term

$$\mp \frac{e}{2mc}\frac{\vec{d}_{2a}\hat{\vec{p}}_1 - 3(\vec{n}_R\vec{d}_{2a})(\vec{n}_R\hat{\vec{p}}_1)}{R^2},$$

whose value is comparable to the term $\sim R^{-3}$ when $R \sim c/\omega_0$.

In the first order of the perturbation theory, the dipole-dipole interaction gives the contribution only when pairs of states of the isolated atoms, which have different parity, enter into initial functions of the zero approximation. Such a situation arises, for example, at the resonance and almost resonance transmission of excitation in collisions of atoms of alkali metals (see [25,26]).

## V. CONCLUSION

In this section, we briefly sum up the results of studying the problem of two quasimolecular electrons in the framework of the second-order effects of quantum electrodynamics and outline a path for further investigations. It is shown that when solving this problem, one has to abide by natural conditions of symmetry of interaction with respect to both electrons. The given circumstance makes it necessary to represent the $c^{-1}$ expansion of the retardation factor in totally symmetrical (with respect to coordinates of both electrons) form (21). In turn, it leads to representation (26) for the relativistic operator of interaction between two electrons $V^{(\pm)}(\vec{r}_1,\vec{r}_2;R)$, in which [unlike (27)] dependence on both orbital and spin variables of pair of electrons is represented in the maximally symmetrical form. Let us indicate the main properties of this operator.

There are two domains of the configuration space where the generalized Breit operator $V^{(\pm)}(\vec{r}_1,\vec{r}_2;R)$ behaves differently depending on the distance $r_{12}$ between the two electrons. For instance, in the united-atom limit, formula (26) becomes the usual Breit expression (1), which correctly describes the retardation effects of the relativistic interaction only at small interparticle distance $r_{12}$. To be more exact, the applicability domain for Breit formula (1) is restricted by the following condition on the coordinate variables:

$$\omega_0 r_{12}/c \ll 1, \tag{44}$$

where $\omega_0$ is the characteristic frequency of spectrum of the interacting electrons. We let $\Omega_I$ denote the corresponding domain in the configuration space, which we call the domain of close electron correlations. However, in the domain $\Omega_{II}$, where the electrons belong to different nuclei and condition (14) is satisfied for all $\Delta r \leqslant R < \infty$, Breit operator (1) fails to describe the relativistic interaction of two electrons even on the qualitative level. At the same time, the relativistic operator $V^{(\pm)}(\vec{r}_1,\vec{r}_2;R)$ (26) constructed here makes it possible to describe the retarded interaction of two electrons in both the domain $\Omega_I$ of close electron correlations and the domain $\Omega_{II}$ 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.

Specific time scale of interaction transfer and specific calculation approximations, making it possible to find small parameters and take into account different types of interaction, are characteristic for each domain ($\Omega_I$, $\Omega_{II}$) of interelectron distances $r_{12}$. Thus, we reiterate not only that we can use the generalized Breit operator $V^{(\pm)}(\vec{r}_1,\vec{r}_2;R)$ to solve the multielectron two-center problems, but also that the quantum electrodynamic treatment of two-electron interaction based on the standard Breit operator (1) is incomplete.

As shown in Sec. III, 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 the quantity (44) [17]. This means that in addition to the characteristic (mean) electron transition time $T_0 = 2\pi/\omega_0$, the unified time scale $T_{\text{int}} = r_{12}/c$, corresponding to the domain $\Omega_I$, is also used. We can interpret this time as an interaction transfer time. Then, the condition $2\pi T_{\text{int}} \ll T_0$, meaning that a substantial change in the electron density in the system of the two interacting electrons occurs during the interaction transfer time, must be satisfied.

At rather large interelectron distances (in the domain $\Omega_{II}$), where the interaction transfer time $T_{\text{int}} = R/c$ is much larger than the mean electron transition time $T_0 = 2\pi/\omega_0$, the natural small parameter is the dimensionless quantity (14). Exchange by virtual photons at such a distance results in the interelectron interaction (26) that, in addition to the Coulomb and Breit interactions (1), contains additional terms caused by the amplification of effects of retardation of the spin interactions of the two quasimolecular electrons. The parameter that determines the degree of amplification of the retardation effects in the electron interaction is the ratio $T_{\text{int}}/T_0$ or $R/\lambda_0$, where $\lambda_0 = 2\pi c/\omega_0$.

The derivation of the explicit representation for the generalized two-particle Breit-Pauli operator $V_{BP}^{(\pm)}$ (37) is performed by means of conversion from the relativistic four-component Dirac bispinors to the nonrelativistic two-component Pauli spinors in the matrix $U_{i\to f}^{(2)}$ (10) of effective energy of interaction $V^{(\pm)}$ (26). It is shown that the correct account of the natural condition of the interaction symmetry with respect to both electrons results in new terms in the operators of spin-orbit (41), spin-spin (40), and retardation (39) interactions which are missed in corresponding operators in [10–13]. Thus, the generalized Breit-Pauli operator (37)–(41) constructed in the present article makes it possible to rigorously take into account orbital and spin degrees of freedom, and retardation effects of interaction of two quasimolecular electrons located at an arbitrary distance from each other. All of this opens up possibilities for mathematically correct calculations of both molecular structures and atomic clusters, and parameters of exchange correlative interaction of atomic particles during the course of collision.

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