

## THE GENERALIZED BREIT OPERATOR OF A LONG-RANGE TYPE IN THE FRAMEWORK OF THE SECOND-ORDER EFFECTS 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 a consistent account for the natural condition of the interaction symmetry with respect to both electrons leads to an additional contribution to the relativistic interaction of the two quasimolecular electrons compared with both the standard Breit operator and the generalized Breit operator known previously. The generalized Breit–Pauli operator and the operator of electric dipole–dipole interaction of two quasimolecular electrons located at an arbitrary distance from each other are obtained. Modern methods of accounting for the relativistic and correlative effects in the problem of ion–atom interactions are discussed.

*Keywords:* Interelectron interaction; retardation effects; Breit operator; quantum electrodynamics; quasimolecular electron.

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### 1. Introduction

For a long period of time, one of the most acute problems of the theory of slow ion–atom collisions has been clarification of mechanisms of multielectronic processes with rearrangement, such as two-electron charge exchange and charge exchange with simultaneous excitation or ionization. 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 internuclear distance  $R$  is rather large. The presence of a small parameter  $1/R$  gives a chance to elaborate a consistent asymptotic theory of such processes. It is no wonder that precisely this path has allowed us to obtain many approved results in the analytical theory of two-electron processes with rearrangement in slow ion–atom and ion–ion collisions

(see, for example, Refs. 1–5 and references therein). The experimental confirmation of a dominating role of effects of the strong exchange-correlative interaction of two electrons, located near different nuclei, in the dynamics of these processes has allowed us to understand and explain the basic properties of such processes on the unified ground.

Investigation into collisions of slow atomic particles with participation of highly charged ions and bare nuclei has become more and more urgent in the light of the further development of physical ideas about mechanisms of multielectronic processes with rearrangement (see, for example, the review Ref. 6). In the case where under favorable conditions the mechanisms of nonadiabatic coupling result in strongly correlated electron transitions with involvement of electrons of internal (nonoptical) shells, the relativistic effects become essential, and a consistent account for them demands the generalization of the adiabatic asymptotic theory of multielectron processes with rearrangement<sup>1–3,7</sup> to the range of relativistic binding energies. It is necessary to stress here that the followed exchange mechanism is typical of all specified two-electron processes with rearrangement (see Refs. 1 and 7 and the references therein): one of the active electrons of atom (ion)  $A^{(Z_a-2)+}$  tunnels to a “foreign” ion (or bare nucleus)  $B^{Z_b+}$ , 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 to the Dirac equation for the two-Coulomb-center problem,<sup>8,9</sup> but also in the 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 the 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, even 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 on the poorly investigated problems of relativistic multiparticle interactions, we note only that the modern quantum field theory of electromagnetic interactions [quantum electrodynamics (QED)], based on the  $S$ -matrix formalism and Feynman diagram technique, gives only the recipe for construction of such an operator in the form of expansion in powers of the fine structure constant  $\alpha$ . As early as 1929, Breit demonstrated<sup>10,11</sup> 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 helium-like atom are small. He obtained the following relativistic operator of the interelectron interaction:<sup>10,11</sup>

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

where  $\boldsymbol{\alpha}_1$  and  $\boldsymbol{\alpha}_2$  are the commuting sets of the Dirac matrices,  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ ,  $r_{12} = |\mathbf{r}_{12}|$ , and the subscripts 1 and 2 distinguish the quantities relating to the first and the second electron, respectively. We have to remember that the applicability of the Breit operator (1) is limited by the condition that the interelectron distance  $r_{12}$  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.<sup>1</sup> Therefore, interest in the problem of two electrons belonging to two hydrogen-like 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. 12–15, where the problem of the interaction of two bound electrons belonging to two hydrogen-like atoms was studied by quantum-electrodynamic methods in the general formulation without imposing any restriction on the interatom distances. However, in turning to these works we discovered<sup>16,17</sup> 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 for a natural condition for 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. 12–15.

This article is organized as follows. In Sec. 2, 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. 4, 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. Section 5 presents a discussion on modern methods of accounting for relativistic and correlative effects in the problem of ion–atom interactions. In the last section, the final results are discussed and compared with the corresponding results of the previous articles devoted to the problem of two electrons.

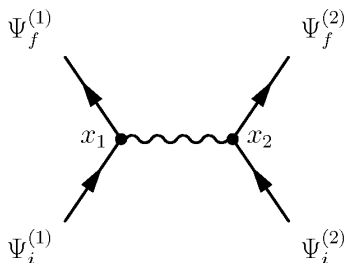


Fig. 1. The Feynman diagram for the second-order effects of QED for interaction of two quasi-molecular electrons.

## 2. Matrix of the Effective Energy of 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<sup>18,19</sup>

$$S_{i \rightarrow f}^{(2)} \equiv \langle f | S^{(2)} | i \rangle = -i \int d^4 x_1 \int d^4 x_2 j_{\text{fi}}^{(2)\mu}(x_2) D_F(x_2 - x_1) j_{\text{fi}\mu}^{(1)}(x_1), \quad (2)$$

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

$$j_{\text{fi}\mu}^{(1)}(x_1) = e \bar{\Psi}_f^{(1)}(x_1) \gamma_\mu^{(1)} \Psi_i^{(1)}(x_1), \quad j_{\text{fi}}^{(2)\mu}(x_2) = e \bar{\Psi}_f^{(2)}(x_2) \gamma^{(2)\mu} \Psi_i^{(2)}(x_2). \quad (3)$$

Here,  $e = -|e|$  is the electronic charge;  $\gamma^\mu$  ( $\mu = 0, 1, 2, 3$ ) are the Dirac matrices in the covariant representation;  $\Psi_i^{(n)}$  and  $\Psi_f^{(n)}$  are wave functions of the respective initial and final states of the  $n$ th electron,  $n = 1, 2$ ;  $\bar{\Psi}_f^{(n)} = \Psi_f^{(n)+} \gamma^0$  is the Dirac-adjoint bispinor; and  $\Psi_f^{(n)+}$  is the Hermitian-adjoint bispinor. In the expression (2), we use the relativistic units  $\hbar = c = 1$ , the notation  $x_1^\mu = (t_1, \mathbf{r}_1)$  and  $x_2^\mu = (t_2, \mathbf{r}_2)$  for the radius four-vectors, and  $d^4 x_1 = d^3 x_1 dt_1$  and  $d^4 x_2 = d^3 x_2 dt_2$  for the four-volume elements. The superscripts (1) and (2) distinguish quantities related to different electrons. The subscripts  $i$  and  $f$  denote quantities pertaining to the initial and final states of the interacting electrons. In the expressions (2) and (3), we use the following representation for the Dirac matrices:

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

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

The wave functions of stationary states

$$\Psi_{i,f}^{(1)}(x_1) = \Psi_{i,f}^{(1)}(\mathbf{r}_1) e^{-iE_{i,f}^{(1)} t_1}, \quad \Psi_{i,f}^{(2)}(x_2) = \Psi_{i,f}^{(2)}(\mathbf{r}_2) e^{-iE_{i,f}^{(2)} t_2} \quad (4)$$

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

$$j_{\hat{n}\mu}^{(1)}(x_1) = j_{\hat{n}\mu}^{(1)}(\mathbf{r}_1)e^{i\omega_{\hat{n}}^{(1)}t_1}, \quad j_{\hat{n}}^{(2)\mu}(x_1) = j_{\hat{n}}^{(2)\mu}(\mathbf{r}_2)e^{i\omega_{\hat{n}}^{(2)}t_2}, \quad (5)$$

where the transition frequency is  $\omega_{\hat{n}}^{(n)} = E_f^{(n)} - E_i^{(n)}$ ,  $n = 1, 2$ .

In the Feynman gauge the propagator

$$D_F(x_2 - x_1) = \int \frac{d^4k}{(2\pi)^4} \left( \frac{-4\pi e^{-ik(x_2-x_1)}}{k^2 + i\varepsilon} \right) \quad (6)$$

corresponds to the internal photon line of the diagram. Here  $k = (\omega, \mathbf{k})$ ,  $\mathbf{k}$  and  $\omega$  are respectively the wave vector and frequency of the photon, and the infinitesimal imaginary term in the denominator fixes the rules for bypassing poles in the complex plane. Having substituted (5) and (6) into (2), we arrive at the following representation for the  $S$  matrix:

$$S_{i \rightarrow f}^{(2)} = -i \int d^4x_1 \int d^4x_2 \int \frac{d^4k}{(2\pi)^4} j_{\hat{n}}^{(2)\mu}(\mathbf{r}_2)e^{i\omega_{\hat{n}}^{(2)}t_2} \times \left( \frac{-4\pi e^{-ik(x_2-x_1)}}{k^2 + i\varepsilon} \right) j_{\hat{n}\mu}^{(1)}(\mathbf{r}_1)e^{i\omega_{\hat{n}}^{(1)}t_1}. \quad (7)$$

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

$$S_{i \rightarrow f}^{(2)} = 4\pi i \int d^3x_1 \int d^3x_2 \int dt_1 \int d\omega \delta(\omega - \omega_{\hat{n}}^{(2)}) \times e^{i(\omega_{\hat{n}}^{(1)} + \omega)t_1} j_{\hat{n}}^{(2)\mu}(\mathbf{r}_2) j_{\hat{n}\mu}^{(1)}(\mathbf{r}_1) \int \frac{d^3k}{(2\pi)^3} \frac{e^{i\mathbf{k}(\mathbf{r}_2 - \mathbf{r}_1)}}{\omega^2 - \mathbf{k}^2 + i\varepsilon}. \quad (8)$$

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

$$S_{i \rightarrow f}^{(2)} = -i \int d^3x_1 \int d^3x_2 \int dt_1 \int d\omega \delta(\omega - \omega_{\hat{n}}^{(2)}) \times e^{i(\omega_{\hat{n}}^{(1)} + \omega)t_1} j_{\hat{n}}^{(2)\mu}(\mathbf{r}_2) \frac{e^{i|\omega||\mathbf{r}_1 - \mathbf{r}_2|}}{|\mathbf{r}_1 - \mathbf{r}_2|} j_{\hat{n}\mu}^{(1)}(\mathbf{r}_1). \quad (9)$$

After integration over time  $t_1$  and the frequencies of virtual photons  $\omega$ , the last expression becomes

$$S_{i \rightarrow f}^{(2)} = -2\pi i \delta(\omega_{\hat{n}}^{(1)} + \omega_{\hat{n}}^{(2)}) \int d^3x_1 \int d^3x_2 j_{\hat{n}}^{(2)\mu}(\mathbf{r}_2) \frac{e^{i|\omega_{\hat{n}}^{(2)}||\mathbf{r}_1 - \mathbf{r}_2|}}{|\mathbf{r}_1 - \mathbf{r}_2|} j_{\hat{n}\mu}^{(1)}(\mathbf{r}_1). \quad (10)$$

Let us now proceed from the scattering matrix  $S_{i \rightarrow f}^{(2)}$  to the matrix  $U_{i \rightarrow f}^{(2)}$  of the effective interaction energy of the system of two charges defined by the equality

$$S_{i \rightarrow f}^{(2)} = -2\pi i U_{i \rightarrow f}^{(2)} \delta(E_f^{(1)} - E_i^{(1)} + E_f^{(2)} - E_i^{(2)}). \quad (11)$$

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

$$E_f^{(1)} + E_f^{(2)} = E_i^{(1)} + E_i^{(2)}, \quad (12)$$

which is the manifestation of symmetry under the continuous time-shift operation. In view of the conservation law (12), let us write  $|\omega_{\bar{n}}^{(1)}|$  and  $|\omega_{\bar{n}}^{(2)}|$  in the simplified form  $|\omega_{\bar{n}}|$  (implying that  $|\omega_{\bar{n}}| = |\omega_{\bar{n}}^{(1)}| = |\omega_{\bar{n}}^{(2)}|$ ). Then by (10) and (11) the matrix of the effective energy of interaction between two electrons is of the form

$$U_{i \rightarrow f}^{(2)} = \int d^3 x_1 \int d^3 x_2 j_{\bar{n}}^{(2)\mu}(\mathbf{r}_2) \frac{e^{i|\omega_{\bar{n}}||\mathbf{r}_1 - \mathbf{r}_2|}}{|\mathbf{r}_1 - \mathbf{r}_2|} j_{\bar{n}\mu}^{(1)}(\mathbf{r}_1). \quad (13)$$

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

### 3. The Generalized Breit Operator of a Long-Range Type

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

$$U_{i \rightarrow f}^{(2)} = e^2 \int d^3 x_1 \int d^3 x_2 \Psi_f^{(2)+}(\mathbf{r}_2) \Psi_f^{(1)+}(\mathbf{r}_1) \frac{1 - \boldsymbol{\alpha}_1 \boldsymbol{\alpha}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \times e^{i|\omega_{\bar{n}}||\mathbf{r}_1 - \mathbf{r}_2|} \Psi_i^{(2)}(\mathbf{r}_2) \Psi_i^{(1)}(\mathbf{r}_1), \quad (14)$$

where  $\boldsymbol{\alpha}_1$  and  $\boldsymbol{\alpha}_2$  are the Dirac matrices acting on different one-electron wave functions:  $\boldsymbol{\alpha}_1$  acts on  $\Psi_i^{(1)}(\mathbf{r}_1)$ , and  $\boldsymbol{\alpha}_2$  acts on  $\Psi_i^{(2)}(\mathbf{r}_2)$ . Since the “retardation factor”  $\exp\{i|\omega_{\bar{n}}|r_{12}\}$ , 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, i.e. an operator  $V$  for which the relation

$$U_{i \rightarrow f}^{(2)} = \langle f | V | i \rangle = \int d^3 x_1 \int d^3 x_2 \Psi_f^{(2)+}(\mathbf{r}_2) \Psi_f^{(1)+}(\mathbf{r}_1) V \Psi_i^{(2)}(\mathbf{r}_2) \Psi_i^{(1)}(\mathbf{r}_1) \quad (15)$$

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). Indeed, for atomic electrons we have  $|\omega_{\bar{n}}| \sim m(\alpha Z_{\text{eff}})^2$  in our units, where  $Z_{\text{eff}}$  is the effective charge of the nucleus, whose interaction with a given electron is equivalent to the interaction of a nucleus, screened by all the other electrons in the atom. Further, take into account that

the characteristic interelectron distance in an atom is  $r_{12} \sim (m\alpha Z_{\text{eff}})^{-1}$ . Hence, the exponent  $|\omega_{\text{fi}}|r_{12}$  in (14) is of the order of  $\alpha Z_{\text{eff}}$ . In fact, the ratio  $v/c$ , being of the order of  $\alpha Z_{\text{eff}}$ , is much smaller than unity for all atomic electrons, including the internal ones. Therefore, we can approximately take into account the retardation and all other relativistic effects by dropping terms of the order  $v^3/c^3$  and higher in the  $v/c$  expansion of the matrix element (14). This approximation results in the known expression (1) for the Breit operator,<sup>10,11,20</sup> which depends not only on the relative position  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$  of the pair of electrons but also on their spins. We claim now that this expression approximates quite well the relativistic electron interaction only in the intra-atomic domain but becomes inapplicable in the domain of large interelectron distances ( $r_{12} \geq \lambda_0 = 2\pi c/\omega_0$ ). In this domain, which we shall call *the domain of far electron correlations*, the effects of retardation of interaction of electrons are essentially amplified.

Let us now consider a two-electron atom (or ion)  $A^{(Z_a-2)+}$  and the bare nucleus  $B^{Z_b+}$  located at an arbitrary distance  $R$  from the atom. Here  $Z_a$  and  $Z_b$  are the charges of the atomic nuclei  $A^{Z_a+}$  and  $B^{Z_b+}$ , which are assumed to be stable in the proposed two-center model. Let  $\mathbf{r}_{na}$  and  $\mathbf{r}_{nb}$  be the position vectors of the  $n$ th electron with respect to the nuclei  $A^{Z_a+}$  and  $B^{Z_b+}$ ,  $n = 1, 2$ . We now assume that one of the electrons of the atom  $A^{(Z_a-2)+}$  — the first electron, for instance — tunnels into the vicinity of the foreign nucleus  $B^{Z_b+}$ , while the second electron is located near its host nucleus,  $A^{Z_a+}$ . If the domains of spatial localizations of the electrons near the different nuclei (the first electron near  $B^{Z_b+}$  and the second one near  $A^{Z_a+}$ ) 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  $\Delta r/R$ :

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

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

In the matrix of effective interaction energy (14), let us consider the factor

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

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,<sup>10,11,20</sup> 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, such as intra-atomic distances in He-like atoms. An asymptotic expansion of the  $K$  factor (17) is constructed below for the case where 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 Refs. 10, 11 and 20, 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 (17) as follows:

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

For electrons belonging to different atoms, this transformation is convenient due to the factorization of the relativistic factor  $\exp\{i|\omega_{\text{fi}}|R/c\}$  of the amplification of the effects of retardation, which are encoded in the dependence of this factor on both the internuclear distance  $R$  and the difference of energies of one-particle states:  $|\omega_{\text{fi}}| = |\omega_{\text{fi}}^{(n)}| = |E_f^{(n)} - E_i^{(n)}|$ ,  $n = 1, 2$ . However, the basic argument in favor of expediency of such transformation consists in the fact that by means of it the problem of expansion of the retardation factor  $\exp\{i|\omega_{\text{fi}}|r_{12}/c\}$  is reduced to expansion of the specialized (for the quasimolecular model of two electrons near different centers) exponential factor  $\exp\{i|\omega_{\text{fi}}|(|\mathbf{r}_1 - \mathbf{r}_2| - R)/c\}$ . The presence of the difference  $r_{12} - R$  in the last exponent indicates that such an expansion should be carried out not only in powers of  $1/c$  but also in powers of the small parameter  $\Delta r/R$ .

In line with this notation, we assume that

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

Internuclear distance therewith can vary over the wide range  $\Delta r \leq R < \infty$ . When the condition (19) is satisfied, the exponent  $|\omega_{\text{fi}}|(r_{12} - R)/c$  on the right-hand side of (18) is a small quantity and we can expand the  $K$  factor (17) in powers of  $1/c$ . So we obtain the expansion to within the terms  $\sim c^{-2}$ :

$$K(\mathbf{r}_1, \mathbf{r}_2; \omega_{\text{fi}}) = e^{i|\omega_{\text{fi}}|R/c} \left\{ f_0(r_{12}) + \frac{i}{c} |\omega_{\text{fi}}| f_1(r_{12}) - \frac{\omega_{\text{fi}}^2}{2c^2} f_2(r_{12}) \right\}. \tag{20}$$

The coefficients

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

of the expansion (20) are in turn power series in  $\Delta r/R$ . Actually, this means that if the domains of space localization of electrons near different centers are rather far



from each other, then one can use the formulas

$$\begin{aligned}
 g_0(\Delta\mathbf{r}, \mathbf{R}) &= R\left(1 + \frac{\mathbf{R}\Delta r}{R^2} + \frac{M}{R}\right), \\
 g_1(\Delta\mathbf{r}, \mathbf{R}) &= \frac{\mathbf{R}\Delta r}{R} + M, \\
 g_2(\Delta\mathbf{r}, \mathbf{R}) &= \left(\frac{\mathbf{R}\Delta r}{R} + M\right)^2
 \end{aligned}$$

and re-expand the functions  $f_0$ ,  $f_1$  and  $f_2$  from (20) in powers of  $\Delta r/R$ . If one does not do such a re-expansion, then one can take into account (in  $c^{-2}$  approximation) the interaction of quasimolecular electrons of all multiplicities in the closed form.

Let us eliminate frequencies in the expression (20) by using the Dirac equations:

$$\hat{H}^{(n)}(\mathbf{r}_n)\Psi_i^{(n)}(\mathbf{r}_n) = E_i^{(n)}\Psi_i^{(n)}(\mathbf{r}_n), \quad \hat{H}^{(n)}(\mathbf{r}_n)\Psi_f^{(n)}(\mathbf{r}_n) = E_f^{(n)}\Psi_f^{(n)}(\mathbf{r}_n). \quad (22)$$

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

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

$$\begin{aligned}
 |\omega_{\text{fi}}|f_1(r_{12}) &= \left|\omega_{\text{fi}}^{(1)}\right|f_1(r_{12}) = \pm\omega_{\text{fi}}^{(1)}f_1(r_{12}) \\
 &= \pm\frac{1}{2}\left(E_f^{(1)} - E_i^{(1)} + E_i^{(2)} - E_f^{(2)}\right)f_1(r_{12}). \quad (23)
 \end{aligned}$$

The plus sign in (23) corresponds to the case  $E_f^{(1)} > E_i^{(1)}$  ( $\omega_{\text{fi}}^{(1)} > 0$ ), and the minus sign to the case  $E_f^{(1)} < E_i^{(1)}$  ( $\omega_{\text{fi}}^{(1)} < 0$ ). We could start with the equality  $|\omega_{\text{fi}}|f_1 = |\omega_{\text{fi}}^{(2)}|f_1$  instead of the equality  $|\omega_{\text{fi}}|f_1 = |\omega_{\text{fi}}^{(1)}|f_1$  in order to symmetrize the quantity  $|\omega_{\text{fi}}|f_1$ . It is easy to see that the representation for  $|\omega_{\text{fi}}|f_1$  obtained in this way is equivalent to the representation (23).

Since we multiply the expression (20) by  $\Psi_i^{(2)}(\mathbf{r}_2)\Psi_i^{(1)}(\mathbf{r}_1)$  from the right and by  $\Psi_f^{(2)+}(\mathbf{r}_2)\Psi_f^{(1)+}(\mathbf{r}_1)$  from the left and subsequently integrate over  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , we can replace the energies  $E_i^{(1)}$  and  $E_i^{(2)}$  in (23) 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  $f_1(r_{12})$ :

$$\begin{aligned} |\omega_{\hat{n}}|f_1(r_{12}) &\rightarrow \pm \frac{1}{2} \left\{ \hat{H}^{(1)} f_1(r_{12}) - f_1(r_{12}) \hat{H}^{(1)} + f_1(r_{12}) \hat{H}^{(2)} - \hat{H}^{(2)} f_1(r_{12}) \right\} \\ &= \pm \frac{1}{2} \left\{ [\hat{H}^{(1)}, f_1(r_{12})] + [f_1(r_{12}), \hat{H}^{(2)}] \right\}. \end{aligned} \tag{24}$$

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

Using the relation  $\omega_{\hat{n}}^{(1)} = -\omega_{\hat{n}}^{(2)}$ , we transform the third term of the expansion (20) into the symmetric form:

$$\begin{aligned} -\omega_{\hat{n}}^2 f_2(r_{12}) &= \left( E_f^{(1)} - E_i^{(1)} \right) \left( E_f^{(2)} - E_i^{(2)} \right) f_2(r_{12}) \\ &\rightarrow f_2(r_{12}) \hat{H}^{(1)} \hat{H}^{(2)} - \hat{H}^{(1)} f_2(r_{12}) \hat{H}^{(2)} \\ &\quad - \hat{H}^{(2)} f_2(r_{12}) \hat{H}^{(1)} + \hat{H}^{(1)} \hat{H}^{(2)} f_2(r_{12}) \\ &= [\hat{H}^{(1)}, [\hat{H}^{(2)}, f_2(r_{12})]]. \end{aligned} \tag{25}$$

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

$$\begin{aligned} K(\mathbf{r}_1, \mathbf{r}_2; \omega_{\hat{n}}) &\rightarrow e^{i|\omega_{\hat{n}}|R/c} \left\{ f_0(r_{12}) \pm \frac{i}{2c} \left( [\hat{H}^{(1)}, f_1(r_{12})] + [f_1(r_{12}), \hat{H}^{(2)}] \right) \right. \\ &\quad \left. + \frac{1}{2c^2} [\hat{H}^{(1)}, [\hat{H}^{(2)}, f_2(r_{12})]] \right\}. \end{aligned} \tag{26}$$

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

Therefore, the  $K$  factor (17) is represented by means of the double expansion (20) 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  $A^{(Z_a-2)+} + B^{Z_b+}$  is described by the relativistic one-electron Hamiltonian for the problem of two Coulomb centers located at the distance  $R$  from each other:

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

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

Hereinafter,  $\hbar \neq 1$ ,  $\hat{\mathbf{p}}_n = -i\hbar \nabla_n$  is the momentum operator of the  $n$ th electron,  $\nabla_n$  is the three-dimensional gradient with respect to the coordinates  $\mathbf{r}_n$  of the electron with the number  $n$ , and the index  $n$  on  $\alpha_n$  and  $\beta_n$  indicates that these matrices act on the function  $\Psi_i^{(n)}(\mathbf{r}_n)$ .

With the performed calculations in mind, it is easy to see that the result (26) can obviously be generalized by introducing the additional terms into the Hamiltonians (27), such as taking into account a finite size and the spin of the nucleus, or screening the nucleus field by the electron shell of the atomic core. However, we have to remember that except for limiting cases (for example, large internuclear distances<sup>8,9</sup>) the eigenvalue problem (22) for such a Hamiltonian cannot be solved in an explicit form.

Let us now calculate the commutators appearing in (26). First of all, note that only one term in  $\hat{H}^{(n)}$ , namely  $c\alpha_n\hat{\mathbf{p}}_n$ , is noncommuting with  $f_1(r_{12})$  and  $f_2(r_{12})$ . For this reason we can disregard all terms not containing the matrices  $\alpha_n$  in the expressions (27) for the operators  $\hat{H}^{(1)}$  and  $\hat{H}^{(2)}$  when they are substituted into the commutators in (26):

$$\begin{aligned} [\hat{H}^{(1)}, f_1] &= c[\alpha_1\hat{\mathbf{p}}_1, f_1], \\ [f_1, \hat{H}^{(2)}] &= c[f_1, \alpha_2\hat{\mathbf{p}}_2], \\ [\hat{H}^{(1)}, [\hat{H}^{(2)}, f_2]] &= c^2[\alpha_1\hat{\mathbf{p}}_1, [\alpha_2\hat{\mathbf{p}}_2, f_2]]. \end{aligned} \tag{29}$$

Having calculated the commutators (29) by the means of the easily checkable formula  $[\alpha_n\hat{\mathbf{p}}_n, f_{1,2}] = -i\hbar(\alpha_n\nabla_n)f_{1,2}$ , we find that the contributions of the second and third terms to the expansion (26) are determined by the following operator expressions:

$$\pm \frac{i}{2c}([\hat{H}^{(1)}, f_1] + [f_1, \hat{H}^{(2)}]) = \pm\hbar R \frac{\alpha_1\mathbf{n} + \alpha_2\mathbf{n}}{2r_{12}^2}, \tag{30}$$

$$\begin{aligned} \frac{1}{2c^2}[\hat{H}^{(1)}, [\hat{H}^{(2)}, f_2]] &= -\frac{\hbar^2}{2}(\alpha_1\nabla_1)(\alpha_2\nabla_2)r_{12} \\ &\quad - \frac{\hbar^2 R^2}{2}(\alpha_1\nabla_1)(\alpha_2\nabla_2)\frac{1}{r_{12}}, \end{aligned} \tag{31}$$

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

Therefore, the quantity  $\langle f|V|i\rangle$  can indeed be represented in the form (15), where the operator  $V$ , which describes the virtual photon exchange between particles in the matrix  $U_{i\rightarrow f}^{(2)}$ , is (here again  $\hbar = 1$ )

$$\begin{aligned} V^{(\pm)}(\mathbf{r}_1, \mathbf{r}_2; R) &= e^2 \exp\left(\frac{i}{c}|\omega_{fi}|R\right) \left\{ \frac{1}{r_{12}} - \frac{\alpha_1\alpha_2 + (\alpha_1\mathbf{n})(\alpha_2\mathbf{n})}{2r_{12}} \right. \\ &\quad \left. \pm R \frac{\alpha_1\mathbf{n} + \alpha_2\mathbf{n}}{2r_{12}^2} - R^2 \frac{\alpha_1\alpha_2 - 3(\alpha_1\mathbf{n})(\alpha_2\mathbf{n})}{2r_{12}^3} \right\}. \end{aligned} \tag{32}$$

In this equality, the plus sign of the term containing the factor  $R$  corresponds to the case  $E_f^{(1)} > E_i^{(1)}$  and the minus sign to the case  $E_f^{(1)} < E_i^{(1)}$ . We calculate the matrix element (15) of the operator (32) with the four-component wave functions  $\Psi_i^{(n)}(\mathbf{r}_n)$  and  $\Psi_f^{(n)}(\mathbf{r}_n)$ . The first term of (32) 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 due to the presence of electron spins.

In the limiting case of a united atom ( $R \rightarrow 0$ ), the operator (32) transforms into the relativistic Breit operator (1) of the interaction of two atomic electrons in helium-like systems. Therefore, we can consider the operator (32) as a direct generalization of the Breit operator<sup>10,11,20</sup> to the domain of arbitrarily large inter-electron distances. Such a generalization is nontrivial because the expression (32), in contrast to the 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 arbitrarily large distance when compared to  $\lambda_0 = 2\pi c/\omega_0$ .

According to the improvement of the Breit operator made in this article, it is worthwhile to call the expression (32) *the generalized Breit operator of a long-range type* (in order to stress the possibility of using it to solve two-electron problems in the physics of slow atomic collisions,<sup>1-3</sup> in the theory of quasimolecular Auger spectroscopy,<sup>4,5</sup> and in several important problems of nonlinear and quantum optics<sup>12-15,21</sup>).

Also, let us call attention to the fact that the obtained operator (32) is symmetric with respect to both interacting particles. This is due to the appropriate symmetrization of all retained terms in the  $c^{-1}$  expansion (20) of the  $K$  factor with respect to both electrons.

In the series of articles<sup>12,13</sup> 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 QED:

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

A principal drawback of this operator is the absence of symmetry in the description of the pair of interacting particles. It is most simply seen from the structure of the third term of (33), which is proportional to  $R$ .

The important remark which follows from comparison of the formulas (32) and (33) consists in the fact that consistent application of the procedure of symmetrization of the  $K$  factor [see (26)] with respect to both electrons leads to the appearance of a new term,  $\pm R(\boldsymbol{\alpha}_1 \mathbf{n})/2r_{12}^2$ , in the final expression (32) for the operator  $V^{(\pm)}(\mathbf{r}_1, \mathbf{r}_2; R)$  when compared with terms of the representation (33). 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 erroneous results when using the operator (33) from Refs. 12-15 in calculations.

### 4. Conversion to Two-Component Pauli Spinors

#### 4.1. Generalized two-particle Breit–Pauli operator

The conversion to approximative two-component wave functions  $\Phi_i^{(n)}$  and  $\Phi_f^{(n)}$  in the matrix  $U_{i \rightarrow f}^{(2)}$  [Eq. (15)] is performed through the transformations<sup>20</sup>

$$\Psi_{i,f}^{(n)}(\mathbf{r}_n) = \begin{pmatrix} \varphi_{i,f}^{(n)}(\mathbf{r}_n) \\ \frac{\boldsymbol{\sigma}_n \hat{\mathbf{p}}_n}{2mc} \varphi_{i,f}^{(n)}(\mathbf{r}_n) \end{pmatrix}, \quad \varphi_{i,f}^{(n)}(\mathbf{r}_n) = \left( 1 - \frac{\hat{\mathbf{p}}_n^2}{8m^2c^2} \right) \Phi_{i,f}^{(n)}(\mathbf{r}_n). \quad (34)$$

Here the two-row spin Pauli matrices  $\boldsymbol{\sigma}_n$  and operators  $\hat{\mathbf{p}}_n$  act on the variables on which the wave functions  $\Phi_i^{(n)}$  and  $\Phi_f^{(n)}$  depend. The formulas (34) demonstrate the convenience of realization of Pauli approximation, when considering the non-relativistic limit of the four-component spinors  $\Psi_{i,f}^{(n)}(\mathbf{r}_n)$ , because in this limit  $c \rightarrow \infty$  and the spinors (34) become effectively two-component.

Let us transform the matrix element

$$\langle f | V^{(\pm)} | i \rangle = \left\langle \Psi_f^{(1)*}(\mathbf{r}_1) \Psi_f^{(2)*}(\mathbf{r}_2) \left| V^{(\pm)}(\mathbf{r}_1, \mathbf{r}_2; R) \right| \Psi_i^{(1)}(\mathbf{r}_1) \Psi_i^{(2)}(\mathbf{r}_2) \right\rangle \quad (35)$$

by means of the functions (34) so that it takes the form

$$\begin{aligned} & \langle \Phi_f^*(1, 2) | V_{\text{BP}}^{(\pm)} | \Phi_i(1, 2) \rangle \\ &= \int d^3x_1 \int d^3x_2 \Phi_f^{(1)*}(\mathbf{r}_1) \Phi_f^{(2)*}(\mathbf{r}_2) V_{\text{BP}}^{(\pm)}(\mathbf{r}_1, \mathbf{r}_2; R) \Phi_i^{(1)}(\mathbf{r}_1) \Phi_i^{(2)}(\mathbf{r}_2), \end{aligned} \quad (36)$$

where  $V_{\text{BP}}^{(\pm)}(\mathbf{r}_1, \mathbf{r}_2; R)$  can be considered as the operator of interaction energy of two quasimolecular electrons at an arbitrary distance from each other. The wave functions  $\Phi_i(1, 2) = \Phi_i^{(1)}(\mathbf{r}_1) \Phi_i^{(2)}(\mathbf{r}_2)$  and  $\Phi_f(1, 2) = \Phi_f^{(1)}(\mathbf{r}_1) \Phi_f^{(2)}(\mathbf{r}_2)$  in (36) are the nonsymmetrized products of the two-component normalized wave functions (34) of separate electrons in the initial and the final state, respectively. The electron coordinates in the functions  $\Psi_{i,f}^{(2)}(\mathbf{r}_2)$  and  $\Psi_{i,f}^{(1)}(\mathbf{r}_1)$  are measured from the nuclei  $A^{Z_a+}$  and  $B^{Z_b+}$ , respectively.

First, let us consider the problem transforming the matrix element (35) of the operator of the Coulomb electron interaction  $e^2/r_{12}$  into the form (36). By substituting the functions (34) into (35) and using the necessary transformations, we obtain the following expression to within terms  $O(1/c^2)$ :

$$\begin{aligned} & e^2 \exp\left(\frac{i}{c} |\omega_{\text{fi}}| R\right) \langle f | \frac{1}{r_{12}} | i \rangle \\ &= e^2 \exp\left(\frac{i}{c} |\omega_{\text{fi}}| R\right) \int \left\{ \Phi_f^{(1)*}(\mathbf{r}_1) \Phi_f^{(2)*}(\mathbf{r}_2) \Phi_i^{(1)}(\mathbf{r}_1) \Phi_i^{(2)}(\mathbf{r}_2) \right. \\ & \quad - \frac{1}{8m^2c^2} \Phi_f^{(1)*}(\mathbf{r}_1) \Phi_f^{(2)*}(\mathbf{r}_2) \Phi_i^{(1)}(\mathbf{r}_1) \left[ \hat{\mathbf{p}}_2^2 \Phi_i^{(2)}(\mathbf{r}_2) \right] \\ & \quad \left. - \frac{1}{8m^2c^2} \Phi_f^{(1)*}(\mathbf{r}_1) \Phi_f^{(2)*}(\mathbf{r}_2) \left[ \hat{\mathbf{p}}_1^2 \Phi_i^{(1)}(\mathbf{r}_1) \right] \Phi_i^{(2)}(\mathbf{r}_2) \right\} \end{aligned}$$

$$\begin{aligned}
 & - \frac{1}{8m^2c^2} \Phi_f^{(1)*}(\mathbf{r}_1) \left[ \hat{\mathbf{p}}_2^2 \Phi_f^{(2)}(\mathbf{r}_2) \right]^* \Phi_i^{(1)}(\mathbf{r}_1) \Phi_i^{(2)}(\mathbf{r}_2) \\
 & - \frac{1}{8m^2c^2} \left[ \hat{\mathbf{p}}_1^2 \Phi_f^{(1)}(\mathbf{r}_1) \right]^* \Phi_f^{(2)*}(\mathbf{r}_2) \Phi_i^{(1)}(\mathbf{r}_1) \Phi_i^{(2)}(\mathbf{r}_2) \\
 & + \frac{1}{4m^2c^2} \left[ \sigma_1 \hat{\mathbf{p}}_1 \Phi_f^{(1)}(\mathbf{r}_1) \right]^* \left[ \sigma_1 \hat{\mathbf{p}}_1 \Phi_i^{(1)}(\mathbf{r}_1) \right] \Phi_f^{(2)*}(\mathbf{r}_2) \Phi_i^{(2)}(\mathbf{r}_2) \\
 & + \frac{1}{4m^2c^2} \Phi_f^{(1)*}(\mathbf{r}_1) \Phi_i^{(1)}(\mathbf{r}_1) \left[ \sigma_2 \hat{\mathbf{p}}_2 \Phi_f^{(2)*}(\mathbf{r}_2) \right]^* \left[ \sigma_2 \hat{\mathbf{p}}_2 \Phi_i^{(2)}(\mathbf{r}_2) \right] \Big\} \frac{d^3x_1 d^3x_2}{r_{12}}. \quad (37)
 \end{aligned}$$

The expression (37) can be transformed into

$$\begin{aligned}
 & \langle \Phi_f^*(1, 2) | V_1 | \Phi_i(1, 2) \rangle \\
 & = \int d^3x_1 \int d^3x_2 \Phi_f^{(1)*}(\mathbf{r}_1) \Phi_f^{(2)*}(\mathbf{r}_2) V_1 \Phi_i^{(1)}(\mathbf{r}_1) \Phi_i^{(2)}(\mathbf{r}_2). \quad (38)
 \end{aligned}$$

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 where taking into account the higher powers of quantity  $1/r_{12}$  results in nontrivial  $\delta$ -functional contributions to the operator of electrostatic energy of two electrons. Obviously, it takes place in the limiting case of the united atom, i.e. when  $R \rightarrow 0$ . Actually, as  $R$  decreases, the field in which electrons move resembles increasingly the field in the united helium-like atom with the total nuclear charge  $Z = Z_a + Z_b$ . This really means that on the interval  $0 \leq R < \Delta r$ , 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 (37) contains the higher powers of the quantity  $1/r_{12}$ , first of all it is necessary to separate out the specified point ( $\mathbf{r}_1 = \mathbf{r}_2$ ), i.e. the origin of coordinates. At  $\mathbf{r}_1 \rightarrow \mathbf{r}_2$  the integral over the sphere around the origin of coordinates gives a finite quantity. As this quantity depends only on the integrand at  $\mathbf{r}_1 = \mathbf{r}_2$ , it can also be represented in the form of a volume integral of the expression containing a three-dimensional Dirac  $\delta$  function,  $\delta(\mathbf{r}_1 - \mathbf{r}_2)$ .

On a more formal level, there are  $\delta$ -functional terms which usually arise when integrated by parts or, more exactly, when the action of the operators  $\hat{\mathbf{p}}_1 = -i\nabla_1$  and  $\hat{\mathbf{p}}_2 = -i\nabla_2$  transfers from the functions  $\Phi_f^{(n)}(\mathbf{r}_n)$  onto the quantity  $1/r_{12}$ . The singular expressions obtained in this way can be represented in the operator form

$$\hat{\mathbf{p}}_1^2 \frac{1}{r_{12}} = \hat{\mathbf{p}}_2^2 \frac{1}{r_{12}} = -(\hat{\mathbf{p}}_1 \hat{\mathbf{p}}_2) \frac{1}{r_{12}} = 4\pi\delta(\mathbf{r}_{12}). \quad (39)$$

Further, the products of the Pauli matrices  $\sigma$  that appear in the course of transformations described above, we write by means of the known matrix relations<sup>20</sup>

$$(\sigma \mathbf{a})(\sigma \mathbf{b}) = (\mathbf{a}\mathbf{b}) + i(\sigma[\mathbf{a} \times \mathbf{b}]), \tag{40}$$

$$(\sigma \mathbf{a})\sigma = \mathbf{a} + i[\sigma \times \mathbf{a}], \quad \sigma(\sigma \mathbf{a}) = \mathbf{a} + i[\mathbf{a} \times \sigma], \tag{41}$$

where  $\mathbf{a}$  and  $\mathbf{b}$  are arbitrary vectors.

The specified transformations allow us to write the expression (37) in the form (38), where the required operator  $V_1$  is given by the equality

$$V_1 = e^2 \exp\left(\frac{i}{c}|\omega_{\bar{n}}|R\right) \left\{ \frac{1}{r_{12}} - \frac{\pi}{m^2 c^2} \delta(\mathbf{r}_{12}) + \frac{1}{4m^2 c^2} \frac{\sigma_2[\mathbf{n} \times \hat{\mathbf{p}}_2] - \sigma_1[\mathbf{n} \times \hat{\mathbf{p}}_1]}{r_{12}^2} \right\}. \tag{42}$$

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

$$V_{1C} = e^2 \exp\left(\frac{i}{c}|\omega_{\bar{n}}|R\right) \frac{1}{r_{12}}, \tag{43}$$

on the right-hand side of (42) tends to the Coulomb electron interaction  $V_C(r_{12}) = e^2/r_{12}$ . Thus, it is reasonable enough that the operator  $V_{1C}$  [Eq. (43)] is an analog of the Coulomb interaction of electrons at an arbitrary distance from each other but, unlike  $V_C(r_{12})$ , depends on the initial and final energies of the system explicitly:  $|\omega_{\bar{n}}| = |\omega_{\bar{n}}^{(n)}| = |E_f^{(n)} - E_i^{(n)}|$ ,  $n = 1, 2$ . 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  $V_1$  [Eq. (42)] later in this article. Here we only point out the key property of the operator  $V_{1C}$  [Eq. (43)], namely its periodic dependence on the internuclear distance  $R$ .

Let us transform the matrix element (35) of the remaining terms of the operator  $V^{(\pm)}$  [Eq. (32)] by means of the wave functions (34). Note that for transformation of the retarded terms containing  $\alpha$  matrices [see (32)], it is sufficient to replace  $\varphi_{i,f}^{(n)}(\mathbf{r}_n)$  by  $\Phi_{i,f}^{(n)}(\mathbf{r}_n)$  because the functions  $\Phi_{i,f}^{(n)}(\mathbf{r}_n)$  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 (42) for the operator  $V_1$ . But, as the integrand contains the strong singularity at the origin of coordinates in the limiting case  $R \rightarrow 0$ , the mathematical treatment for atomic ( $0 \leq R < \Delta r$ ) and quasimolecular ( $\Delta r < R < \infty$ ) domains differs slightly.

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, this means that, unlike in the case of a single helium-like atom ( $R \rightarrow 0$ ) considered in Ref. 20, higher powers of the quantities

$$\frac{(\mathbf{a}\mathbf{n})(\mathbf{b}\mathbf{n})}{r_{12}}, \quad \frac{R(\mathbf{a}\mathbf{n})}{r_{12}^2}, \quad \frac{R^2(\mathbf{a}\mathbf{n})(\mathbf{b}\mathbf{n})}{r_{12}^3}, \tag{44}$$

where  $\mathbf{a}$  and  $\mathbf{b}$  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  $0 \leq R < \Delta r$ ) 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

$$(\hat{\mathbf{p}}_1 \mathbf{a})(\hat{\mathbf{p}}_2 \mathbf{b}) \frac{1}{r_{12}} = -\frac{1}{r_{12}^3} \left\{ \mathbf{ab} - \frac{3(\mathbf{ar}_{12})(\mathbf{br}_{12})}{r_{12}^2} \right\}, \quad (45)$$

containing the constant vectors  $\mathbf{a}$ ,  $\mathbf{b}$ . However, the last formula is valid only in the case where the wave functions in the matrix elements (35) and (36) are not spherically symmetric. For spherically symmetric functions, the matrix element of the operator on the right-hand side of (45) becomes zero. This can be verified at once by elementary integration over angles.

Let us now proceed to investigation of singularities of the higher powers of the quantities (44) and (45) when  $R$  tends to zero. The limiting expressions obtained here prove to be improper and can contain  $\delta$ -functional singularities at the origin of coordinates.

Consistent and mathematically rigorous treatment of the specified singularities can be carried out only in the framework of the theory of generalized functions.<sup>22</sup> However, one can elucidate the structure of the basic singularities, using leading considerations based on systematic use of symmetry properties of the considered system. So, for example, in the spherically symmetric case, which can be realized only in the limiting case of the united atom ( $R \rightarrow 0$ ), the substitution ( $x = x_1 - x_2$ ,  $y = y_1 - y_2$ ,  $z = z_1 - z_2$ )

$$(\nabla_1 \mathbf{a})(\nabla_2 \mathbf{b}) \frac{1}{r_{12}} = \left( a_x b_x \frac{\partial^2}{\partial x^2} + a_y b_y \frac{\partial^2}{\partial y^2} + a_z b_z \frac{\partial^2}{\partial z^2} \right) \frac{1}{r_{12}} \quad (46)$$

can be made in the integrand. Indeed, due to symmetry considerations it follows that the terms, containing mixed partial derivatives like  $\partial^2/\partial x \partial y$ , disappear when integrating over angular variables. Also, all three terms on the right-hand side of (46) give equal contributions due to the spherical symmetry. Therefore,

$$(\nabla_1 \mathbf{a})(\nabla_2 \mathbf{b}) \frac{1}{r_{12}} = \frac{1}{3} (\mathbf{ab}) \Delta \frac{1}{r_{12}} = -\frac{4\pi}{3} (\mathbf{ab}) \delta(\mathbf{r}_{12}). \quad (47)$$

The expressions (45) and (47) thus obtained can be combined into the formula

$$(\hat{\mathbf{p}}_1 \mathbf{a})(\hat{\mathbf{p}}_2 \mathbf{b}) \frac{1}{r_{12}} = -\frac{1}{r_{12}^3} \left\{ \mathbf{ab} - \frac{3(\mathbf{ar}_{12})(\mathbf{br}_{12})}{r_{12}^2} \right\} + \frac{4\pi}{3} (\mathbf{ab}) \delta(\mathbf{r}_{12}), \quad (48)$$

which is valid for an arbitrary case.



The structure of other singularities, arising from transformations described above, can be studied by means of the same considerations, which have led us to the representation (48), and by the subsequent reduction of similar terms. There is the specific delicacy which consists in the fact that all higher powers of the quantities (44), which contain  $R$  (or  $R^2$ ) in the coefficients, give zero contributions in the limit  $R \rightarrow 0$  due to the factor  $R$  (or  $R^2$ ). Certainly, nontrivial  $\delta$ -functional singularities will arise at  $R \rightarrow 0$  only from those higher degrees of the quantities (44) 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 (32), 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:

$$V_{BP}^{(\pm)} = V_{1C} + \tilde{V}_{BP}^{(\pm)} = V_{1C} + V_D + V_{LL}^{(\pm)} + V_{SS} + V_{SL}. \tag{49}$$

Here, the following notations are used:

$$V_D = -\pi \left( \frac{e\hbar}{mc} \right)^2 \exp \left( \frac{i}{c} |\omega_{fi}| R \right) \delta(\mathbf{r}_{12}), \tag{50}$$

$$\begin{aligned} V_{LL}^{(\pm)} = & -\frac{e^2}{2m^2c^2} \exp \left( \frac{i}{c} |\omega_{fi}| R \right) \\ & \times \left\{ \frac{\hat{\mathbf{p}}_1 \hat{\mathbf{p}}_2 + \mathbf{n}(\mathbf{n} \hat{\mathbf{p}}_1) \hat{\mathbf{p}}_2}{r_{12}} + \frac{R^2}{r_{12}^3} [\hat{\mathbf{p}}_1 \hat{\mathbf{p}}_2 - 3\mathbf{n}(\mathbf{n} \hat{\mathbf{p}}_1) \hat{\mathbf{p}}_2] \right\} \\ & \pm \frac{e^2}{2mc} \exp \left( \frac{i}{c} |\omega_{fi}| R \right) \frac{R}{r_{12}^2} [\mathbf{n} \hat{\mathbf{p}}_1 + \mathbf{n} \hat{\mathbf{p}}_2], \end{aligned} \tag{51}$$

$$\begin{aligned} V_{SS} = & \left( \frac{e\hbar}{2mc} \right)^2 \exp \left( \frac{i}{c} |\omega_{fi}| R \right) \left\{ \frac{1}{r_{12}^3} [\boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2 - 3(\boldsymbol{\sigma}_1 \mathbf{n})(\boldsymbol{\sigma}_2 \mathbf{n})] \right. \\ & \left. + \frac{R^2}{r_{12}^5} [15(\boldsymbol{\sigma}_1 \mathbf{n})(\boldsymbol{\sigma}_2 \mathbf{n}) - 9\boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2] - \frac{8\pi}{3} (\boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2) \delta(\mathbf{r}_{12}) \right\}, \end{aligned} \tag{52}$$

$$\begin{aligned} V_{SL} = & \frac{e^2 \hbar}{4m^2c^2} \exp \left( \frac{i}{c} |\omega_{fi}| R \right) \\ & \times \left\{ \frac{-(\boldsymbol{\sigma}_1 + 2\boldsymbol{\sigma}_2)[\mathbf{n} \times \hat{\mathbf{p}}_1] + (\boldsymbol{\sigma}_2 + 2\boldsymbol{\sigma}_1)[\mathbf{n} \times \hat{\mathbf{p}}_2]}{r_{12}^2} \right. \\ & \left. + \frac{3R^2}{r_{12}^4} (\boldsymbol{\sigma}_1[\mathbf{n} \times \hat{\mathbf{p}}_1] - \boldsymbol{\sigma}_2[\mathbf{n} \times \hat{\mathbf{p}}_2]) \right\}. \end{aligned} \tag{53}$$

All terms of the operator  $V_{BP}^{(\pm)}$  [Eq. (49)] 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  $V_D$  [Eq. (50)] and  $V_{LL}^{(\pm)}$  [Eq. (51)] have a clear orbital origin. Therefore, the physical meaning of the operator  $V_D$  is easily

seen from its  $\delta$ -like structure: in the limit  $R \rightarrow 0$ ,  $V_D$  is transformed into the two-particle singular part  $-\pi(e\hbar/mc)^2\delta(\mathbf{r}_{12})$  of the known Darwin (contact) interaction of electrons with nuclei and with each other.<sup>10,11,20</sup> From the  $\delta$ -functional structure of (50), it also follows that the operator  $V_D$  should be taken into account only in the atomic domain  $0 \leq R < \Delta r$ .

Let us discuss the physical meaning of the operator  $V_{LL}^{(\pm)}$  [Eq. (51)]. When  $R$  tends to zero, it turns into the usual operator of the retarded interaction between two electrons in the united He-like atom.<sup>20</sup> Therefore, it is reasonable to consider the operator  $V_{LL}^{(\pm)}$  as an operator of the retarded interaction of two quasimolecular electrons at an arbitrary distance from each other.

In order to obtain the same result for the operator  $V_{LL}^{(\pm)}$  from the classical Hamiltonian of the system of interacting charges, which move in the external electromagnetic field,<sup>23</sup> one should replace classical momentums of particles by the corresponding quantum-mechanical operators of momentums in this Hamiltonian.<sup>12</sup> The specified agreement between classical and quantum theories is the base, on which the more perfect relativistic quantum-mechanical theory of ion-atom interactions can be constructed.

Let us give the expression for the operator of retarded interaction of two quasimolecular electrons that was found in Refs. 12–15. In our notation it is of the form

$$\begin{aligned}
 V_{LL} = & -\frac{e^2}{2m^2c^2} \exp\left(\frac{i}{c}|\omega_{\text{fi}}|R\right) \\
 & \times \left\{ \frac{\hat{\mathbf{p}}_1\hat{\mathbf{p}}_2 + \mathbf{n}(\mathbf{n}\hat{\mathbf{p}}_1)\hat{\mathbf{p}}_2}{r_{12}} + \frac{R^2}{r_{12}^3}[\hat{\mathbf{p}}_1\hat{\mathbf{p}}_2 - 3\mathbf{n}(\mathbf{n}\hat{\mathbf{p}}_1)\hat{\mathbf{p}}_2] \right\} \\
 & + \frac{e^2}{mc} \exp\left(\frac{i}{c}|\omega_{\text{fi}}|R\right) \frac{R}{r_{12}^2} \mathbf{n}\hat{\mathbf{p}}_1. \quad (54)
 \end{aligned}$$

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. As one would expect, the operator  $V_{LL}^{(\pm)}$  [Eq. (51)] constructed in the present article is universal and symmetrical in description of both particles. It is seen directly from its structure.

The comparison of the formulas (51) and (54) 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 (51), but also by the additional retarded term

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

which is proportional to  $R$ . Thus, the expression (51) gives a more complete description of the retardation effects in the interaction of electrons than the expression (54) found in the previous articles.<sup>12–15</sup>

Let us now discuss the physical meaning of the operator  $V_{SS}$  [Eq. (52)]. First of all, note that in the limiting case  $R \rightarrow 0$  it is transformed into the usual operator of the spin-spin interaction of electrons in a He-like atom.<sup>20</sup> Thus,  $V_{SS}$

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 the expression (52) is in agreement with the corresponding result of Refs. 12–15 only in the quasimolecular domain  $\Delta r < R < \infty$ . Note, however, that the singularities of the integrand of (35) in the atomic domain  $0 \leq R < \Delta r$  were not studied in these articles. As is known,<sup>18,20</sup> the singular part of the operator  $V_{SS}$  [Eq. (52)] is a manifestation of the so-called spin–contact interaction between electrons (Fermi interaction) and is related to the  $\delta$ -functional singularity of the expression (48) in the origin of coordinates. As well as in the case of the operator  $V_D$  [Eq. (50)], the  $\delta$ -functional term  $[\sim (\boldsymbol{\sigma}_1 \boldsymbol{\sigma}_2) \delta(\mathbf{r}_{12})]$  entering into (52) gives the nontrivial contribution to the matrix element (36) only at  $R \rightarrow 0$ . In the other cases, when the overlap of wave functions from various centers can be neglected, this term disappears at  $\Delta r \leq R < \infty$ .

Finally, let us clarify the physical meaning of the operator  $V_{SL}$  [Eq. (53)]. In the limiting case  $R \rightarrow 0$  it becomes the corresponding spin–orbit term in the Breit–Pauli operator,<sup>18,20</sup> which describes the interaction between spin and orbital magnetic moments of electrons in a He-like atom. Thus, the last term of (49),  $V_{SL}$  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,  $-3R^2(\boldsymbol{\sigma}_2[\mathbf{n} \times \hat{\mathbf{p}}_2])/r_{12}^4$ , entering into the last square brackets of the expression (53) is lost in Refs. 13 and 14. It is absent in the review Ref. 15 as well [see the formula (3.8)]. As is seen from (53), 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 Refs. 14 and 15.

The following remark needs to be made regarding the expression obtained for the generalized Breit–Pauli operator  $V_{BP}^{(\pm)}$ . Although we are mainly interested in the quasimolecular domain ( $\Delta r < R < \infty$ ), the formulas (49)–(53) are written in the form valid in all interval of variation of  $R$  ( $0 \leq R < \infty$ ). When  $R$  tends to zero the operator  $V_{BP}^{(\pm)}$  [Eq. (49)] becomes the corresponding two-particle part of the known Breit–Pauli operator in the coordinate space.<sup>18,20</sup> 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 [Eqs. (49)–(53)] is reduced to providing the mathematical correctness of the limiting transition to the case of a single helium-like atom ( $R \rightarrow 0$ ) investigated in Ref. 20.

Finally, we emphasize that one should not assign any meaning (of the presence of especially strong coupling, for example) to the formal transformation of singular parts of the operators  $V_D$  [Eq. (50)] and  $V_{SS}^{(\pm)}$  [Eq. (52)] into infinity (at  $R = 0$  and  $\mathbf{r}_1 = \mathbf{r}_2$ ). The integral values of all correction terms  $\tilde{V}_{BP}^{(\pm)}$  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,  $V_{1C}$  [Eq. (43)], which is an analog of the Coulomb interaction.

#### 4.2. *Electric dipole–dipole interaction of two quasimolecular electrons*

The role of various terms in the interaction operator (49) is determined by the type of quantum transition in the spectrum of the quasimolecule  $(AB)^{(Z_a+Z_b-2)+}$ . 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 a purely orbital origin. Further, we shall consider the case  $\omega_0 R/c \sim 1$ , where 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 Ref. 24 (see also Ref. 25). In the case considered here, when the position vectors  $\mathbf{r}_{1b}$  and  $\mathbf{r}_{2a}$  of electrons 1 and 2 are measured from the nuclei  $B^{Z_b+}$  and  $A^{Z_a+}$ , respectively, and the axes  $z_A$  and  $z_B$  of the corresponding systems of coordinates are parallel to  $\mathbf{R}$ , the bipolar expansion of the operator  $1/r_{12}$  takes the form

$$\frac{1}{r_{12}} = \frac{1}{R} + \frac{(\mathbf{n}_R \mathbf{r}_{2a}) - (\mathbf{n}_R \mathbf{r}_{1b})}{R^2} + \frac{3(\mathbf{n}_R \mathbf{r}_{2a})^2 - r_{2a}^2 + 3(\mathbf{n}_R \mathbf{r}_{1b})^2 - r_{1b}^2}{2R^3} + W(\mathbf{r}_{1b}, \mathbf{r}_{2a}) + O(R^{-4}). \quad (55)$$

Here,  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the position vectors of the first and second electrons in an arbitrary system of coordinates, and  $\mathbf{n}_R$  is the unit vector oriented in the direction of  $\mathbf{R}$ . The correlative term  $W(\mathbf{r}_{1b}, \mathbf{r}_{2a})$  depends on the products of coordinates of both electrons:

$$W(\mathbf{r}_{1b}, \mathbf{r}_{2a}) = \frac{\mathbf{r}_{1b} \mathbf{r}_{2a} - 3(\mathbf{n}_R \mathbf{r}_{1b})(\mathbf{n}_R \mathbf{r}_{2a})}{R^3}, \quad (56)$$

and other terms of (55) depend on coordinates of only one of the electrons 1 and 2. The replacement of the initial operator  $r_{12}^{-1}$  by the multipolar series (55) is valid when the condition  $R \gg r_{1b} + r_{2a}$  is satisfied. The bipolar expansions of  $r_{12}^{-2}$  and  $r_{12}^{-3}$  have similar structure and can be obtained from the multipolar expansion (55), (56) for  $r_{12}^{-1}$  without special difficulties.

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

$$V_{1C,\text{dip}} + V_{LL,\text{dip}}^{(\pm)} = \exp\left(\frac{i}{c}|\omega_{\text{fl}}|R\right) \left\{ \frac{\mathbf{d}_{1b} \mathbf{d}_{2a} - 3(\mathbf{n}_R \mathbf{d}_{1b})(\mathbf{n}_R \mathbf{d}_{2a})}{R^3} \right\}$$

$$\pm \frac{e}{2mc} \left[ \frac{\mathbf{d}_{1b}\hat{\mathbf{p}}_2 - 3(\mathbf{n}_R\mathbf{d}_{1b})(\mathbf{n}_R\hat{\mathbf{p}}_2)}{R^2} - \frac{\mathbf{d}_{2a}\hat{\mathbf{p}}_1 - 3(\mathbf{n}_R\mathbf{d}_{2a})(\mathbf{n}_R\hat{\mathbf{p}}_1)}{R^2} \right] - \frac{e^2}{m^2c^2} \frac{\hat{\mathbf{p}}_1\hat{\mathbf{p}}_2 - (\mathbf{n}_R\hat{\mathbf{p}}_1)(\mathbf{n}_R\hat{\mathbf{p}}_2)}{R} \Big\}, \tag{57}$$

where  $\mathbf{d}_{1b} = e\mathbf{r}_{1b}$  and  $\mathbf{d}_{2a} = e\mathbf{r}_{2a}$  are the operators of the electric dipole moments of separate electrons. The operator (57) 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 [see the formula (3.9) in Ref. 14] consists in the fact that the expression (57) contains the additional retarded term

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

whose value is comparable with 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 near-resonance transmission of excitation in collisions of atoms of alkali metals.<sup>26,27</sup>

### 5. Accounting for Relativistic Effects in a Problem of Ion–Atom Interactions

There are some ways to account for relativistic effects in two-electron problems of the theory of slow atomic collisions connected with nonresonance transitions of electrons from one center to another. In the case where the atom (or ion)  $A^{(Z_a-2)+}$  and the bare nucleus  $B^{Z_b+}$  are not too heavy, one can introduce additional terms of the generalized Breit–Pauli operator  $\tilde{V}_{BP}^{(\pm)}$  [Eqs. (49)–(53)] into the nonrelativistic Hamiltonian  $H_{nr}^{(0)1,2}$  of the system  $(AB)^{(Z_a+Z_b-2)+}$ :

$$H_r = H_{nr} + \tilde{V}_{BP}^{(\pm)} = H_{nr}^{(1)} + H_{nr}^{(2)} + V_{1C} + \tilde{V}_{BP}^{(\pm)}. \tag{58}$$

Here  $H_{nr}^{(1)}$  and  $H_{nr}^{(2)}$  are the Hamiltonians of separate electrons in the field of two fixed point charges  $Z_a$  and  $Z_b$  located at a distance  $R$  from each other.<sup>28</sup> Thus, we obtain the Schrödinger equation for two quasimolecular electrons in the configuration space

$$H_r\Phi_n(\mathbf{r}_1, \mathbf{r}_2; R) = E_n^{(r)}(R)\Phi_n(\mathbf{r}_1, \mathbf{r}_2; R), \tag{59}$$

where  $E_n^{(r)}$  is the energy of the stationary state. The wave functions  $\Phi_n$  should satisfy the antisymmetry condition.

It is significant that, in contrast to the operator  $V_{1C}$  [Eq. (43)], it makes sense to use the operator  $\tilde{V}_{BP}^{(\pm)}$  [Eqs. (49)–(53)] only in the first order of the perturbation theory. The same applies to the expression (32). The cause consists in the fact that when deriving (32) and (49)–(53) we essentially used, firstly, the expansion

(20) and, secondly, the smallness of “lower” components of the Dirac bispinors. Both are valid as long as we consider that there are positive frequency one-electron Dirac wave functions in the matrix elements (35) and (36). When transiting to the second order of the perturbation theory, the summation over the complete set of one-electron states including negative frequency states arises.

For not-too-heavy quasimolecules, the position of energy levels (terms) is basically determined by the Hamiltonian  $H_{\text{nr}}$ , and  $\tilde{V}_{\text{BP}}^{(\pm)}$  leads to splitting of levels of  $H_{\text{nr}}$ , which gives the so-called fine structure of energy levels  $E_n^{(r)}$  of the system  $(\text{AB})^{(Z_a+Z_b-2)+}$ . In such a situation, it is natural to first find the wave functions and energy levels in the nonrelativistic approximation, and then take into account  $\tilde{V}_{\text{BP}}^{(\pm)}$  by means of one or another method of the perturbation theory. Here, the functions of zeroth-order approximation are eigenfunctions of the Hamiltonian  $H_{\text{nr}}$  in which the operators of the relativistic interactions are lacking.

Let us now briefly analyze the possibilities of application of the obtained effects to calculation of matrix elements of exchange correlative interaction of multiply charged ions with heavy (relativistic) atoms. First of all, note that for all two-electron processes with rearrangement which are mentioned in the Introduction, the following exchange mechanism is characteristic: one of the active electrons of the atom  $\text{A}^{(Z_a-2)+}$  tunnels to the ion  $\text{B}^{Z_b+}$ , followed by strongly correlated (as a rule, a dipole–multipole) simultaneous transition of two electrons located near different centers. When one is calculating the exchange correlative interaction being responsible for simultaneous transition of two electrons, it is necessary to know the asymptotics (at  $R \rightarrow \infty$ ) of the two-Coulomb-center wave function of the electron of the atom  $\text{A}^{(Z_a-2)+}$  near the “foreign” nucleus  $\text{B}^{Z_b+}$ . Such asymptotics has previously been found<sup>7</sup> in the quasiclassical approximation.

In a general case, the matrix element of the exchange interaction is determined as a nondiagonal matrix element of the electron Hamiltonian (58) between electron wave functions of the system  $(\text{AB})^{(Z_a+Z_b-2)+}$  which correspond to the cases of various localizations of electrons in the initial and final states (see, for example, Refs. 1 and 2). For the electrons localized near different nuclei, the correct two-electron wave function of the zeroth approximation, satisfying the Pauli exclusion principle, can be written in the form of an antisymmetrized product of the two-center wave functions of separate electrons.<sup>7</sup> We shall consider in detail the calculation of the exchange interaction, responsible for the course of two-electron processes with rearrangement (such as two-electron charge exchange, or charge exchange with simultaneous excitation or ionization), in the next articles. Here we only note that with the increase of charges of the nuclei  $Z_a$  and  $Z_b$  relativistic effects become more and more significant, and the direct numerical solution of the Schrödinger equation (59) with the generalized Breit–Pauli operator (58) is necessary. However, such an approach is extremely complicated and onerous for the problem considered here.

The alternative approach, which is obviously acceptable for the heavy multiply charged quasimolecules  $(\text{AB})^{(Z_a+Z_b-2)+}$ , consists in construction of the adiabatic

asymptotic (at large internuclear distance  $R$ ) theory of two-electron processes with rearrangement on the basis of the generalized Dirac–Breit equation. Within this approach the motion of separate electrons in the quasimolecule is described by the one-electron Dirac Hamiltonian of the two-center problem (27), and the interelectron interaction is given by the generalized Breit operator  $V^{(\pm)}$  [Eq. (32)]. As a result, we arrive at the generalized quasirelativistic Dirac–Breit equation

$$\begin{aligned} H\Psi_n(\mathbf{r}_1, \mathbf{r}_2; R) &= (H^{(0)} + V^{(\pm)})\Psi_n(\mathbf{r}_1, \mathbf{r}_2; R) \\ &= (H^{(1)}(\mathbf{r}_1) + H^{(2)}(\mathbf{r}_2) + V^{(\pm)})\Psi_n(\mathbf{r}_1, \mathbf{r}_2; R) \\ &= E_n(R)\Psi_n(\mathbf{r}_1, \mathbf{r}_2; R), \end{aligned} \tag{60}$$

which describes the motion of two electrons interacting with each other in the field of two fixed Coulomb centers with the charges  $Z_a$  and  $Z_b$ . Here  $\Psi_n(\mathbf{r}_1, \mathbf{r}_2; R)$  is the 16-component spinor wave function (four components for each of the electrons 1 and 2), and  $E_n$  is the total energy (including the rest energy) of the stationary state of the system of two interacting quasimolecular electrons. In addition to the equation (60), the wave functions  $\Psi_n(\mathbf{r}_1, \mathbf{r}_2; R)$  should satisfy the antisymmetry condition. The operator  $H^{(0)} = H^{(1)}(\mathbf{r}_1) + H^{(2)}(\mathbf{r}_2)$  completely takes into account the one-electron relativistic effects (except for radiative corrections), and  $V^{(\pm)}$  [Eq. (32)] includes all two-electron relativistic corrections to within terms  $\sim \alpha^2$ .

Let us discuss the possibilities arising when one is using the equation (60) for the description of strongly correlated motion of electrons in the quasimolecule  $(AB)^{(Z_a+Z_b-2)+}$  in the framework of the second-order effects of QED. Firstly, such a description allows one to clarify the basic features and possible mechanisms of processes with rearrangement, to take into account orbital and spin degrees of freedom of atomic electrons, the  $jj$  scheme of coupling of the angular moments (which is the most natural for heavy atoms), and effects of retardation of interaction of two quasimolecular electrons located at an arbitrary distance from each other. Secondly, the considerable achievement of such consideration is an elaboration of the method of deriving new integral relations,<sup>8</sup> relating asymptotic solutions to the relativistic problem of two spaced Coulomb centers  $(Z_a, e, Z_b)$  which correspond to different regions of electron motion. In particular, the integral relations allow us to find the approximate analytical solution to the relativistic problem  $(Z_a, e, Z_b)$  which satisfies the Dirac equation with the potential of two spaced Coulomb centers to within small terms. This means that in this approximation most of the one-particle relativistic effects are already taken into account in zeroth approximation. Using the operator (32) and asymptotic formulas for solutions to the relativistic problem  $(Z_a, e, Z_b)$  found previously,<sup>8,9</sup> one can calculate the parameters of exchange correlative interaction of atomic particles in the course of collision. In point of fact, all of this gives a natural basis both for the generalization of the adiabatic asymptotic theory of two-electronic processes with rearrangement<sup>1</sup> to a range of the relativistic binding energies and for the correct formulation of some problems of the modern theory of an electronic structure of the complicated molecules and atomic clusters.<sup>28</sup>

## 6. Conclusion

In this section, we shall 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 the 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  $c^{-1}$  expansion of the retardation factor in the totally symmetrical (with respect to coordinates of both electrons) form (26). In turn, this leads to the representation (32) for the relativistic operator of interaction between two electrons  $V^{(\pm)}(\mathbf{r}_1, \mathbf{r}_2; R)$ , in which [unlike (33)] dependence on both orbital and spin variables of the 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  $V^{(\pm)}(\mathbf{r}_1, \mathbf{r}_2; R)$  behaves differently, depending on the distance  $r_{12}$  between the two electrons. For instance, in the united-atom limit, the formula (32) 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 the Breit formula (1) is restricted by the following condition on the coordinate variables:

$$\frac{\omega_0 r_{12}}{c} \ll 1, \quad (61)$$

where  $\omega_0$  is the characteristic frequency of the spectrum of the interacting electrons. 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 the condition (19) is satisfied for all  $\Delta r \leq R < \infty$ , the Breit operator (1) fails to describe the relativistic interaction of two electrons even on the qualitative level. At the same time, the relativistic operator  $V^{(\pm)}(\mathbf{r}_1, \mathbf{r}_2; R)$  [Eq. (32)] 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 scales of interaction transfer and specific calculation approximations, making it possible to find small parameters and take into account different types of interaction, are characteristic of each domain ( $\Omega_I$ ,  $\Omega_{II}$ ) of interelectron distances  $r_{12}$ . Thus, we reiterate not only that we can use the generalized Breit operator  $V^{(\pm)}(\mathbf{r}_1, \mathbf{r}_2; R)$  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. 3, 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 (61).<sup>20</sup> 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  $\Omega_{\text{I}}$ , is 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  $\Omega_{\text{II}}$ ), 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 (19). Exchange by virtual photons at such a distance results in the interelectron interaction (32), which, apart from 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  $V_{\text{BP}}^{(\pm)}$  [Eq. (49)] is performed by means of conversion from the relativistic four-component Dirac bispinors to the nonrelativistic two-component Pauli spinors in the matrix  $U_{i \rightarrow f}^{(2)}$  [Eq. (15)] of effective energy of the interaction  $V^{(\pm)}$  [Eq. (32)]. It is shown that the correct account for the natural condition of the interaction symmetry with respect to both electrons results in new terms in the operators of spin–orbit (53), spin–spin (52) and retardation (51) interactions which are missed in the corresponding operators in Refs. 12–15. Thus, the generalized Breit–Pauli operator [Eqs. (49)–(53)] constructed in the present article allows one 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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