in terms of perturbation theory. In the approximation linear in the charge, the scattering amplitude is described by the Born formula with the interaction

$$\hat{U}=-\frac{e}{c}\mathrm{Av}+i\frac{e\hbar}{2mc}\operatorname{div}\mathrm{A}, \tag{16}$$

where $\mathrm{v}=\hbar\mathbf{k}/m$ is the initial velocity of the particle and m is its mass. The condition of applicability of the Born approximation to the problem considered has the form

$$e\Phi/\hbar c\ll 1. \tag{17}$$

For the amplitude we obtain

$$f(\mathbf{q})=\frac{1}{4\pi}\frac{e\Phi}{\hbar c}[(\mathbf{kn})+(\mathbf{k'n})]\iint_{\Sigma}\exp(-i\mathbf{qr})\,dS. \tag{18}$$

Here $\mathbf{k}$ and $\mathbf{k'}=\mathbf{k}+\mathbf{q}$ are the wave vectors of the particle before and after scattering, $\mathbf{n}$ is the normal to the plane of the solenoid, and Σ is the portion of this plane bounded by the magnetic lines of force.

According to Eq. (18) the amplitude for scattering by 180° is strictly zero. If $k\gg 1/l$, where l is the length of the solenoid, scattering occurs mainly at small angles; here $\mathbf{k'}\approx\mathbf{k}$, and Eq. (18) is a limiting case of the eikonal formula.

For $k\ll 1/l$ we have

$$f=\frac{1}{4\pi}\frac{e\Phi}{\hbar c}[\mathbf{kn}+\mathbf{k'n}]S. \tag{19}$$

In particular, if $\mathbf{k}\|\mathbf{n}$, then

$$f(\theta)=\frac{1}{4\pi}kS\frac{e\Phi}{\hbar c}(1+\cos\theta), \tag{20}$$

and the total cross section for scattering is

$$\sigma=\frac{1}{3\pi}k^2S^2\left(\frac{e\Phi}{\hbar c}\right)^2. \tag{21}$$

If the solenoid has the shape of a thin torus with a hole radius a, the Born amplitude takes the form

$$f(\mathbf{q})=a\frac{e\Phi}{\hbar c}J_1(a[\mathbf{q}^2-(\mathbf{qn})^2]^{1/2})\frac{1}{[\mathbf{q}^2-(\mathbf{qn})^2]^{1/2}}\frac{\mathbf{kn}+\mathbf{k'n}}{2}. \tag{22}$$

In the case where $\mathbf{k}\|\mathbf{n}$ we have

$$f(\theta)=\frac{ka}{2}\frac{e\Phi}{\hbar c}J_1(k|\sin\theta|a)\frac{1}{ka|\sin\theta|}(1+\cos\theta). \tag{23}$$

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[1)]The solution of the scattering problem at small angles is given in Ref. 6.

[1]Y. Aharonov and D. Bohm, Phys. Rev. 115, 485 (1959); 123, 1511 (1961); 130, 1625 (1963).
[2]E. L. Feinberg, Usp. Fiz. Nauk 78, 53 (1962) [Sov. Phys. Uspekhi 5, 753 (1963)].
[3]H. Erlichson, Amer. J. Phys. 38, 162 (1970).
[4]M. Peshkin, I. Talmi, and J. L. Tassie, Ann. Phys. (N.Y.) 12, 426 (1961).
[5]A. I. Vaĭnshtein and V. V. Sokolov, Yad. Fiz. 22, 618 (1975) [Sov. J. Nucl. Phys. 22, 319 (1975)].
[6]L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Nauka, 1974, Section 131, p. 617. English translation, earlier edition, Pergamon Press, 1959.
[7]L. D. Landau and E. M. Lifshitz, Teoriya polya (Theory of Fields), Nauka, Moscow, 1967, Section 61, p. 203.

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Contribution to the theory of excitation transfer in slow collisions of like atoms

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The exchange contribution, responsible for excitation transfer, to the term splitting is investigated. It is shown that the previously developed theory, in which no account was taken of the symmetry with respect to electron permutation, is inaccurate. In the case of alkali-metal atoms, the exchange contribution determines the effective excitation-transfer cross section at 10^3 K. The van der Waals contribution is less than the exchange contribution. The cross section is of the order of 10^{-14} cm^2.

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We investigate in this paper the excitation-transfer process

$$A^*+B\to A+B^*. \tag{1}$$

In collisions of identical atoms ($A\equiv B$), the effective cross section of this process is large and, in analogy with the resonant charge-exchange process, it determines the coefficient of diffusion of the excited atoms A^* in their own gas. If a dipole transition to the ground state from the excited state A^* is allowed, then transfer of excitation is the result of dipole-dipole interaction of the atoms, which decreases $\propto R^{-3}$ when the atoms are diluted (R is the distance between nuclei). The process

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(1) was investigated for this case, in a number of studies.[1-3] On the other hand, if the dipole transition $A^* \to A$ is forbidden, then the principal role is assumed by interactions of induced dipoles[4,5] ($\propto R^{-6}$ as $R \to \infty$) and by the exponentially decreasing exchange interaction.[6]

In this paper we investigate the asymptotic behavior, as $R \to \infty$, of the exchange interaction for a quasimolecule consisting of two identical single-electron atoms. The previously proposed exchange-interaction theory[6] is incomplete in that it does not take into account the symmetry with respect to electron permutation. The quasimolecule wave functions used by Smirnov[6] were not symmetrized with respect to permutations of electrons from different atoms. This symmetrization leads in our case to a different asymptotic dependence of the exchange interaction and to the necessity of using a different method for its calculation.

We confine ourselves here to the case when the excited state A^* is not degenerate. The cross section of the process (1) for single-electron atoms is then

$$\sigma = {}^1/_4\sigma^{(+)} + {}^3/_4\sigma^{(-)}, \tag{2}$$

where $\sigma^{(\pm)}$ are the cross sections for excitation transfer at total quasimolecule spin 0 and 1, respectively. Thus, it is necessary to determine separately for the singlet and triplet cases the exchange interaction that leads to excitation transfer. The sought interaction is determined by that region of the electron coordinates on the axis between the nuclei in which perturbation theory cannot be used. It is therefore necessary to calculate first the wave function in the indicated region.

We use throughout the system of atomic units ($e^2 = m = \hbar = 1$).

ASYMPTOTIC EXPANSION OF THE WAVE FUNCTION

The wave function on the internuclear axis as $R \to \infty$ can be determined by the method of Gor'kov and Pitaevskiĭ[7] and of Herring and Flicker.[8] The earlier generalization of this method in the case of arbitrary atoms[9,6] is suitable, as we shall see, only for interactions between atoms with equal (or close) ionization potentials. In our case, the difference of the potentials of ionization from the ground J_1 and excited J_2 states is of the order of these quantities themselves.

We seek the wave function in the form

$$\Psi_1(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{2A}(\mathbf{r}_{1A})\varphi_{1B}(\mathbf{r}_{1B})\chi_1(\mathbf{r}_1, \mathbf{r}_2);$$
$$\varphi_{2A} \xrightarrow[r_A \to \infty]{} b r_A^{1/\beta - 1} \exp(-\beta r_A), \quad \varphi_{1B} \xrightarrow[r_B \to \infty]{} a r_B^{1/\alpha - 1} \exp(-\alpha r_B), \tag{3}$$

where φ_{2A} and φ_{1B} are the unperturbed atomic wave function respectively of the excited state (2) on the atom A and the ground state (1) on the atom B; χ_1 is a new function that takes into account the interaction between the atoms (see Fig. 1). For this function we have according to Refs. 7–9 the equation

$$2\frac{\partial \chi_1}{\partial \eta} + W_1 \chi_1 = 0, \tag{4}$$

$$\xi = z_1/\alpha + z_2/\beta, \quad \eta = z_1/\alpha - z_2/\beta;$$
$$\alpha = (2J_1)^{1/2}, \quad \beta = (2J_2)^{1/2}, \quad W_1 = \frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}}, \tag{5}$$

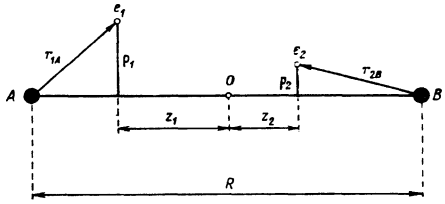

FIG. 1. Arrangement of the electrons and nuclei for the collision of the atoms A and B.

where $z_{1,2}$ are the coordinates of the electrons along the internuclear axis, reckoned from the center of the system, which is the midpoint of the internuclear axis (see Fig. 1). Expression (5) for W_1 is valid only in the asymptotic region $r_{1B} \sim r_{2A} \sim R$.

The boundary condition $\chi_1 \to 1$ is imposed on the broken line $z_1 = -R/2$ and $z_2 = R/2$ (the electrons land in their own atoms) on the $z_{1,2}$ plane (see Fig. 2). Inasmuch as we have changed over in (4) to the variables ξ and η, it is necessary to determine the mapping of this line on the (ξ, η) plane. We easily find that this line also goes over into a broken line $\eta_0(\xi)$ given by the expression (see Fig. 2)

$$\eta_0(\xi) = |\xi - \xi_0| - \frac{\alpha+\beta}{2\alpha\beta}R, \quad \xi_0 = \frac{\alpha-\beta}{2\alpha\beta}R. \tag{6}$$

We then obtain

$$\chi_1 = \exp\left[-\frac{1}{2}\int_{\eta_0(\xi)}^{\eta} W_1(\xi, \eta')\,d\eta'\right] \tag{7}$$

or, after elementary integration,

$$\chi_1 = \frac{1}{(1-\zeta_1)^{1/\alpha}(1+\zeta_2)^{1/\beta}}\left(\frac{r_{12} - \mathbf{n}\mathbf{r}_{12}}{R}\right)^{1/(\alpha+\beta)} \times \begin{cases} 2^{1/\alpha}\exp\left(-\frac{1+\zeta_1}{2\alpha}\right)\left[1+\zeta_2+\frac{\beta}{\alpha}(1+\zeta_1)\right]^{1/\beta - 1/(\alpha+\beta)}, & \frac{\zeta_1}{\alpha}+\frac{\zeta_2}{\beta} < \frac{\alpha-\beta}{\alpha\beta} \\ 2^{1/\beta}\exp\left(-\frac{1-\zeta_2}{2\beta}\right)\left[1-\zeta_1+\frac{\alpha}{\beta}(1-\zeta_2)\right]^{1/\alpha - 1/(\alpha+\beta)}, & \frac{\zeta_1}{\alpha}+\frac{\zeta_2}{\beta} > \frac{\alpha-\beta}{\alpha\beta} \end{cases};$$
$$\mathbf{n} = \mathbf{R}/R, \quad \zeta_{1,2} = 2z_{1,2}/R, \quad \zeta_1 < \zeta_2. \tag{8}$$

The derivative of this function has a discontinuity ($\propto R^{-2}$) at $\xi = \xi_0$.

The integration in (7) is carried out at constant ξ. If $\alpha = \beta$, then the condition $\xi = \text{const}$ corresponds to constancy of the center of gravity of the electrons. To satisfy the boundary conditions it is necessary in this

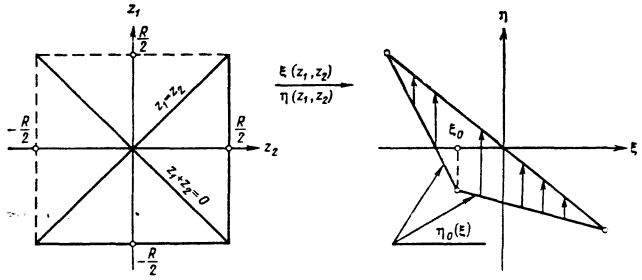

FIG. 2. Regions of electron motion on the internuclear axis prior to their encounter, in terms of the variables $z_{1,2}$ and ξ, η. The arrows on the (ξ, η) plane indicate the direction of integration in formula (7).

case to move the electrons to the atoms with their center of gravity unchanged. If the center of gravity is closer to the atom $B(z+z_2>0)$, then in this case the electron 2 reaches the atom B earlier, so that the function χ_1 in the region $z_1+z_2>0$ is determined by the condition $r_{2B}\to 0$. In the region $z_1+z_2<0$ the electrons interchange roles. Consequently, in the two regions $z_1+z_2\gtrless 0$ (at $\alpha=\beta$) we have two different expressions for χ_1. On the other hand, if $\alpha\neq\beta$, then the condition $\xi=\text{const}$ corresponds to a more complicated motion of the electrons with changing η. Fig. 2 shows a simple formal method of satisfying the boundary conditions in this case.

Expressions (8) coincide with the corresponding expressions obtained earlier;[9,8] all that differ are the equations of the lines that separate these expressions. In Refs. 9 and 6 the two expressions analogous to (8) are separated by the line $z_1+z_2=0$, a fact true only at $\alpha=\beta$.

The function (8) is insufficient for the calculation of the sought exchange interaction, since it is valid only for the region of electron coordinates prior to their encounter when each moves to its own atom. We, on the other hand, must know this function also in the region after the encounter of the electrons. At the very least, it is seen immediately that (8) is incorrect for the region where the electrons are close to each other, since the gradient r_{12}^{-1} of the interelectron interaction is not small here, and this should influence the function χ. We cannot leave out of the Schrödinger equation the higher derivatives of this function (as was done in Refs. 6 and 9 in the derivation of an equation analogous to (4)).

It was shown earlier[10,11] that the determination of the wave function in the region $r_{12}\ll R$ and $r_{1A}, r_{2B}\sim R$ can be reduced to the problem of scattering of electrons by each other, and this problem has an exact solution. For the problem considered here it is necessary to find the wave function not only at $r_{12}\ll R$, but also in the entire region of the electron motion after their encounter on the internuclear axis. It was previously found that[10,11]

$$\chi_1=\Phi(\mathbf{r}_1,\mathbf{r}_2)\,\Phi_{\text{отн}}(\mathbf{r}_{12}); \tag{9}$$

$$\Phi=\frac{1}{(1-\zeta_1)^{1/\alpha}(1+\zeta_2)^{1/\beta}}\{\ldots\},\quad z_1\geqslant z_2; \tag{10}$$

$$\Phi_{\text{отн}}=\frac{\Gamma(1+1/(\alpha+\beta))}{[(\alpha+\beta)R/2]^{1/(\alpha+\beta)}}F\left(-\frac{1}{\alpha+\beta};\ 1;\ -\frac{\alpha+\beta}{2}(r_{12}-\mathbf{nr}_{12})\right). \tag{11}$$

The expression in the curly brackets of (10) coincides with the expression in (8). If we use in (11), at $r_{12}\sim R$, the asymptotic form of the confluent hypergeometric function $F(\ldots x)$ as $x\to\infty$, then we obtain expression (8) for χ_1.

Let us show that the function (9) is valid in the entire region after the encounter of the electrons: $r_{12}\sim R$. Introducing in the Schrödinger equation for the two electrons the relative coordinate $\mathbf{r}_{12}$ and the coordinate $\mathbf{r}$ of their center of gravity, and discarding the Laplacian with respect to $\mathbf{r}$ (there are no singularities whatever with respect to the coordinate of the center of gravity), we obtain for χ_1

$$\left[-\Delta_{12}-\alpha\frac{\partial}{\partial z_1}+\beta\frac{\partial}{\partial z_2}+W_1\right]\chi_1=0. \tag{12}$$

The function (9)–(11) is a solution of precisely this equation.

It is easily seen that (9)–(11) is a solution of Eq. (12) (accurate to quantities $\propto R^{-1}$) in the entire region after the encounter of the electron. This can be verified by directly substituting the function (9)–(11) in (12) and recognizing that

$$|\nabla_{12}\Phi|\sim R^{-1}|\Phi|$$

and that these quantities can be neglected.

From among the properties of the solution (9)–(11), we note the following. In the region after the encounter of the electrons and at $r_{12}\sim R$ we cannot discard the Laplacian with respect to the relative coordinate. When the electrons are scattered by each other, the function χ acquires a gradient $\propto R^{-1/2}$ (whereas the gradient of the function (8) is $\propto R^{-1}$), which retains its form in the entire region $z_1>z_2$ past the encounter of the electrons near the internuclear axis. The function (8) is identically equal to zero at $z_1>z_2$ if the electrons are located exactly on the R axis.

In the region past the encounter of the electrons and $\rho_{12}\ll R$ we must use the expansion

$$r_{12}-\mathbf{nr}_{12}\approx\rho_{12}^2/2z_{12},\ \boldsymbol{\rho}_{12}=\boldsymbol{\rho}_1-\boldsymbol{\rho}_2,\ z_{12}=z_1-z_2;$$

$$F\left[-\frac{1}{\alpha+\beta};\ 1;\ -\frac{\alpha+\beta}{2}(r_{12}-\mathbf{nr}_{12})\right]\approx F\left[-\frac{1}{\alpha+\beta};\ 1;\ -\frac{\alpha+\beta}{4z_{12}}\rho_{12}^2\right];$$

$$\rho_{12}\ll R,\quad z_{12}\sim R,\quad z_{12}>0, \tag{13}$$

where $\rho_{1,2}$ are the distances from the electrons to the internuclear axis.

We note that the obtained asymptotic expansion of the wave function and of the term spacings given below is valid for internuclear distances R much larger than the total dimension of the electron shells, i.e., for

$$R\gg 2/\alpha^2+2/\beta^2.$$

ASYMPTOTIC FORM OF THE EXCHANGE INTERACTION THAT LEADS TO EXCITATION TRANSFER

The Schrödinger equation for the wave function of the system of two identical atoms is

$$(H-E_{g,u}^{(\pm)})\,\Psi_{g,u}^{(\pm)}(\mathbf{r}_1,\mathbf{r}_2)=0, \tag{14}$$

where the superscripts (±) label the spin state of the quasimolecule ((+)–singlet, (–)–triplet), while the subscripts g and u label the symmetry with respect to permutation of the states. For nondegenerate excited states it is necessary thus to consider four terms.

The total wave functions are equal to

$$\Psi_{g,u}^{(\pm)}=2^{-1/2}[\Psi_A^{(\pm)}\pm\Phi_B^{(\pm)}], \tag{15}$$

where the functions $\Phi_{A,B}$ describe states when the excitation is on the atom A or B. They are symmetrized with respect to permutation of the electrons and equal

to

$$\Phi_A^{(\pm)}=2^{-1/2}[\varphi_{2A}(\mathbf{r}_1)\varphi_{1B}(\mathbf{r}_2)\chi_{1(2A)}^{2(1B)}\pm\varphi_{2A}(\mathbf{r}_2)\varphi_{1B}(\mathbf{r}_1)\chi_{1(1B)}^{2(2A)}],$$
$$\Phi_B^{(\pm)}=2^{-1/2}[\varphi_{1A}(\mathbf{r}_1)\varphi_{2B}(\mathbf{r}_2)\chi_{1(1A)}^{2(2B)}\pm\varphi_{1A}(\mathbf{r}_2)\varphi_{2B}(\mathbf{r}_1)\chi_{1(2B)}^{2(1A)}]. \quad (16)$$

The indices of the function χ mark the electron positions: 1(2A) means that the electron 1 is located in the excited state on the atom A. All these functions are obtained from the functions (8)–(11) by suitable permutations $z_1 \rightleftarrows z_2$ and (or) $\alpha \rightleftarrows \beta$.

We multiply Eq. (14) for Ψ_g by Ψ_u, the equation for Ψ_u by Ψ_g, subtract one from the other, integrate the result over the domain Ω. We obtain

$$(E_u-E_g)\int_\Omega(\Phi_A^2-\Phi_B^2)\,d\tau_1\,d\tau_2=\int_\Omega(\Psi_gH\Psi_u-\Psi_uH\Psi_g)\,d\tau_1\,d\tau_2. \quad (17)$$

We shall use this relation to determine the sought energy difference E_u-E_g.

We introduce two operations: electron permutation P_{12} and inversion I of the coordinates of all the electrons in the center of the system O (see Fig. 1). As a result of applying the combined operation IP_{12}, any point of the plane (z_1,z_2) (see Fig. 2) is mapped on the line $z_1+z_2=0$. Let Ω in (17) be the Gor'kov-Pitaevskiĭ volume,[7] defined by $z_1\leq z_2$ (on the (z_1,z_2) plane of Fig. 2 this is the area below the line $z_1=z_2$). It is easily seen that for this volume the two integrals in (17) are equal to zero. In fact, both integrands are symmetrical with respect to the operation P_{12}, since all the wave functions in them are taken at one value of the spin. With respect to the operation I, however, they are antisymmetrical, since they contain products of functions of unequal symmetry g and u (the Hamiltonian H for the system of two identical atoms is symmetrical with respect to I and P_{12}). Consequently, the integrands in (17) are antisymmetrical with respect to the operation IP_{12}, or reverse sign when a point from the (z_1,z_2) plane is mapped on the line $z_1+z_2=0$. Therefore the two integrals in (17) are in fact equal to zero.

We see thus that after introducing the permutation symmetry it becomes impossible to use Smirnov's method.[6] We consider therefore another volume. Let the volume Ω in (17) be defined by the inequality $z_1+z_2<0$. The operation IP_{12} takes each point of this volume to the outside of the volume and this operation cannot be used for the transformation of the integrals (17). Using the symmetry with respect to permutation of the electrons, we readily obtain

$$E_u-E_g=I_1/I_2, \quad (18)$$

$$I_1=\oint_{z_1+z_2=0}\Phi_A\frac{\partial\Phi_B}{\partial z_1}\Big|_{-z_1=z_2=z}dz\,d\rho_1\,d\rho_2, \quad (19)$$

$$I_2=\frac{1}{4}\int_{z_1+z_2<0}(|\Phi_A|^2-|\Phi_B|^2)\,d\tau_1\,d\tau_2. \quad (20)$$

Differentiating only the exponentials, we get

$$I_1=\left(\frac{\alpha-\beta}{2}\right)\Big[\oint_{z_1+z_2=0}\varphi_{2A}(\mathbf{r}_1)\varphi_{1A}^*(\mathbf{r}_1)\varphi_{2B}^*(\mathbf{r}_2)\varphi_{1B}(\mathbf{r}_2)\chi_{1(1A)}^{2(2B)}\chi_{1(2A)}^{2(1B)}\,dz\,d\rho_1\,d\rho_2$$
$$\pm\oint_{z_1+z_2=0}\varphi_{1A}^*(\mathbf{r}_1)\varphi_{1B}(\mathbf{r}_1)\varphi_{2A}(\mathbf{r}_2)\varphi_{2B}^*(\mathbf{r}_2)\chi_{1(1A)}^{2(2B)}\chi_{1(1B)}^{2(2A)}\,dz\,d\rho_1\,d\rho_2\Big]; \quad (21)$$

the plus and minus signs pertain to the singlet and triplet, respectively.

We note a necessary property possessed by the obtained expression. It follows from (21) that as $\alpha\to\beta$ the separation $E_u-E_g\to0$, as it should. In fact, as $\alpha\to\beta$ we should arrive at the case when atoms in identical states interact, and when there are only two terms that differ in the value of the total spin. The first integral in (21) is given by the coordinate region of the electrons when they are located in their atoms. This integral therefore determines the contribution of the induced dipoles to the splitting. The calculation of this contribution is a special problem[4] and will not be considered here. We calculate only the exchange contribution given by the second integral in (21):

$$I_1^{\text{exch}}=\pm\left(\frac{\alpha-\beta}{2}\right)\oint_{z_1+z_2=0}\varphi_{1A}^*(\mathbf{r}_1)\varphi_{1B}(\mathbf{r}_1)\varphi_{2A}(\mathbf{r}_2)\varphi_{2B}^*(\mathbf{r}_2)\chi_{1(1A)}^{2(2B)}\chi_{1(1B)}^{2(2A)}\,dz\,d\rho_1\,d\rho_2. \quad (22)$$

Using the same calculation method as before,[6-9] and using the tabulated integral of the confluent hypergeometric function,[12] we obtain

$$I_1^{\text{exch}}=\pm C_1R^{2/\alpha+2/\beta-1/(\alpha+\beta)-1}e^{-(\alpha+\beta)R}; \quad (23)$$

$$C_1=\frac{a^2b^2(\alpha-\beta)}{2\alpha e^{1/\alpha}(4\beta)^{1+1/(\alpha+\beta)}}\left(\frac{\alpha+\beta}{2\alpha}\right)^{2/\beta-1/(\alpha+\beta)}\Gamma\left(1+\frac{1}{\alpha+\beta}\right)$$
$$\times\int_0^1\left[1-\frac{\alpha-\beta}{\alpha+\beta}x^2\right]^{1/\beta-1/(\alpha+\beta)}\left[1+\frac{8\alpha\beta x}{(\alpha+\beta)^2}-x^2\right]^{1/(\alpha+\beta)}dx. \quad (24)$$

The constants C_1 for collisions of alkali-metal atoms are given in Table I.

The most difficult is the calculation of the integral I_2 defined by formula (20). It is given by the intra-atomic regions of the electron coordinates and it is therefore natural to use perturbation theory for its calculation:

$$\psi_A(\mathbf{r}_1,\mathbf{r}_2)\approx\psi_A^{(0)}+\sum_k{}'\frac{W_{0k}\psi_A^{(k)}}{E_k-E_0}+\ldots,$$
$$\psi_A^{(0)}=\varphi_{2A}(\mathbf{r}_1)\varphi_{1B}(\mathbf{r}_2),\quad \psi_B^{(0)}=\varphi_{1A}(\mathbf{r}_1)\varphi_{2B}(\mathbf{r}_2) \quad (25)$$

and an analogous expansion for $\psi_B(\mathbf{r}_1,\mathbf{r}_2)$. We expand also the perturbation

$$W=\frac{f_3(\mathbf{r}_1,\mathbf{r}_2)}{R^3}+\frac{f_4(\mathbf{r}_1,\mathbf{r}_2)}{R^4}+\ldots; \quad (26)$$

$$f_3=\mathbf{r}_{1A}\mathbf{r}_{2B}-3(\mathbf{r}_{1A}\mathbf{n})(\mathbf{r}_{2B}\mathbf{n}), \quad (27)$$

$$f_4=\tfrac{3}{2}\{(\mathbf{r}_2\mathbf{n}_2+\mathbf{r}_1\mathbf{n}_1)[5(\mathbf{r}_1\mathbf{n}_1)(\mathbf{r}_2\mathbf{n}_2)-2(\mathbf{r}_1\mathbf{r}_2)]+r_1^2\mathbf{r}_2\mathbf{n}_2-r_2^2\mathbf{r}_1\mathbf{n}_1\}, \quad (28)$$

TABLE I. The constants used and calculated for alkali-metal pairs (a.u.).

	Li(2s)+Li(3s)	Na(3s)+Na(4s)	K(4s)+K(5s)	Rb(5s)+Rb(6s)	Cs(6s)+Cs(7s)
α	0.630	0.626	0.567	0.556	0.536
β	0.385	0.378	0.357	0.351	0.342
a	0.76	0.75	0.53	0.49	0.42
b	0.085	0.075	0.050	0.043	0.035
ΔE	0.0676	0.0772	0.0588	0.0581	0.0533
C_1	$4.3\cdot10^{-5}$	$3.2\cdot10^{-5}$	$6.7\cdot10^{-6}$	$4.3\cdot10^{-6}$	$2.0\cdot10^{-5}$
C_2	$\sim1.9\cdot10^3$	$\sim1.7\cdot10^3$	$\sim4.1\cdot10^3$	$\sim4.7\cdot10^3$	$\sim6.3\cdot10^3$
D	$\sim2.3\cdot10^{-8}$	$\sim1.9\cdot10^{-8}$	$\sim1.6\cdot10^{-9}$	$\sim9.1\cdot10^{-10}$	$\sim3.2\cdot10^{-10}$

Note. The quantities a and b were taken from Smirnov's paper,[6] C_1 was calculated by formula (24), C_2 by (36), and D by (35).

where the axes of quantization on the atoms A and B ($\mathbf{n}_1$ and $\mathbf{n}_2$) are oppositely directed from each atom to the other.

The contribution made to I_2 by the unperturbed atomic functions is

$$I_2^{(0)}=\frac{1}{4}\int_{x_1<x_2}[|\varphi_{2A}(\mathbf{r}_1)|^2|\varphi_{1B}(\mathbf{r}_2)|^2-|\varphi_{1A}(\mathbf{r}_1)|^2|\varphi_{2B}(\mathbf{r}_2)|^2]d\tau_1 d\tau_2, \quad (29)$$

where x_1 and x_2 are the coordinates of the electrons along the axes $\mathbf{n}_1$ and $\mathbf{n}_2$, measured from their own nuclei.

Consider the operation I_{12}—the inversion of the coordinates of both electrons in the nuclei of their own atoms. Under this operation, each point of the region $x_1<x_2$ goes over into the region $x_1>x_2$. Since the integrand in (29) is symmetrical with respect to I_{12} (the squares of the moduli of the atomic functions are symmetrical with respect to coordinate inversion), it follows that the integral (29) is equal to half the integral in the entire region, which, in accord with the normalization condition, is equal to zero. Consequently, $I_0^{(0)}=0$.

The contribution made to I_2 by products of the functions of the zeroth and first orders is

$$I_2^{(1)}=\frac{1}{2}\sum_{n,m}^{\infty}\frac{\langle 1,m(B)|W|2,n(A)\rangle}{E_n+E_m-2E_1}\int_{x_1<x_2}\varphi_{2A}(\mathbf{r}_1)\varphi^*_{nA}(\mathbf{r}_1)\varphi_{1B}(\mathbf{r}_2)\varphi^*_{mB}(\mathbf{r}_2)d\tau_1 d\tau_2$$
$$-\frac{1}{2}\sum_{n,m}^{\infty}\frac{\langle 2,m(B)|W|1,n(A)\rangle}{E_n+E_m-2E_1}\int_{x_1<x_2}\varphi_{1A}(\mathbf{r}_1)\varphi^*_{nA}(\mathbf{r}_1)\varphi_{2B}(\mathbf{r}_2)\varphi^*_{mB}(\mathbf{r}_2)d\tau_1 d\tau_2. \quad (30)$$

In the second sum we interchange the designations $\mathbf{r}_1 \rightleftarrows \mathbf{r}_2$, $n \rightleftarrows m$, $A \rightleftarrows B$. The latter is possible because the atoms A and B are identical. We obtain

$$I_2^{(1)}=\frac{1}{2}\sum_{n,m}^{\infty}\frac{\langle 1,m(B)|W|2,n(A)\rangle}{E_n+E_m-2E_1}$$
$$\times\Big[\int_{x_1<x_2}\varphi_{2A}(\mathbf{r}_1)\varphi^*_{nA}(\mathbf{r}_1)\varphi_{1B}(\mathbf{r}_2)\varphi^*_{mB}(\mathbf{r}_2)d\tau_1 d\tau_2$$
$$-\int_{x_1>x_2}\varphi_{2A}(\mathbf{r}_1)\varphi^*_{nA}(\mathbf{r}_1)\varphi_{1B}(\mathbf{r}_2)\varphi^*_{mB}(\mathbf{r}_2)d\tau_1 d\tau_2\Big]. \quad (31)$$

The integrands in these integrals are now identical, and only the integration regions are different. These regions go over into each other when the operation I_{12} is applied. It is seen therefore that of the first term of the expansion (26) of the perturbation W causes the sum (31) to vanish, since this term is symmetrical with respect to I_{12}. In fact, the matrix element $(f_3)_{2n}^{1m}$ differs from zero when m and n are such that the product of the four wave functions is symmetrical with respect to I_{12}, and consequently the difference of the integrals in (31) is equal to zero.

For the next perturbation-expansion term, which is antisymmetrical with respect to I_{12}, the product of the four wave functions is also antisymmetrical, so that the sum (31) can be easily transformed into

$$I_2^{(1)}=C_3R^{-3}, \quad (32)$$

$$C_3=\sum_{n,m}^{\infty}\frac{\langle 1,m(B)|f_1|2,n(A)\rangle}{E_n+E_m-2E_1}\int_{x_1<x_2}\varphi_{2A}(\mathbf{r}_1)\varphi^*_{nA}(\mathbf{r}_1)\varphi_{1B}(\mathbf{r}_2)\varphi^*_{mB}(\mathbf{r}_2)d\tau_1 d\tau_2. \quad (33)$$

We write down the entire splitting in the form

$$(E_u-E_g)^{\text{exch}}=\pm DR^{2/\alpha+2/\beta-1/(\alpha+\beta)+3}e^{-(\alpha+\beta)R}, \quad (34)$$

$$D=C_1/C_2, \quad (35)$$

where the constants $C_{1,2}$ are given by (24) and (33). The pre-exponential factor in (34) is R^4 times larger than the value obtained earlier.[6] We note that in this case the Heitler-London method does not predict correctly even the exponential part of the splitting (34). According to this method, the splitting is proportional to $\exp(-2\beta R)$.

ESTIMATES OF THE CONSTANTS AND OF THE EXCITATION-TRANSFER CROSS SECTION

The exact calculation of the sum (33) is quite complicated. The construction of this sum is more complicated than that of the sums encountered in the theory of Van-der-Waals forces, since the term in (33) can have alternating signs. We confine ourselves here only to an estimate of the constants C_2 and D.

Experience with the calculations of the Van-der-Waals constants shows that the order of magnitude of the sum (33) can be estimated by the first term:

$$C_3\sim\frac{r_{13}(r^2)_{21}}{|\Delta E|}\sim\frac{\bar{r}^3}{\Delta E}\sim\frac{8}{\alpha^6|\Delta E|}. \quad (36)$$

The subscript 3 marks here the lowest state to which a dipole transition from the ground state 1 is possible; $\Delta E=E_3-E_1$ is the energy difference of these states. Replacement of the matrix-element product $r_{13}(r^2)_{21}$ by the cube of the average dimension of the ground state $\bar{r}^3=(2/a^2)^3$ is more likely to increase the constant C_2. Table I lists the values of these constants for alkali metals, and also of the constant D, as calculated with the aid of the constants C_1 and C_2.

For cesium atoms Cs(6s)+Cs(7s) we have

$$(E_u-E_g)^{\text{exch}}=\pm 3.2\cdot 10^{-10}\cdot R^{11.44}\cdot e^{-0.878R}$$

and for lithium Li(2s)+Li(3s) we have

$$(E_u-E_g)^{\text{exch}}=\pm 2.3\cdot 10^{-8}\cdot R^{10.38}\cdot e^{-1.013R}.$$

The excitation-transfer cross section is[6]

$$\sigma=\tfrac{1}{2}\pi R_0^2, \quad |E_u-E_g|_{R=R_0}=0.28\,v, \quad (37)$$

where v is the relative collision velocity. Since the splittings differ only in sign for the different spins, we have in formula (2) $\sigma^{(+)}=\sigma^{(-)}$.

Table II lists the excitation-transfer cross sections calculated from formula (37) for lithium and cesium atoms at a temperature 10^3 K. The error in the determination of the cross section is much less than the error in the determination of the constant D, since the splitting changes strongly when the internuclear distance is changed. The error in the determination of the cross section is apparently not larger than 50%. It

TABLE II.

	σ (10^3 K), 10^{-14} cm^2	R_0, a.u	$2/\alpha^2+2/\beta^2$, a.u	$\Delta E^{\text{exch}}(R_0)$, a.u.	$\Delta C/R_0^6$, a.u.
$Li_7(2s)+Li_7(3s)$	2.3	23	19	$2.8\cdot10^{-4}$	$1.2\cdot10^{-4}$
$Cs_{133}(6s)+Cs_{133}(7s)$	4.2	31	24	$6.4\cdot10^{-5}$	–

is seen from the table that the radius R_0 of the transition is only slightly larger than the combined dimension of the electron orbits $2/\alpha^2+2/\beta^2$, i.e., the asymptotic theory determines the cross section at the limit of applicability of the theory. It is also seen that the Van-der-Waals contribution to the splitting[5] at $R=R_0$ is less than the exchange contribution. The temperature dependence of the cross section is weak, $\sigma \sim \ln^2 T$, as seen from (37).

[1]In: Voprosy teorii atomykh stolknoveniĭ (Problems of Atomic Collisions), ed. Yu. A. Vdovin, Atomizdat, 1970.
[2]T. Watanabe, Phys. Rev. A 138, 1573 (1965): A 140, 135 (1965).
[3]E. L. Duman, B. M. Smirnov, and M. I. Chibisov, Zh. Eksp. Teor. Fiz. 53, 314 (1967) [Sov. Phys. JETP 26, 210 (1968)].
[4]M. I. Chibisov, Opt. Spektrosk. 32, 3 (1972).
[5]T. Caves, J. Chem. Phys. 59, 6177 (1973).
[6]B. M. Smirnov, Zh. Eksp. Teor. Fiz. 53, 305 (1967) [Sov. Phys. JETP 26, 204 (1968)]; Atomye stolkoveniya i élementarnye protsessy v plazme (Atomic Collisions and Elementary Processes in Plasma), Atomizdat, 1968; Asimptoticheskie metody v teorii atomnykh stolknoveniĭ (Asymptotic Methods in the Theory of Atomic Collisions), Atomizdat, 1973).
[7]L. P. Gor'kov and L. P. Pitaevskiĭ, Dokl. Akad. Nauk SSSR 151, 822 (1963) [Sov. Phys. Dokl. 8, 788 (1964)].
[8]C. Herring and M. Flicker, Phys. Rev. A 134, 362 (1964).
[9]B. M. Smirnov and M. I. Chibisov, Zh. Eksp. Teor. Fiz. 48, 939 (1965) [Sov. Phys. JETP 21, 624 (1965)].
[10]E. A. Andreev, Teor. Acta Chim. (Berlin) B 30, 191 (1973).
[11]M. I. Chibisov and G. V. Shlapnikov, Dokl. Akad. Nauk SSSR 231, 1339 (1976) [Sov. Phys. Dokl. 21, 1339 (1976)].
[12]D. L. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics) Fizmatgiz, 1963 [Pergamon, 1968].

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Strong fluctuations of electromagnetic waves in a random medium with finite longitudinal correlation radius of the inhomogeneities

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The propagation of electromagnetic waves in a medium with random inhomogeneities of the refractive index is considered in the parabolic-equation approximation. The statistical wave intensity moments $\langle I^n \rangle$ of arbitrary order are expressed as Feynman continual integrals (in operator form). Expressions are obtained for the higher intensity moments with account taken of the finite longitudinal correlation radius of the refractive-index fluctuations, for both weak and intense intensity fluctuations. The limits of applicability of the Markov approximation, in which this correlation radius is assumed equal to zero, are obtained in the course of the calculation of the intensity moments $\langle I^n \rangle$.

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I. INTRODUCTION

The passage of electromagnetic waves in a randomly refracting medium with inhomogeneities of a scale that is large compared with the wavelength is accompanied in a number of cases by concentration of the scattered radiation in a narrow angle interval around the initial propagation direction; this leads to a fast growth of the field intensity fluctuations, followed by their saturation at a certain level. This effect can arise when radio waves propagate through the ionosphere or through interplanetary or interstellar plasma, or when light passes through a turbulent atomosphere.[1,2]

A theoretical description of strong intensity fluctuations is based on methods that go beyond the scope of perturbation theory, and have been first reported in Refs. 3–6. These methods yield equations, in closed form, for the statistical moments of the field, suitable also in the region of strong fluctuations. The approach developed in one of the papers[4] is based on a model in which the longitudinal correlation radius of the permittivity ε can be neglected in comparison with all the remaining longitudinal scales; it is also based on the assumption that the fluctuations of ε have a Gaussian probability distribution. Such a model makes it possible to describe the wave-propagation process as a Markov random process, and has therefore been dubbed the Markov approximation.

The question of the applicability limits of the Markov approximation in the derivation of the mean field $\bar{u}$ and of the coherent-field function Γ_2 was considered in Refs. 7 and 8, while its use for the description of amplitude-phase fluctuations in the geometric approximation was dealt with in Ref. 9, where a successive-approximation method was developed in which the Markov approximation serves as the first step. This method has made it possible to estimate the limits of applicability of the Markov approximation for the first two moments of the field, but not for the higher moments, owing to the complexity of the resultant equations.

The method used in the present paper was proposed by Fradkin[10] in quantum field theory and yields an expression for an arbitrary moment of the field, in the

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