Nonresonant exchange between two electrons

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An analytic expression is obtained for the matrix element of two-electron exchange in collision between an atom and an ion with different nuclear charges. A quasiclassical approximation is used that should lead to a higher accuracy (than the asymptotic expansion) at not too large distances between the nuclei. The specific case of He + C^{4+} collision is considered.

§1. INTRODUCTION

Interest has increased recently in electron exchange occurring in collisions between atoms and multiply charged ions

$$A^{Z_a-m}+B^{Z_b}\to A^{Z_a}+B^{Z_b-m}\quad (m\geqslant 1). \tag{1}$$

The effective cross sections for exchange of two, three, and even four electrons were measured in Refs. 1–3. These processes are effective mechanisms for obtaining particles with excitation energy of tens of electron volts. They play a significant role in the investigation of problems of controlled thermonuclear fusion,[4] production of an inverted medium emitting in the UV and x-ray regions,[5,6] x-ray and nuclear spectroscopy, astrophysics, and others.

The process most thoroughly investigated, experimentally and theoretically, is at present one-electron charge transfer. If the atom's outer shell has several equivalent electrons, a relatively effective reaction channel, besides one-electron, is two-electron capture. The latter process has a number of features not possessed by one-electron charge transfer and has been less studied. An exception is the case of resonant two-electron exchange, theoretically studied in Refs. 7 and 8.

The main difficulty in the understanding of the physics of two-electron processes is that an important role is played in their dynamics by correlation effects, but these constitute an independent theoretical problem.

We investigate in this paper nonresonant exchange of two electrons in slow collisions of an atom and an ion. This process was already investigated earlier in Refs. 9–11. In Refs. 9 and 10 are cited the results of a measurement of the effective cross section of the reaction

$$\mathrm{He}+\mathrm{C}^{4+}\to\mathrm{He}^{2+}+\mathrm{C}^{2+}. \tag{2}$$

The same references describe a detailed variational calculation of the terms of this system and of the cross section of the process as a whole. Grozdanov and Janev[11] applied the theory of resonant two-electron exchange,[7,8] without substantial modification, to nonresonant exchange. This theory is applicable to systems consisting of two electrons in the field of two purely Coulomb centers. For reactions with the core electrons [e.g., reaction (2)], the theory calls for further elaboration. The analytic approach used in our paper permits a study, in general form, of the efficiency of asymmetric two-electron exchange with allowance for the presence of the core. In addition, we calculate the exchange matrix element by a method valid for smaller internuclear distances and providing a more accurate result than the usual asymptotic approach.

In symmetric two-electron exchange the term splitting is determined by a configuration such that the electrons are transferred to different nuclei. For asymmetric exchange (when an atom collides with an unlike ion) this relative simple situation may also not occur. It is realized, as follows from preceding studies,[7,8] when the first ionization potential of each atom is smaller than the second potential of any of these atoms. This is indeed the case considered here. This condition is satisfied for the reaction (2) investigated in this paper. We use the atomic system of units $e^2=m=\hbar=1$.

§2. CALCULATION OF THE TWO-ELECTRON-EXCHANGE MATRIX ELEMENT

We start from the fact that in reaction (1) the core electrons of the ions A^{Z_a} and B^{Z_b} do not change their state, i.e., they can be regarded as "frozen." The problem reduces then to consideration of the motion of two "outer" electrons in the field of the two ions A^{Z_a} and B^{Z_b}. Let $\Psi_a((\mathbf{r}_1,\mathbf{r}_2)$ be the two electron wave function of the ion A^{Z_a-2}, and $\Psi_b(\mathbf{r}_1,\mathbf{r}_2)$ the two-electron wave function of the ion B^{Z_b-2}. Our problem is to calculate the exchange matrix element[12]

$$H_{ab}=\langle\Psi_a|H|\Psi_b\rangle-\langle\Psi_a|\Psi_b\rangle\langle\Psi_a|H|\Psi_a\rangle, \tag{3}$$

where H is the total Hamiltonian of the system, which takes in our case the form

$$H=-\frac{\Delta_1}{2}-\frac{\Delta_2}{2}+V_a(r_{1a})+V_a(r_{2a})+V_b(r_{1b})+V_b(r_{2b})+\frac{1}{r_{12}}+\frac{Z_aZ_b}{R}. \tag{4}$$

Here Z_a and Z_b are the effective charges of the atomic cores of A^{Z_a} and B^{Z_b}, r_{ia}, r_{ib} $(i=1,2)$ are the distances of the ith electron from the cores A and B, $V_a(r_{1a})$ and $V_b(r_{1b})$ are the potentials of the interaction of the electron "1" with the cores of A and B, respectively; $V_a(r_{2a})$ and $V_b(r_{2b})$ are the analogous quantities for the electron "2." We denote by lm_1 and lm_2 the orbital momenta and their projections on the axis joining the electrons that participate in the charge transfer and are centered on A^{Z_a}. Let L and S be their total orbital and spin momenta, and M_L and M_S the corresponding projections on the axis joining the nuclei. The quantum numbers of the electrons relative to the center B^{Z_b} will be designated l', m_1',...,M_S'. The wave function that describes the system in the initial state can then be represented in the form (we are considering a case when the A^{Z_a} and B^{Z_b} ion cores have closed electron shells)

$$\Psi_a=\frac{1}{\sqrt{2}}\sum_{m_1,m_2}\begin{bmatrix} l & l & L \\ m_2 & m_1 & M_L \end{bmatrix}(\Phi_{1a}(\mathbf{r}_1,\mathbf{r}_2)$$
$$+(-1)^S\Phi_{2a}(\mathbf{r}_1,\mathbf{r}_2))\chi_{SM_S}, \tag{5}$$

where χ_{SM_S} are the two-electron spin functions $\Phi_{1a}(\mathbf{r}_1,\mathbf{r}_2)$ and $\Phi_{2a}(\mathbf{r}_1,\mathbf{r}_2)=\Phi_{1a}(\mathbf{r}_1,\mathbf{r}_2)$ are the two-electron coordinate wave functions. The final-state wave function $\Psi_b(\mathbf{r}_1,\mathbf{r}_2)$ is constructed similarly. Substituting the functions Ψ_a and Ψ_b in (3), we obtain

$$H_{ab}=\frac{1}{2}\sum_{\substack{m_1,m_2\\ m_1',m_2'}}\begin{bmatrix} l & l & L \\ m_2 & m_1 & M_L \end{bmatrix}$$
$$\times\begin{bmatrix} l' & l' & L' \\ m_2' & m_1' & M_L' \end{bmatrix}((-1)^S H_{ab}^{(1)}+H_{ab}^{(2)}), \tag{6}$$

$$H_{ab}^{(1)}=\langle\Phi_{1a}|H|\Phi_{2b}\rangle+\langle\Phi_{2a}|H|\Phi_{1b}\rangle$$
$$+\langle\Psi_a|H|\Psi_a\rangle(\langle\Phi_{1a}|\Phi_{2b}\rangle+\langle\Phi_{2a}|\Phi_{1b}\rangle), \tag{7}$$

$$H_{ab}^{(2)}=\langle\Phi_{1a}|H|\Phi_{1b}\rangle+\langle\Phi_{2a}|H|\Phi_{2b}\rangle$$
$$+\langle\Psi_a|H|\Psi_a\rangle(\langle\Phi_{1a}|\Phi_{1b}\rangle+\langle\Phi_{2a}|\Phi_{2b}\rangle). \tag{8}$$

We put next

$$\Phi_{1a}(\mathbf{r}_1,\mathbf{r}_2)=\varphi_{1ab}(\mathbf{r}_1)\varphi_{2a}(\mathbf{r}_2),\quad \Phi_{2b}(\mathbf{r}_1,\mathbf{r}_2)=\varphi_{2ba}(\mathbf{r}_2)\varphi_{1b}(\mathbf{r}_1), \tag{9}$$

where $\varphi_{1ab}(\mathbf{r}_1)$ is the wave function of the "first" (outer) electron of the atom A^{Z_a-2} (the second subscript b of the function φ_{ab} denotes that its value near the center B is considered), $\varphi_{2a}((\mathbf{r}_2)$ is the wave function of the "second" (inner) electron of the ion A^{Z_a-1}, and similarly for the function $\Phi_{2b}(\mathbf{r}_1,\mathbf{r}_2)$. The terms $\Phi_{2b}((\mathbf{r}_1,\mathbf{r}_2)$ and $H_{ab}^{(1)}$ and $H_{ab}^{(2)}$ obtained in (6) correspond to two different two-electron transfer mechanisms. The term $H_{ab}^{(1)}$ corresponds to "parallel" transfer of the first electron from the state 1 of ion A to state 1 of ion B, and of the second electron from the state 2 of ion A to state 2 of ion B. The matrix element $H_{ab}^{(1)}$ corresponds to "crossover" transfers, when the first electron goes over from state 1 of ion A to state 2 of ion B, and the converse for the second electron. We confine ourselves hereafter to the case when the first ionization potentials of each are smaller than the second potentials of any of these atoms, i.e., when n_{1a}, $n_{1b}>n_{2a}$, n_{2b}, where $1/2n_{1a,2a}$ and $1/2n_{1b,2b}^2$ are the first and second ionization potentials of A and B, respectively. The matrix element $H_{ab}^{(1)}$ has an $R\to\infty$ an asymptotic form $\exp[-(1/n_{1a}+1/n_{1b})R]$, while

$$H_{ab}^{(2)}\underset{R\to\infty}{\sim}\exp\left[-\left(\frac{1}{n_{1a}}+\frac{1}{n_{2a}}+\frac{1}{n_{1b}}+\frac{1}{n_{2b}}\right)\frac{R}{2}\right).$$

We shall take into account only the principal matrix element of $H_{ab}^{(1)}$, which decreases more slowly than the matrix element H_{ab}, in analogy with the case of resonant two-electron exchange.[7,8]

The functions $\varphi_{1a,2a}$ and $\varphi_{1b,2b}$ must be known in the region where they are a maximum, and can be regarded known as unperturbed atomic functions. The functions $\varphi_{1ab,2ab}$ ($\varphi_{1ba,2ba}$) must be known in the region where the electron is removed from its center to the foreign ion. The construction of these functions is the subject of the next section.

§3. DETERMINATION OF THE ELECTRON WAVE FUNCTIONS

We recognize that the first electron is situated in the field of two centers, A^{Z_a-1} and B^{Z_b}. Therefore its wave function φ_{ab} satisfies the following Schrödinger equation:

$$(-\Delta/2+U_a(r_a)+V_b(r_b)-E)\varphi_{ab}(\mathbf{r}_b)=0, \tag{10}$$

where U_a and V_b are the potentials of the interaction of the electron with particles A^{Z_a-1} and B^{Z_b}.

It follows from the formulation of the problem that we must know the wave function φ_{ab} in the vicinity of the center B. In this region the principal role in Eq. (10) is played by the potential of the electron interaction with the center B, while the potential U_a can be regarded as a small perturbation. Equation (10) can then be solved with the aid of a Green function, namely,

$$\varphi_{ab}(\mathbf{r}_b)=-\int d^3r_b' G_b(\mathbf{r}_b,\mathbf{r}_b';E)U_a(r_b')\varphi_{ab}(\mathbf{r}_b'), \tag{11}$$

where G_b is the Green function for the motion of one electron in the potential V_b.

The solution of (10) must satisfy definite boundary conditions and was obtained in Ref. 13 for the intercenter region, where the potentials U_a and V_b can be replaced by their Coulomb asymptotic values. The solution obtained is of the form

$$\varphi_{ab}(\mathbf{r}_a)=\frac{1}{r_a}q(\mathbf{r}_a)Y_{lm_1}(\theta_a,\varphi_a), \tag{12}$$

$$q=\frac{A_1}{(n_{1a}p(r_a))^{1/2}}\left(\frac{(Z_a-1)n_{1a}^2}{2e}\right)^{n_{1a}(Z_a-1)}\exp\left[-\int_{r_1}^{r_a}|p(r')|dr'\right], \tag{13}$$

$$p^2(r_a)=2\left(-|E|+\frac{Z_a-1}{r_a}+\frac{Z_b}{|\mathbf{r}_a-\mathbf{R}|}\right),\quad r_a\sim R,\quad p(r_1)=0. \tag{14}$$

This solution is so constructed that at $r_a\sim1$ it goes over into the asymptotic form of the atomic wave function

$$\varphi_{ab}\xrightarrow[1\sim r_a\ll R]{}\varphi^0=A_1r^{n_{1a}(Z_a-1)-1}e^{-r_a/n_{1a}}Y_{lm_1}(\theta_a,\varphi_a). \tag{15}$$

The boundary conditions for (10) will be chosen by "joining" the solution of Eq. (10) with the solution (12) in the region r_a, $r_b\sim R$. By the same token it becomes automatically normalized to the asymptotic relation (15).

We emphasize that the solution (12) was obtained by a quasiclassical method. This is important, since it becomes possible to take correctly into account the charge of the electron energy under the barrier. The quasiclassical approach yields a solution that is valid at not too large internuclear distances R. The only restriction on R is that it be larger than the distance at which the potential barrier between the centers vanishes.

To solve the integral equation (11) we must consider certain properties of the Green function. The total Green function G_b for the centrosymmetric potential V_b can be expanded into partial radial Green functions g_{l_1} (Ref. 14):

$$G_b(\mathbf{r}_b, \mathbf{r}_b'; E) = \sum_{l_1=0}^{\infty} \frac{2l_1+1}{2\pi} P_{l_1}(\cos\gamma) \frac{g_{l_1}(r_b, r_b')}{r_b r_b'}, \tag{16}$$

where γ is the angle between $\mathbf{r}_b$ and $\mathbf{r}_b'$, and the radial Green functions are

$$g_{l_1}(r_b, r_b') = {}^1\!/_2 n_{1a} f_{1l_1}(r_<) f_{2l_1}(r_>), \tag{17}$$

$$f_{1l_1} \xrightarrow[r_b\to\infty]{} r_b^{-n_{1a}Z_b} e^{r_b/n_{1a}} \qquad f_{2l_1} \xrightarrow[r_b\to\infty]{} r_b^{n_{1a}Z_b} e^{-r_b/n_{1a}},$$

$$r_{\gtrless} = \max, \min\{r_b, r_b'\}. \tag{18}$$

The functions f_{l_1} are solutions of the equation

$$\left[\frac{d^2}{dr_b^2} + 2\left(E - V_b(r_b) - \frac{l_1(l_1+1)}{r_b^2}\right)\right] f_{l_1}(r_b) = 0, \tag{19}$$

with f_{l_1} regular at zero and f_{2l_2} regular at infinity.

We return to Eq. (11). The function φ_{ab} attenuates exponentially in the direction from nucleus A to nucleus B, and the Green function G_b, conversely, from the nucleus B to the nucleus A. Their product in the integral of (11) is a maximum in the internuclear region, so that just this region of values $r_b' R$ determines the value of the integral. Since we need the region $r_b \sim 1$, we must use the asymptotic form of the Green function (16) at $r_b' \gg r_b$. We obtain this asymptotic form by putting in (17) $r_< \to r_b$ and $r_< \to r_b'$ and using for $f_{2l_1}(r_b')$ its asymptotic form (18). The required asymptotic expression for the Green function is then

$$G_b \underset{r_b' \gg r_b}{\approx} \frac{n_{1a}}{4\pi} (r_b')^{n_{1a}Z_b - 1} e^{-r_b'/n_{1a}}$$

$$\times \sum_{l_1=0}^{\infty} (2l_1+1) P_{l_1}(\cos\theta_b) \frac{f_{1l_1}(r_b)}{r_b}, \tag{20}$$

where θ_b is the angle between the internuclear axis and the vector r_b. This expression was factorized relative to the variables r_b and r_b'. When it is substituted in (11), we obtain no longer an equation but an explicit expression for the wave function in the region $r_b \sim 1$ needed by us (i.e., the solution of this equation):

$$\varphi_{ab}(\mathbf{r}_b) \underset{r_b \ll R}{\approx} D_a(R) \sum_{l_1=0}^{\infty} (2l_1+1) P_{l_1}(\cos\theta_b) \frac{f_{1l_1}(r_b)}{r_b}. \tag{21}$$

It is assumed that the projection of the angular momentum of the electron in the state φ_{ab} is zero. The normalization constant $D_a(R)$ in (21) is obtained by joining the function (21) with the function (12), (13). To this end it is necessary, generally speaking, to calculate the sum contained in (21). For values of r_b inside the core of particle B, this problem is practically unsolvable. To determine $D_a(R)$, however, we must sum in the region of such large r_b, where the core can already be neglected and where only the Coulomb part of the potential V_b remains. In this region the Green function (16) should coincide with the pure Coulomb Green function obtained by Hostler and Prat,[15] with an asymptotic form with respect to the variable r_b'

$$G_b^{\mathrm{C}} \underset{r_b' \gg r_b}{\approx} \frac{2^{n_{1a}Z_b}}{2\pi n_{1a}^{n_{1a}Z_b}} \Gamma(1 - n_{1a}Z_b)(r_b')^{n_{1a}Z_b - 1}$$

$$\times e^{-r_b'/n_{1a}} e^{-r_b/n_{1a}} F\left(1 - n_{1a}Z_b; 1; \frac{r_b(1-\cos\theta_b)}{n_{1a}}\right), \tag{22}$$

where $F(\ldots)$ is a confluent hypergeometric function, while $M(\ldots)$ and $W(\ldots)$ are Whittaker functions. Comparing (22) and (20), we obtain the value of the sought sum outside the core:

$$\sum_{l_1=0}^{\infty} (2l_1+1) P_{l_1}(\cos\theta_b) \frac{f_{1l_1}(r_b)}{r_b}$$

$$= \left(\frac{2}{n_{1a}}\right)^{n_{1a}Z_b+1} \Gamma(1 - n_{1a}Z_b) e^{-r_b/n_{1a}}$$

$$\times F\left(1 - n_{1a}Z_b; 1; \frac{r_b(1-\cos\theta_b)}{n_{1a}}\right). \tag{23}$$

For a pure Coulomb center V_b, when there is no core, this expression is valid in the entire vicinity of particle B. In reaction (2) this center is the He^{2+} ion.

To find $D_a(R)$ in an arbitrary case we must use the asymptotic form of (22) with respect to the variable r_b' and a quasiclassical approximation for the function $M(\ldots)$, since we must match the result to the quasiclassical function (12), (13). We then obtain for the sum in Eq. (21)

$$\sum_{l_1=0}^{\infty} \ldots = \frac{4}{n_{1a}^2} \left(\frac{2}{n_{1a}}\right)^{n_{1a}Z_b - 1} \left(\frac{e}{n_{1a}Z_b}\right)^{n_{1a}Z_b}$$

$$\times \exp\left(\int_{x_1}^{x_b} p_b\,dx' - \frac{\rho'^2}{2n_{1a}x}\right),$$

$$R \gg r_b \gg 2r_b n_{1a}^2, \tag{24}$$

where x_b is the distance from B along the internuclear axis, ρ' is the distance from the nuclear axis, and

$$p_b^2 \equiv (2|E| - 2Z_b/r).$$

Substituting (24) in (21) and comaring (21) with (12), (13) we obtain ultimately for the wave function

$$\varphi_{ab} \approx D_a(R) \sum_{l_1=0}^{\infty} (2l_1+1) P_{l_1}(\cos\theta_b) \frac{f_{1l_1}(r_b)}{r_b}, \tag{25}$$

$$D_a(R) = \frac{A_1 n_{1a}}{2} \left(\frac{2l+1}{4\pi}\right)^{1/2} \left(\frac{2}{n_{1a}^2 Z_b}\right)^{n_{1a}(Z_a-1)}$$

$$\times \left(\frac{n_{1a}^2 Z_b}{2e}\right)^{n_{1a}Z_b} Q(R, n_{1a}, Z_b, Z_a), \tag{26}$$

$$Q(R, n_{1a}, Z_b, Z_a) = R^{2n_{1a}(Z_a-1)-1} \exp\left[-\frac{R}{n_{1a}}\right]$$

$$\times \left[\left(\frac{R}{2Z_b n_{1a}^2}\right)^{1/2} + \left(\frac{R}{2Z_b n_{1a}^2} + 1\right)^{1/2}\right]^s; \tag{27}$$

$$s \equiv \frac{2(Z_b - Z_a + 1)}{(1/n_{1a}^2 + 2Z_b/R)^{1/2}}.$$

We have used here the previously obtained (13) expansion of the barrier integral

$$\int_{x_1}^{x_2} p\,dx.$$

In the juncture region, the integral of (13) is written in a form similar to the integral in (24).

For a pure Coulomb perturbing center B we have in place of (25)

$$\varphi_{ab}(\mathbf{r}_b)=\left(\frac{2}{n_{1a}}\right)^{n_{1a}Z_b+1}\Gamma(1-n_{1a}Z_b)D_a(R)$$

$$\times e^{-r_b/n_{1a}}F\left(1-n_{1a}Z_b;\,1;\frac{r_b(1-\cos\theta_B)}{n_{1a}}\right). \tag{28}$$

Although (25) contains an infinite sum, it is convenient for our calculations since the determination of the exchange matrix element calls for calculation of the matrix element of a one-electron dipole transition from the state (25) to the ground state of the ion B. When the matrix element is calculated for such a transition, only a finite number of terms remain in the sum of (25) in view of the selection rules.

§4. TERM SPLITTING

We consider the following model for the potential V_b of the interaction between and electron and an ion with a core [C^{4+}in the reaction (2)]:

$$V_b=-Z_b/r_b+C/r_b^2. \tag{29}$$

The energy levels in this potential are known exactly, and the wave functions are expressed in terms of confluent hypergeometric functions.[16] The functions f_{1l_1} contained in the sum (21) are expressed in this case in terms of a Whittaker function

$$f_{1l_1}(r)=\left(\frac{2}{n_{1a}}\right)^{n_{1a}Z_b}\frac{\Gamma(1+s_{l_1}-n_{1a}Z_b)}{\Gamma(2s_{l_1}+2)}M_{n_{1a}Z_b;\,s_{l_1}+1/2}\left(\frac{2r}{n_{1a}}\right), \tag{30}$$

where

$$s_{l_1}=[(l_1+1/2)^2+2C]^{1/2}-1/2. \tag{31}$$

To find C, we choose the B^{Z_b-1}, wave function for the ground state into which the electron removed from A goes over to be equal to the wave function of one of the states in a field (29) having the same angular quantum numbers l' and m' as the real state. The radial quantum numbers must apparently be chosen such that the number of zeros of the model and real (e.g., Hartree-Fock) wave functions coincide.

Matching the energy levels of the ground states does not guarantee equality of the other levels. However, the description of the entire spectrum of the particle B^{Z_b-1} by a single model potential (29) ensures the necessary orthogonality of the wave functions of the different states of the particle B^{Z_b-1}. If the zeros of the model and real wave functions are chosen equal in number, the agreement between the real and the model spectra will on the whole be best, with the possible exception of several model terms that lie considerably lower than the real ones. This, however, does not influence strongly the final result.

The normalized wave functions $\varphi_{2a}(\mathbf{r}_1)$ and $\varphi_{2b}(\mathbf{r}_1)$ of the ground states of the ions A^{Z_a-1} and B^{Z_b-1} respectively as specified within the framework of the model potential (29) in the form

$$\varphi_{2a}(\mathbf{r}_2)=A_2r_2^{s_{l_1}}e^{-r_2/n_{2a}}Y_{lm_2},$$

$$A_2=\left(\frac{2}{n_{2a}}\right)^{s_{l_1}+3/2}\Gamma^{-1/2}(2s_{l_1}+3), \tag{32}$$

$$\varphi_{2b}(\mathbf{r}_1)=B_2r_1^{s_{l_1'}}e^{-r_1/n_{2b}}Y_{l'm_2'},$$

$$B_2=\left(\frac{2}{n_{2b}}\right)^{s_{l_1'}+3/2}\Gamma^{-1/2}(2s_{l_1'}+3). \tag{33}$$

The excited-state wave functions for the model potential (29) are constructed in analogy with those of the excited states in a Coulomb field and differ from the latter only in that the integer values of the orbital-momentum quantum numbers are replaced by fractional values.

An important property of the two-electron wave functions $\Phi_{1a}=\varphi_{1ab}(\mathbf{r}_1)\varphi_{2a}(\mathbf{r}_2)$ and $\Phi_{2b}=\varphi_{1ba}(\mathbf{r}_2)\varphi_{2b}(\mathbf{r}_1)$ constructed here is that they are orthogonal. Therefore a nonzero contribution to the matrix element (7) is made only by the electron-electron interaction r_{12}^{-1}. The regions of importance for the matrix element (7) are those where r_1 and r_2 are small and the electron-electron interaction r_{12}^{-1} must be expanded in reciprocal powers of the large internuclear distance R, retaining only the first correlation term

$$r_{12}^{-1}\approx R^{-3}(\mathbf{r}_1\mathbf{r}_2-3(\mathbf{r}_1\mathbf{n})(\mathbf{r}_2\mathbf{n})),\quad \mathbf{n}=\mathbf{R}/R. \tag{34}$$

Next, substituting in (7) the corresponding explicit expressions for the wave functions $\varphi_{1ab}, \varphi_{1ba}, \varphi_{2a}$, and φ_{2b} and taking into account only the principal term of the asymptotic expansion of $H_{ab}^{(1)}$ in powers of R^{-1} (i.e., the term stemming from $m_1=m_1'=0$), we ultimately obtain the following expression of the term splitting:

$$\Delta E=2H_{ab}^{(1)}=DQ(R,n_{1a},Z_b,Z_a)Q(R,n_{1b},Z_a,Z_b)R^{-3}, \tag{35}$$

where

$$D=(-1)^{s+l}2C_lC_{l'}\left\{[1+(-1)^{L+L'}]\begin{bmatrix} l & l & L\\ 1 & 0 & 1\end{bmatrix}\right.$$

$$\times\begin{bmatrix} l' & l' & L'\\ 1 & 0 & 1\end{bmatrix}[T_{l'}^{(-)}(n_{1a},n_{2b},Z_b)$$

$$+T_{l'}^{(+)}(n_{1a},n_{2b},Z_b)][T_l^{(-)}(n_{1b},n_{2a},Z_a)+T_l^{(+)}(n_{1b},n_{2a},Z_a)]$$

$$+2\begin{bmatrix} l & l & L\\ 0 & 0 & 0\end{bmatrix}\begin{bmatrix} l' & l' & L'\\ 0 & 0 & 0\end{bmatrix}[K_{l'}^{(-)}(n_{1a},n_{2b},Z_b)$$

$$+K_{l'}^{(+)}(n_{1a},n_{2b},Z_b)]$$

$$\left.\times[K_l^{(-)}(n_{1b},n_{2a},Z_a)+K_l^{(+)}(n_{1b},n_{2a},Z_a)]\right\}, \tag{36}$$

$$C_{l'}(A_1,B_2,n_{1a},Z_a,Z_b)$$

$$=\frac{n_{1a}(2l'+1)}{2}A_1B_2\left(\frac{2}{n_{1a}^2Z_b}\right)^{n_{1a}(Z_a-1)}\left(\frac{n_{1a}Z_b}{e}\right)^{n_{1a}Z_b}, \tag{37}$$

$$T_{l'}^{(\pm)}(n_{1a},n_{2b},Z_b)=[2(l'\pm1)+1]\frac{\Gamma(1+s_{l'\pm1}-n_{1a}Z_b)}{\Gamma(2s_{l'\pm1}+2)}$$

$$\times\begin{pmatrix} l' & l'\pm1 & 1 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} l' & l'\pm1 & 1 \\ -1 & 0 & 1 \end{pmatrix} \dot{J}_{l'}^{(\pm)}(n_{1a}, n_{2b}, Z_b), \quad (38)$$

$$\tilde{K}_{l'}^{(\pm)}(n_{1a}, n_{2b}, Z_b) = [2(l'\pm1)+1] \times \frac{\Gamma(1+s_{l'\pm1}-n_{1a}Z_b)}{\Gamma(2s_{l'\pm1}+2)}\begin{pmatrix} l' & l'\pm1 & 1 \\ 0 & 0 & 0 \end{pmatrix}^2 \times \dot{J}_{l'}^{(\pm)}(n_{1a}, n_{2b}, Z_b), \quad (39)$$

$$\dot{J}_{l'}^{(\pm)}(n_{1a}, n_{2b}, Z_b) = \int_0^\infty dr r^{s_{l'}+2} e^{-r/n_{2b}} M_{n_{1a}Z_b;\, s_{l'\pm1}\pm1/2}\left(\frac{2r}{n_{1a}}\right), \quad (40)$$

$$C_l \equiv C_{l'}(B_1, A_2, n_{1b}, Z_b, Z_a), \quad T_l^{(\pm)} \equiv T_{l'}^{(\pm)}(n_{1b}, n_{2a}, Z_a),$$
$$K_l^{(\pm)} \equiv K_{l'}^{(\pm)}(n_{1b}, n_{2a}, Z_a), \quad \dot{J}_l^{(\pm)} \equiv \dot{J}_{l'}^{(\pm)}(n_{1b}, n_{2a}, Z_a). \quad (41)$$

The quantities $\begin{pmatrix} \cdots \\ \cdots \end{pmatrix}$ are Wigner $3j$ symbols that appear in the matrix elements (38) and (39) as a result of integration over the angle variables. The radial integrals $J_{l'}^{(\pm)}$ defined by (40) can be calculated analytically with the aid of the tabulated integrals of the Whittaker function[17]

$$\dot{J}_{l'}^{(\pm)}(n_{1a}, n_{2b}, Z_b) = \left(\frac{2}{n_{1a}}\right)^{s_{l'\pm1}+1}\left(\frac{n_{1a}n_{2b}}{n_{1a}+n_{2b}}\right)^{s_{l'}+s_{l'\pm1}+} \Gamma(s_{l'}+s_{l'\pm1}+4)$$
$$\times {}_2F_1\left(1+s_{l\pm1}-n_{1a}Z_b; s_l+s_{l\pm1}+4; 2s_{l\pm1}+2; \frac{2n_{2b}}{n_{2b}+n_{1a}}\right), \quad (42)$$

where ${}_2F_1(\ldots)$ is a complete hypergeometric function.

From expressions (35)–(42) for the term splitting, which are valid for the nonresonant case, it is easy to obtain an expression for the term splitting in the resonant case. To this end it suffices to put in (35)–(42)

$$Z_a = Z_b = Z, \quad n_{1a,\,2a} = n_{1b,\,2b}, \quad l = l', \quad L = L', \quad A_{1,2} = B_{1,2}. \quad (43)$$

Let us investigate the results in the limit $R \gg 2Z_{a,b}n_{1a,1b}^2$, when it should go over into the asymptotic result,[8,11] for the case of interaction of a helium atom with an α particle. In this particular case $C \to 0$ ($s_0 \to 0$, $s_1 \to 1$, $n_{2a,2b} = 1/Z_{a,b} = 1/Z$) and (35) takes the form

$$\Delta E = 2^8 A^2 \Gamma^2(1-nZ)\left(\frac{nZ^{1/2}}{nZ+1}\right)^{10}\left(\frac{2}{ne}\right)^{2nZ}\left(\frac{nZ-1}{nZ+1}\right)^{2nZ-4} \times R^{2n(2Z-1)-5}e^{-2R/n}, \quad (44)$$

or one-half the corresponding result of Ref. 8: a factor $2^{-1/2}$ was lost from Eq. (2) of Ref. 8.

§5. RESULTS OF CROSS-SECTION CALCULATIONS AND COMPARISON WITH EXPERIMENT

In this section we calculate the cross section of the charge-transfer reaction (2) at low energies. The time-dependent equations for the amplitudes of the quantum transitions can be written in the two-level approximation[16] in the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = a_1(t)\Psi_a(\mathbf{r}_1, \mathbf{r}_2) + a_2(t)\Psi_b(\mathbf{r}_1, \mathbf{r}_2), \quad (45)$$

$$i\dot{a}_1 = H_{11}a_1 + V_{12}a_2, \quad i\dot{a}_2 = V_{21}a_1 + H_{22}a_2, \quad (46)$$

where the total Hamitonian $H = H_0 + V$ and the matrix elements are

$$V_{ik} = \int \Psi_i^*(\mathbf{r}_1, \mathbf{r}_2) V \Psi_k(\mathbf{r}_1, \mathbf{r}_2) d^3r_1\, d^3r_2, \quad \{i, k\} \equiv \{a, b\};$$
$$H_{ii} = E_i + V_{ii}, \quad V_{12} = V_{21} = H_{ab}(R(t)). \quad (47)$$

The system (46) must be solved under the initial condition $a_1(-\infty) = 1$, $a_2(-\infty) = 0$. The transition probability is then $W = |a_2(+\infty)|^2$.

The calculations of the exchange interaction $H_{ab}^{(1)}$ for reaction (2) with the aid of Eqs. (35)–(40) have shown that the $2s^2$ state of the C^{2+} ion is most effectively populated, so that the two-level approximation can be used. The amplitudes A_1 and B_1 in the asymptotic expression (15) for the respective wave functions of the He atom and the C^{2+} ion were determined earlier[18,19] by comparing (15) with the numerical Hartree-Fock-Clementi wave functions[20]

$$A_1 = 2.87, \quad B_1 = 9.05, \quad n_{1a} = 0.744,$$
$$n_{1b} = 0.533, \quad n_{2b} = 0.458. \quad (48)$$

We assume the collision trajectory to be a straight line: $R = (\rho^2 + v^2t^2)^{1/2}$, where ρ is the impact parameter.

Figure 1 shows the cross section of the process (2), calculated by us by numerically solving the system (46) and by using the Landau-Zener model (the numerical value of the splitting at the term quasicrossing point is $\Delta E(R_0 = 3.265) = 0.038$. From our calculations, as well as from earlier ones,[21,22] it follows that the increase of the cross section compared with the Landau-Zener value is due to peripheral collisions, i.e., collisions with an impact parameter ρ close to the interatomic, at which the term crossing takes place. For these collisions, the transition probability increases as a result of interference between two crossing points. The range of ρ for which interference is significant increases with increasing collision rate, for the transition region increases in this case. This is indeed the reason why the cross section calculated from the system (46) is considerably closer to experiment than the cross section of the Landau-Zener model.

Figure 1 shows also the results of other studies.[9,10,23] The time-dependent problem was solved in Refs. 9 and 10 by the method of strong coupling of 11 states. The nuclei were

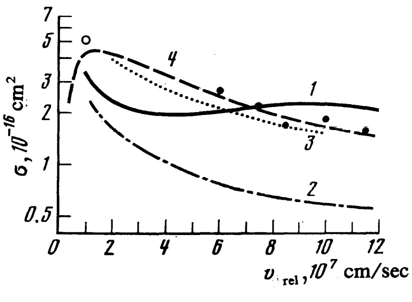

FIG. 1. Curve 1 was obtained by us with the aid of the system (46), 2—obtained by us in the Landau-Zener approximation; 3—obtained in Refs. 8 and 10 by the method of strong coupling of 11 states; 4—obtained in Ref. 11 in the Landau-Zener approximation. Experiment: ●—from Ref. 23.

assumed to move along straight lines. Account was taken in the matrix elements of both the radial and the rotational coupling. It can be seen from the figure that allowance for only two terms yields an oscillating cross section (curve 1). Expansion of the basis leads apparently to a smoothing of the oscillations (curve 3).

In Ref. 11 the exchange matrix element was calculated under the assumption that the C^{4+} ion is a Coulomb center, and the cross section for the process (2) was calculated by the Landau-Zener formula. However, the energy spectra of systems with and without cores, as already indicated above, are substantially different, while the cross sections calculated by the Landau-Zener formula are several times smaller than the exact ones. It follows hence that the agreement between the theory and the experiment in Ref. 11 is apparently accidental.

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