kW), while Fig. 6d shows the same but with the dye-laser wavelength tuned with the aid of a Fabry–Perot resonator. When the frequency of the rhodamine laser was varied in the range 562–585 nm, the anti-Stokes and Stokes radiation was tuned in the ranges 455–469 and 737–773 nm. As follows from the spectrograms, the efficiency of the conversion of the weak pumping is of the order of 50% in energy.

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[1)]The increments $\lambda_{1,2}$ were given in[2] for the case $K_{22} \gg K_{11}$.
[2)]Expressions for C_{2S} and C_{1a}^* can be easily obtained from (6) and (7) by making the substitutions $K_{11} \to K_{11}(\omega_1, \omega_{1a})$, $K_{12} \to -K_{12}(\omega_2, \omega_{1a})$ and $C_{1a} \to C_{1a}^*$.
[3)]The solution of the transcendental equation (30) and the calculation of the integral (27) were carried out with a computer.
[4)]The difference between the threshold intensities cannot be explained by the frequency dependence of the cross sections of the spontaneous Raman scattering, and is apparently connected with the somewhat different geometry of the beams of the slow and weak pumps under the experimental conditions.
[5)]Curves 1 and 2 (Fig. 4) were obtained in[1] by an approximate calculation in the phase-locking regions (see Sec. III, subsection 3), i.e., under the assumption $\theta \approx 0$ and $\delta \ll 1$.

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Resonance two-electron charge exchange

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The process of resonance exchange of two electrons in an atom–ion collision is considered. At large internuclear distances the process proceeds mainly as a superposition of two inelastic transitions for each separate electron. A substantial contribution to the charge exchange is also made by parallel electron transitions in which the energy of each electron does not change. For the purpose of computing the probability of these transitions, the asymptotic behavior of the wave function resulting from the simultaneous removal of two electrons from the atom is investigated.

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1. The probability of resonance charge exchange of any number of electrons in a collision between an atom and its multiply charged ion can be computed if the spacing between the energy terms of the even and odd—with respect to the interchange of the nuclei—states is known.[1] At collision velocities lower than the orbital velocities of the bound electrons, the transition occurs at large interatomic distances, so that it is necessary to know the asymptotically exact value of the term spacing. This spacing exponentially decreases as the atoms move away from each other.

The term spacing for a two-electron exchange was earlier computed in the papers[2,3] and estimated in[4]. In[2] the computation was carried out, using unperturbed atomic wave functions, i.e., according to the Heitler-London scheme. In[3,4] it is pointed out that, in order to obtain the asymptotic form of the term splitting for large internuclear distances, it is necessary to construct the correct wave function of the outer atomic electron in the vicinity of the perturbing ion.

In[3,4] the contribution made by the crossover transitions to the splitting is investigated: An electron from the outer (inner) orbit of the atom a crosses to an inner (outer) orbit of the atom b. These transitions are inelastic for each separate electron (the transition of both electrons as a whole is elastic). The dominant contribution to the transition probability is made here by the configuration in which the electrons move apart on different nuclei, and the independent electron approximation as a zeroth approximation is valid.[3,5–7] Inelastic

transitions are possible only as a result of the interaction of the electrons with each other, an interaction which, for the configuration under consideration, is proportional to R^{-3}. The term splitting is then equal to the matrix element of this interaction, and turns out to be smaller than the splitting obtained in[3,4] by a factor of R^3 (R is the internuclear distance).

The method, proposed by Komarov and Yanev in[3], for computing this dominant part of the splitting turns out to be unsuitable in practice, since it requires the determination of the wave function correct up to terms $\sim R^{-3}$ with respect to the zeroth approximation. The nonzero result obtained in[3] with a function of the zeroth approximation turns out to be incorrect. This is shown in the Appendix to this paper. The estimate made in[4] is also incorrect, since it does not take the orthogonality, discussed below, of the wave functions into account.

In the present paper we compute still another contribution to the splitting, namely, the contribution made by parallel transitions: An electron from the outer (an inner) orbit of the atom a crosses over to the outer (an inner) orbit of the atom b. For atomic particles for which the first and second ionization potentials are nearly equal, this contribution attenuates, as the atoms are separated, virtually according to the same exponential law as the dominant contribution. Both contributions can be computed simultaneously for any atoms, using the wave function of only the zeroth approximation, since they are determined by different regions of the electron coordinates. The computation of the second contribution requires the investigation of the asymptotic behavior of the atomic wave function resulting from the simultaneous removal of two electrons.

TWO-ELECTRON ASYMPTOTIC BEHAVIOR OF THE ATOM IN THE FIELD OF THE ION

Let us consider a two-electron atom, at a distance R from which the same doubly-ionized positive ion is located. The Schrödinger equation for the two electrons can be written in the form $(H - E_{u,g})\psi_{u,g} = 0$,

$$H=-\frac{\Delta_1+\Delta_2}{2}-\frac{Z}{r_{1a}}-\frac{Z}{r_{2a}}-\frac{Z}{r_{2b}}-\frac{Z}{r_{1b}}+\frac{1}{r_{12}}+\frac{Z^2}{R}. \tag{1}$$

Here $r_{1a,2a}$, $r_{1b,2b}$ are respectively the distances of the electrons from the nuclei a and b; Z is the charge of the nuclei. The eigenfunctions are either even (g), or odd (u) with respect to the operation of reflection of the coordinates of the two electrons in the plane perpendicular to, and passing through the middle of, the internuclear axis. These functions go over, as the nuclei are separated, into combinations of the atomic functions $\psi_{a,b}(\mathbf{r}_1, \mathbf{r}_2)$. These latter functions are the solutions to the set of equations

$$\begin{aligned}&\left(H-\frac{E_u+E_g}{2}\right)\psi_a=\frac{E_u-E_g}{2}\psi_b,\\ &\left(H-\frac{E_u+E_g}{2}\right)\psi_b=\frac{E_u-E_g}{2}\psi_a,\\ &\psi_{g,u}=\frac{1}{\sqrt{2}}(\psi_a\pm\psi_b).\end{aligned} \tag{1a}$$

It is not all for configurations that this system can be treated as homogeneous by discarding the right-hand sides. If both electrons are located, for example, near the atom a, then the equation for ψ_b is inhomogeneous, since the right-hand side is greater than the terms on the left-hand side. For the computation of the splitting, we shall need those configurations for which the right-hand sides in (1a) are small, and the system can be assumed to be homogeneous.

Let us determine the dominant term of the asymptotic expansion of the functions $\psi_{a,b}$ in inverse powers of R, an expansion which will be valid when both electrons are moved away through a distance $\sim R$. For this purpose, let us first consider the asymptotic form of the atomic function in the case when, for example, the electron 1 is moved away considerably farther than the electron 2, but through a distance much shorter than R. We evidently have

$$\begin{aligned}&\psi_a^{(0)}=\psi_{1a}^{(0)}+\psi_{2a}^{(0)}, \quad \psi_{1a}^{(0)}\approx a_1 r_{1a}^{(Z-1)/\beta_1-1}e^{-\beta_1 r_{1a}}\varphi_{0a}(r_{2a}),\\ &\psi_2=\psi_1(r_1\rightleftarrows r_2),\ R\gg r_{1a}\gg r_{2a}\sim 1,\\ &\varphi_{0a}\underset{r_{2a}\gg 1}{\approx} a_2 r_{2a}^{Z/\beta_2-1}e^{-\beta_2 r_{2a}}, \quad \beta_{1,2}=(2|E_{1,2}|)^{1/2}.\end{aligned} \tag{2}$$

Here $|E_{1,2}|$ are the first and second ionization potentials of the atom; φ_{0a} is the wave function of the ground state of the singly charged ion of the atom a (or the inner orbit of this atom).

To construct the function ψ_{1a} in the region $r_{1a}\sim r_{2a}\sim R$, let us set $\psi_{1a}=\psi_{1a}^{(0)}\chi_{1a}(r_1, r_2)$ and use for the determination of χ the method used in the papers[8-10]. Let us substitute this product into the homogeneous system (1a) (after setting $E_u+E_g=2E_0=2(E_1+E_2)$), neglect the second derivatives of the function χ, and differentiate only the exponential functions occurring in the function (2). Then for the new function χ, we obtain the equation

$$2\frac{\partial\chi_{1a}}{\partial\xi}+\left[\frac{1}{r_{12}}-\frac{1}{r_{1a}}+Z\left(\frac{1}{R}-\frac{1}{r_{1b}}\right)+Z\left(\frac{1}{R}-\frac{1}{r_{2b}}\right)\right]\chi_{1a}=0; \tag{3}$$
$$\xi=r_{1a}/\beta_1+r_{2a}/\beta_2;\ \eta=r_{1a}/\beta_1-r_{2a}/\beta_2.$$

Here E_2 is the second ionization potential of the atomic particle a, and we have also taken into account the fact that the electronic energy is equal to $E - Z(Z-2)R^{-1}$. The solution to Eq. (3) determines the function χ up to an arbitrary function of η and the angles which the vectors $\mathbf{r}_{1a}$ and $\mathbf{r}_{2a}$ make with R and with each other. Let us choose this function such that it satisfies the boundary conditions: $\chi \to 1$ for $R \gg r_{1a} \gg r_{2a}$, while for $r_{1a}\sim R$ and $r_{2a} \ll r_{1a}$ the function χ should go over into a one-electron function taking the field of the ion into account.[5] Such a solution to Eq. (3) is equal to

$$\chi_{1a}=\chi_{1a}^{(1)}\chi_{1a}^{(2)}\chi_{1a}^{(3)}, \tag{4}$$

$$\chi_{1a}^{(1)}=\exp\left\{-\frac{Zr_{1a}}{\beta_1 R}\right\}\left[\frac{r_{1b}+r_{1a}-R\cos\theta_1}{R(1-\cos\theta_1)}\right]^{Z/\beta_1},$$

$$\chi_{1a}^{(2)}=\exp\left\{-\frac{Zr_{2a}}{\beta_2 R}\right\}\left[\frac{r_{2b}+r_{2a}-R\cos\theta_2}{R(1-\cos\theta_2)}\right]^{Z/\beta_2}, \tag{5}$$

$$\chi_{1a}^{(3)}=\left(\frac{\beta_2 r_{1a}}{\beta_2 r_{1a}-\beta_1 r_{2a}}\right)^{1/\beta_1} \tag{6}$$
$$\times\left[\frac{(\beta_2 r_{1a}-\beta_1 r_{2a})(\beta_{12}+\beta_1-\beta_2\cos\theta_{12})}{\beta_2\beta_{12}r_{12}+\beta_2 r_{1a}(\beta_1-\beta_2\cos\theta_{12})+\beta_2 r_{2a}(\beta_2-\beta_1\cos\theta_{12})}\right]^{1/\beta_{12}},$$
$$\beta_{12}=(\beta_1^2+\beta_2^2-2\beta_1\beta_2\cos\theta_{12})^{1/2},\ r_1\geqslant r_2,\ \beta_1<\beta_2.$$

Here θ_1 and θ_2 are the angles the vectors $\mathbf{r}_{1a}$ and $\mathbf{r}_{2a}$ make with $\mathbf{R}=\mathbf{R}_b-\mathbf{R}_a$; θ_{12} is the angle between $\mathbf{r}_{1a}$ and $\mathbf{r}_{2a}$. The functions $\chi_{1a}^{(1),(2)}$ take the influence of the Coulomb field of the ion into account. The function $\chi_{1a}^{(3)}$ takes the interelectron interaction into account, and describes the two-electron asymptotic behavior of the isolated atom in the region $r_{1a}\gtrsim r_{2a}\gg 1$. The expansion of this function in powers of $r_2/r_1<1$ is easily obtained by substituting into Eq. (3) the well-known expansion of r_{12}^{-1} in terms of the Legendre polynomials. Then solving this equation, and setting $\chi(\xi=\eta)=1$, we obtain

$$\chi_{1a}^{(3)}=\exp\Big[-\frac{1}{\beta_1}\sum_{k=2}^{\infty}\frac{1}{k}\Big(\frac{r_{2a}}{r_{1a}}\Big)^{k}\sum_{n=1}^{k-1}\Big(\frac{\beta_1}{\beta_2}\Big)^{k-n}P_n(\cos\theta_{12})\Big], \qquad (7)$$
$$r_{1a}\geqslant r_{2a},\ \beta_1<\beta_2.$$

The first term of the expansion of this function in powers of r_2/r_1 describes the polarizing influence of the removed electron 1 on the electron 2 left behind. The expansions of the functions (7) and (6) naturally coincide.

It is well known that the two-electron wave function of the states with zero total momentum depends only on the three variables r_1, r_2, and θ_{12} (or r_1, r_2, and r_{12}). The approximate equation (3) is valid for states with any momenta of the individual electrons and any total momenta. Nevertheless, according to (6), the function χ depends only on the three variables indicated above.

The method used allowed the determination of the dominant term of the expansion of the wave function in powers of r_1^{-1} and r_2^{-1}. The standard one-electron asymptotic form (2) is an expansion in powers of $(r_</r_>)$. To go over to the two-electron from the one-electron asymptotic form, it is necessary to sum the series (7), which is actually done here by method of the papers[8-10].

The function χ depends on the chosen form of the exponential factor, which has the form (2) when $|\mathbf{r}_1+\mathbf{r}_2|\gg 1$ and $r_{2a}<r_{1a}$. Consequently, χ is defined only for this region, outside of which it has singularities. If $r_{2a}>r_{1a}$, then the component ψ_2 becomes dominant in the atomic function.

The approximation used for the determination of $\chi^{(3)}$ is also inapplicable for $r_2\to r_1$, since we cannot discard here the second derivatives because of the strong interelectron interaction. Let us expand the function ψ_{1a} for $r_{1a}\to r_{2a}$ in the region $r\sim R\gg r_{12}\gg 1$ (here $2r=r_{1a}+r_{2a}$ is the coordinate of the center of gravity). Expanding the function (6), we obtain

$$\psi_{1a}\approx B\Phi(r;\ r_{1a}=r_{2a})\,e^{-(\beta_1+\beta_2)r}f_1(\mu)f_2(\nu),\quad f_1\underset{\mu\gg 1}{\longrightarrow}\mu^{1/(\beta_2-\beta_1)}e^{(\beta_2-\beta_1)\mu/4},$$
$$\Phi=\chi_{1a}^{(1)}(r_{1a})\chi_{1a}^{(2)}(r_{2a})\,r_{2a}^{z/\beta_2-1}\,r_{1a}^{(z-1)/\beta_1-1}\,r^{-1/(\beta_2-\beta_1)},\quad f_2\underset{\nu\gg 1}{\longrightarrow}e^{-(\beta_2-\beta_1)\nu/4},$$
$$\mu\equiv r_{12}+\mathbf{nr}_{12},\quad \nu\equiv r_{12}-\mathbf{nr}_{12},\quad \mathbf{n}\equiv\mathbf{r}/r, \qquad (8)$$
$$B=2^{1/(\beta_1-\beta_2)}a_1a_2\Big(\frac{\beta_2}{\beta_2-\beta_1}\Big)^{1/\beta_1+1/(\beta_2-\beta_1)},\quad r\sim R\gg r_{12}\gg 1.$$

For the region $r_{12}\ll R$, let us introduce in Eq. (1) the coordinates $\mathbf{r}_{12}$ and $\mathbf{r}$. Retaining in this region the dependence of the wave function on the position of the center of gravity in the form as written in the formula (8), we obtain an equation for only the relative motion:

$$\Big[-\Delta_{12}+\frac{1}{r_{12}}+\frac{(\beta_2-\beta_1)^2}{4}\Big]\psi_{1a}=0 \qquad (9)$$

with the boundary conditions (8). It can be seen after this that the problem of the determination of the wave function in the region of relatively close disposition of the electrons is entirely analogous to the problem of the continuation of the one-electron functions $\chi^{(1),(2)}$ into the vicinity of the nucleus of the ion.[3] Separating the variables in (9) in parabolic coordinates, μ and ν,[10] and retaining for f_2 the asymptotic dependence (8), we find for $\nu\sim 1$ the function f_1 which satisfies the boundary condition (8) and which is finite at $r_{12}=0$[5]:

$$f_1(\mu)=\Big(\frac{\beta_2-\beta_1}{2}\Big)^{1/(\beta_1-\beta_2)}\Gamma\Big(1+\frac{1}{\beta_2-\beta_1}\Big)e^{(\beta_2-\beta_1)\mu/4}F\Big(\frac{1}{\beta_1-\beta_2};\,1;\,(\beta_1-\beta_2)\frac{\mu}{2}\Big). \qquad (10)$$

Here F is the confluent hypergeometric function.[10]

Let us write the complete function in the form

$$\psi_{1a}=\psi_{1a}^{(0)}\chi_{1a}^{(1)}\chi_{1a}^{(2)}\chi_{1a}^{(3)},$$
$$\chi_{1a}^{(3)}\approx Ar^{-1/(\beta_2-\beta_1)}F\Big(\frac{1}{\beta_1-\beta_2};\,1;\,\frac{\beta_1-\beta_2}{2}(r_{12}+\mathbf{nr}_{12})\Big),\quad r_{12}\ll r, \qquad (11)$$
$$A=\beta_2^{1/\beta_1+1/(\beta_2-\beta_1)}(\beta_2-\beta_1)^{-2/(\beta_2-\beta_1)}\Gamma\Big(1+\frac{1}{\beta_2-\beta_1}\Big).$$

In Eq. (3) all the angles enter only as parameters. Therefore, the value of χ at any point in configuration space depends on the values of this function on the radial lines r_{1a} and r_{2a}. Consequently, in the region $r_{2a}>r_{1a}$ and $\theta_{12}=0$ the expression (6) is not valid, since we cannot reach this region from the region $r_{2a}<r_{1a}$ and $\theta_{12}=0$ (where the boundary conditions are prescribed) along a path bypassing the strong electron-electron interaction region, where the approximation (3) is invalid. The function (11) accomplishes the continuation of the function (6) into this "shadow" region.

For what follows it is necessary to write out the value of the function $\chi^{(3)}$ for the $\theta_{12}=0$ case, when both of the electrons are located on the same straight line (on the internuclear axis, for example):

$$\chi_{1a}^{(3)}=\beta_2^{1/\beta_1+1/(\beta_2-\beta_1)}\,r_{1a}^{1/\beta_1}(r_{1a}-r_{2a})^{1/(\beta_2-\beta_1)}(\beta_2r_{1a}-\beta_1r_{2a})^{-1/\beta_1-1/(\beta_2-\beta_1)},$$
$$r_{1a}\gtrsim r_{2a}\sim(r_{1a}-r_{2a}),$$
$$\chi_{1a}^{(3)}=Ar^{-1/(\beta_2-\beta_1)}F\Big(\frac{1}{\beta_1-\beta_2};\,1;\,(\beta_1-\beta_2)(r_{1a}-r_{2a})\Big),\quad 0<(r_{1a}-r_{2a})\ll r, \qquad (12)$$
$$\chi_{1a}^{(3)}=A\cdot 2^{1/(\beta_2-\beta_1)}(r_{1a}+r_{2a})^{-1/(\beta_2-\beta_1)},\quad r_{2a}>r_{1a}.$$

Here we have taken into account the fact that for $\theta_{12}=0$ and $r_{2a}>r_{1a}$ we have $r_{12}+\mathbf{n}\cdot\mathbf{r}_{12}=0$ and $F=1$. It can be seen that the interelectron interaction significantly changes the wave function for $r_{12}\sim r$ after passing through the region $r_{12}\ll r$.

The functions $\chi^{(1),(2)}$, which take the influence of the field of the ion into account, diverge when the electrons reach the vicinity of the ion. For these configurations Eq. (3) is inapplicable. The continuation of the functions $\chi^{(1),(2)}$ into the vicinity of the ion has been carried out in[5-7]. Using the results of these papers, let us write the wave function for the configuration in which the electrons have separated on different nuclei in the form

$$\psi_{1a}\approx D(R)\varphi_{0a}(r_{2a})e^{-\beta_1(\tilde{\xi}+\tilde{\eta})/2}F\left(1-\frac{Z}{\beta_1};\,1;\,\beta_1\tilde{\eta}\right),\quad r_{2a}\sim r_{1b}\sim 1. \tag{13}$$

$$\varphi_{0a}=\frac{Z^{3/2}}{\sqrt{\pi}}e^{-Zr_{2a}},\quad D(R)=a_1\Gamma\left(1-\frac{Z}{\beta_1}\right)\left(\frac{2\beta_1 R}{e}\right)^{Z/\beta_1}R^{Z/\beta_1-1}e^{-\beta_1 R},$$

$$\tilde{\xi}=r_{1b}+\mathbf{n}_R\mathbf{r}_{1b},\quad \tilde{\eta}=r_{1b}-\mathbf{n}_R\mathbf{r}_{1b}.$$

Here $\tilde{\xi}$ and $\tilde{\eta}$ are the parabolic coordinates of one electron with the center at the nucleus of the ion b and φ_{0a} is the wave function of the ground state of the residual ion a, after the departure of the electron 1 to the nucleus b. The expression for the function ψ_2 is obtained from ψ_1 by interchanging the electrons.

It is very important for what follows to indicate the Hamiltonian of which the function (13) is an eigenfunction. As can be seen from the method of continuation of the functions $\chi^{(1),(2)}$ into the vicinity of the nucleus of the ion, [5] the complete wave function ψ_{1a} is a solution to the Schrödinger equation for the isolated detached-electron + ion system without any allowance for the interaction of the system with the nucleus a and the remaining electron. Therefore, (13) is an eigenfunction of the Hamiltonian

$$H_0=-\frac{\Delta_1}{2}-\frac{Z}{r_{1b}}-\frac{\Delta_2}{2}-\frac{Z}{r_{2a}}. \tag{14}$$

The function ψ_{2b} for this configuration is also an eigenfunction of the Hamiltonian (14). Therefore, these functions are orthogonal to each other as functions of different (though degenerate) states:

$$\int\psi_{1a}\psi_{2b}\,d^3r_1\,d^3r_2\cong\left|\int\varphi_0(r_{1b})e^{-\beta_1(\tilde{\xi}+\tilde{\eta})/2}F\left(1-\frac{Z}{\beta_1};\,1;\,\beta_1\tilde{\eta}\right)d^3r_1\right|^2=0. \tag{15}$$

This result can easily be obtained by directly evaluating the integral involving the confluent hypergeometric function. [10]

THE SPLITTING OF THE TERMS

Let us use for the computation of the term splitting the definition

$$E_u-E_g=\int(\psi_u H\psi_u-\psi_g H\psi_g)\,d^3r_1\,d^3r_2. \tag{16}$$

The integration here is performed over the entire two-electron configuration space. Let us write this formula in terms of the atomic functions:

$$E_u-E_g=\Delta E_1+\Delta E_2,$$
$$\Delta E_1=-2\int(\psi_{1a}H\psi_{2b}+\psi_{2a}H\psi_{1b})\,d^3r_1\,d^3r_2\sim e^{-2\beta_1 R}, \tag{17}$$
$$\Delta E_2=-2\int(\psi_{1a}H\psi_{1b}+\psi_{2a}H\psi_{2b})\,d^3r_1\,d^3r_2\sim e^{-(\beta_1+\beta_2)R}.$$

The term ΔE_1 is the contribution of the crossover transitions: an electron of the outer orbit of the atom a crosses over to an inner orbit of the atom b, and vice versa. The term ΔE_2 is the contribution of the parallel transitions: transitions from an outer to an outer and from an inner to an inner orbit.

Let us first compute ΔE_1. The integrand here is greatest when the electrons separate on different nuclei. It decreases exponentially when even one electron moves away from its nucleus. In this region we have, according to (14), that

$$H\psi_b=\left[E_0(R)+\frac{W}{R^3}\right]\psi_b, \tag{18}$$

$$W=\mathbf{r}_{1b}\mathbf{r}_{2a}-3(\mathbf{n}_R\mathbf{r}_{1b})(\mathbf{n}_R\mathbf{r}_{2a}). \tag{19}$$

Substituting (18) into (17), and using the orthogonality of the functions, noted in the preceding section, we obtain

$$\Delta E_1=-\frac{4}{R^3}\int\psi_{1a}W\psi_{2b}\,d^3r_1\,d^3r_2. \tag{20}$$

Substituting into this matrix element the expression for the two-electron atomic functions in the form of a product of the one-electron functions (13), we obtain

$$\Delta E_1=\frac{8D^2(R)}{R^3}\left|\int\varphi_0 e^{-\beta_1(\tilde{\xi}+\tilde{\eta})/2}(\mathbf{n}\mathbf{r}_{1b})F\left(1-\frac{Z}{\beta_1};\,1;\,\beta_1\tilde{\eta}\right)d^3r_1\right|^2. \tag{21}$$

It can be seen from this that the contribution to the splitting results from the superposition of the two transitions, which are inelastic for each separate electron. One of the electrons moves away from the atom to the foreign nucleus. After this the electrons interact and, exchanging energy, go over to the new nucleus, each into a different orbit: the energy of the electron detached from the atom a decreases, and gets into an inner orbit of the atom b, the excess energy being transferred to the second electron, which from an inner orbit of the atom b goes over into the outer orbit of the atom b.

Evaluating the integrals in (21) (in parabolic coordinates) with the aid of table integrals of the confluent hypergeometric function, [10] we obtain

$$\Delta E_1=B_1R^{(4Z-2)/\beta_1-3}e^{-2\beta_1 R}, \tag{22}$$

$$B_1=\frac{a_1^2\Gamma^2(1-Z/\beta_1)}{2\beta_1^5}\left(\frac{2\beta_1}{e}\right)^{2Z/\beta_1}\left(\frac{2\sqrt{Z\beta_1}}{Z+\beta_1}\right)^{10}\left(\frac{Z-\beta_1}{Z+\beta_1}\right)^{2Z/\beta_1-4}. \tag{23}$$

For the pair H^++H^-, it is necessary to take into account in this formula the change in the first ionization potential because of the Coulomb attraction of the ions, i.e., to set

$$\beta_1=(\beta_{10}^2+2/R)^{1/2},\ \beta_{10}=0.235\ \text{for}\ H^++H^-. \tag{24}$$

According to the formula (23), the coefficient B_1 becomes infinite under the conditions when, because of the interaction of the atoms, a one-electron resonance is realized, and the one-electron charge exchange becomes the most important. Under these conditions the method used here to construct the wave function ceases to be correct, since the atomic function near the foreign nucleus becomes of the order of unity.

The expression (22) is the contribution to the splitting from the principal configuration, in which the transition-inducing interaction between the electrons is weak ($\sim R^{-3}$). It is necessary, therefore, to compute ΔE_2, i.e., the contribution from the symmetric transitions, which are determined by the configuration in which both electrons move away from the atoms far into the subbarrier region.

We compute $E_u - E_g$, using the Komarov–Yanev relation[3]:

$$E_u - E_g = 2\int_{\Omega} (\psi_g H \psi_u - \psi_u H \psi_g)\, d\tau_1\, d\tau_2. \tag{25}$$

The integration domain Ω is determined here by the condition[3] $x_2 \leq -x_1$, where x_1 and x_2 are the electron coordinates along the internuclear axis, measured from the center of the system, i.e., from the point halfway between the nuclei. The interchange of the electrons does not take any point of this space beyond its boundary. Therefore, we can use the exchange symmetry and transform (25) into the form

$$E_u - E_g = 2\int d\tau_1 \oint [\psi_u \nabla_2 \psi_g - \psi_g \nabla_2 \psi_u]\, dS_\Omega, \quad S_\Omega \to x_2 = -x_1 \tag{26}$$

where S_Ω is the hyperplane $x_2 = -x_1$.

Let us substitute the atomic functions into this expression, differentiating only the exponential functions. After this we obtain

$$\Delta E_2 = 4(\beta_1+\beta_2)\int_0^{R/2} dx_1 \oint dS_1 \oint \psi_{1a}\psi_{1b}\, dS_2, \tag{27}$$

$$\Delta E_1 = 2\int d\tau_1 \oint_{x_2=-x_1} [\psi_{1a}\nabla_2\psi_{2b} - \psi_{2b}\nabla_2\psi_{1a}]\, dS_2. \tag{28}$$

The result of the evaluation of the integral (27) with the use of the wave functions (2), (4)–(6), and (12) can be written in the form

$$\Delta E_2 = B_2 R^p e^{-(\beta_1+\beta_2)R}, \quad p = 2Z\left(\frac{1}{\beta_1}+\frac{1}{\beta_2}\right) - \frac{2}{\beta_1} - \frac{1}{\beta_2-\beta_1} - 1, \tag{29}$$

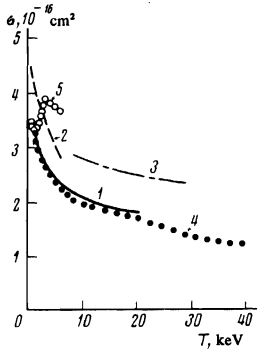
$$B_2 = \frac{a_1^2 a_2^2}{2}\left(\frac{\beta_1+\beta_2}{\beta_1\beta_2}\right)(\beta_2-\beta_1)^{-2/(\beta_2-\beta_1)} e^{-Z(1/\beta_1+1/\beta_2)} \frac{\Gamma(1-1/\beta_1)\Gamma^2(1+1/(\beta_2-\beta_1))}{\Gamma(2-1/\beta_1+1/(\beta_2-\beta_1))}$$
$$\times {}_2F_1\left(\frac{1}{\beta_1}+\frac{1}{\beta_2-\beta_1};\ 1-\frac{1}{\beta_1};\ 2-\frac{1}{\beta_1}+\frac{1}{\beta_2-\beta_1};\ \frac{\beta_2+\beta_1}{2\beta_2}\right). \tag{30}$$

Here ${}_2F_1$ is the complete hypergeometric function.

It is shown in the Appendix to this paper that the integral (28) vanishes in the approximation under consideration. This was to be expected, since the expression (28) is of the order of $|\psi_{1a}(r_{1b}\sim 1;\ r_{2a}\sim 1)|^2$, whereas the exact result (22) is smaller by a factor of R^3. This means that, computing ΔE_1 with the aid of (28), we obtain a nonzero result only after determining the atomic wave function to within quantities $\sim R^{-3}$ relative to its principal asymptotic value computed here.

Thus, the physical ideas developed in[3] describe symmetric transitions, each consisting of two elastic transitions for each individual electron.

The constant B_2 diverges, according to (30), as $\beta_1 \to 1$, which is due to the divergence of the expressions (5) for the "field" functions $\chi^{(1),(2)}$. The fact that this constant diverges implies that the integral (27) is, for $\beta_1 \to 1$, given by the region $x_1 \approx R/2$. To this corresponds the configuration in which the electrons separate on different nuclei, but, in contrast to the crossover transitions, the electron removed from each atom is in an inner orbit. For this case, special investigations of the wave function of the outer electron in the absence of an inner electron are necessary.



Dependence of the cross section for the resonance two-electron charge exchange $^3He^{++} + {}^3He^0 = {}^3He^0 + {}^3He^{++}$ on the energy of the impinging ions. Theory: 1) present work; 2) according to[2]; 3) according to[11]. Experiment: 4) according to[12]; 5) according to[13].

As can be seen from the formulas (17), (22), and (29), the term of the symmetric state g lies deeper than the antisymmetric term u. This is explained by the presence in the wave function ψ_u of an additional nodal hyperplane when the electrons are located in planes perpendicular to the internuclear axis and symmetric with respect to the central plane.

CHARGE EXCHANGE CROSS SECTION FOR HELIUM

For the interaction of a helium atom with an α-particle, the term splitting turns out, according to the formulas (22), (23) and (29), (30), to be equal to

$$\Delta E = \Delta E_1 + \Delta E_2;\ \beta_1 = 1.344;\ \beta_2 = 2;\ a = 2.95;$$
$$\Delta E_1 = 52.7\, R^{-0.537} e^{-2.688R};\ \Delta E_2 = 35.4\, R^{0.962} e^{-3.344R} \text{ for } He + He^{++}. \tag{31}$$

The cross section for the charge exchange $He + He^{++} \to He^{++} + He$ was computed with the aid of the relation[4]

$$\sigma = \frac{\pi\rho^2}{2},\ \left(\frac{\pi\rho}{2}\right)^{1/2}\left[\frac{\Delta E_1}{(2\beta_1)^{1/2}} + \frac{\Delta E_2}{(\beta_1+\beta_2)^{1/2}}\right]_{R=\rho} = 0.28v, \tag{32}$$

where v is the relative collision velocity. The results of the computations are presented in the figure. In the operating region of interatomic distances, the contribution, ΔE_2, from the symmetric transitions to the splitting is 2–2.5 times smaller than the contribution, ΔE_1, of the crossover transitions. The coincidence of the cross section computed here with the cross section obtained in[14] is accidental, since the variational calculations[14,15] give an incorrect sign for the splitting $E_u - E_g$ (the even term g turns out to be higher than the odd term u). The splittings are close in absolute value and many times smaller than the splitting obtained in[3].

The method of unperturbed atomic functions guarantees, as is well known, a considerably high accuracy in the computation of molecular energies. Therefore, the calculation in[2] reproduces well the cross section for velocities close to 10^6 cm/sec, when the operating distances are the internuclear distances, which are close to the atomic dimension.

It is necessary to note that because of the very sharp

decrease of the splitting of the terms as the atoms move away from each other, the cross section is only slightly sensitive to the absolute value of this splitting.

In conclusion, the author expresses his profound gratitude to O. B. Firsov for a discussion of the questions touched upon here.

APPENDIX

The integral (28) is determined by the configuration in which the wave functions have parabolic symmetry. It is therefore more convenient to calculate ΔE_1 on the basis of a relation similar to the relation (25), but with the integration domain Ω defined in elliptic coordinates, $\bar{\mu}$ and $\bar{\nu}$, which, near each of the nuclei, go over into parabolic coordinates. Let us define Ω in (25) by the condition $\bar{\nu}_2 \leqslant -\bar{\nu}_1$, after which the surface S_Ω becomes a hyperboloid of revolution. In the configuration of interest to us the condition $\bar{\nu}_2 = -\bar{\nu}_1$ goes over, in the parabolic coefficients $\bar{\xi}$ and $\bar{\eta}$ near the nuclei, into the condition $\bar{\eta}_1^{(a)} = \bar{\eta}_2^{(b)}$. Here $\bar{\xi}^{(a)}$, $\bar{\eta}^{(a)}$ and $\bar{\xi}^{(b)}$, $\bar{\eta}^{(b)}$ are parabolic coordinates constructed respectively at the the nuclei a and b (the azimuthal axes of quantization at the different nuclei are oriented in different directions). Using the relation $\nabla f dS = \bar{\eta}(\partial f/\partial\eta) d\bar{\xi} d\varphi$ for the parabolic coordinates and the function (13), let us reduce (28) to the form

$$\Delta E_1 \sim \int_0^\infty e^{-2\lambda t} t(1+\lambda t)\left[\left(\frac{1}{\beta_1}-\frac{1}{Z}\right) F^2(\alpha; 1; \beta_1 t) + \frac{1}{\beta_1 Z}\frac{\partial}{\partial t} F^2(\alpha; 1; \beta_1 t)\right] dt,$$
$$\lambda = (Z+\beta_1)/2;\ \alpha = 1 - Z/\beta_1. \qquad \text{(A.1)}$$

Let us integrate once by parts the term containing the derivative of the square of the confluent hypergeometric function. After this, using the equality

$$\int_0^\infty e^{-\lambda t} t F^2(\alpha; 1; \beta_1 t)\, dt = -\frac{\partial}{\partial\lambda}\int_0^\infty e^{-\lambda t} F^2(\alpha; 1; \beta_1 t)\, dt,$$

we obtain with the aid of table integrals the expression

$$\Delta E_1 \sim \left[x(x+1)\frac{\partial^2}{\partial x^2} - (x-1)\frac{\partial}{\partial x} - 1\right](x+1)^{2\alpha-1} x^{-2\alpha} F(\alpha; \alpha; 1; x^{-2})\big|_{\alpha=1-x}$$
$$x = Z/\beta_1 > 1. \qquad \text{(A.2)}$$

Let us go over to the variable $y = x^{-2}$ and reduce (A.2) to the form

$$\Delta E_1 = \frac{4y^{1/2}(\sqrt{y}+1)^{1-2/\sqrt{y}}}{1-\sqrt{y}}\left[y(1-y)\frac{d^2F}{dy^2} + (1-3y+2\sqrt{y})\frac{dF}{dy} - \frac{(\sqrt{y}-1)^2}{y}F\right]\Bigg|_{\alpha=1-1/\sqrt{y}} = 0;$$
$$y = 1/x^2 = (\beta_1/Z)^2. \qquad \text{(A.3)}$$

The identical vanishing, when $y < 1$, of this expression is due to that differential equation which is satisfied by the complete hypergeometric function $F(1-1/\sqrt{y};\ 1-1/\sqrt{y};\ 1;\ y)$.[10]

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