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RESONANT CHARGE EXCHANGE INVOLVING HIGHLY EXCITED ATOMS

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Transition of a classical electron between two Coulomb centers is analyzed on the basis of computer simulations. The contribution to the electron transfer cross section from a tunnel electron transition is evaluated with the strong mixing of highly excited electron states due to motion of Coulomb centers taken into account. The rate of transition of a highly excited electron between two Coulomb cores with a fixed separation is evaluated together with the cross section of resonant charge exchange in slow collisions. Typical times of change of the electron momentum as a result of electron motion in the field of two Coulomb centers are determined.

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1. INTRODUCTION

The resonant charge exchange process is of importance for transport processes in nonequilibrium weakly ionized gases, in particular, for cosmic plasmas where, along with charged atomic particles, excited atoms are present with a remarkable concentration (see, e.g., [1]). The problem of resonant charge exchange with a transition of a highly excited electron is studied starting from Sena's papers [2, 3]. He has shown that the transition of a classical electron has an over-barrier character, and the maximum cross section of the resonant charge exchange in this case is

$$\sigma_0 = \pi R_0^2/2,$$

where R_0 is the distance between colliding particles when the barrier separating the fields of the first and second cores disappears. This occurs in slow collisions when, at distances below R_0, the probability of the electron location near each core after the collision is $1/2$. At an arbitrary collision velocity v, the cross section σ of the resonant charge exchange can be represented as [2]

$$\sigma = \sigma_0 f(v/v_0),$$

where the typical electron velocity v_0 follows from the relation

$$m_e v_0^2 = \frac{e^2}{R_0}$$

(m_e is the electron mass and e is its charge) and the universal function $f(x)$ tends to unity at small x and behaves as $1/x$ at large x.

One can solve this problem more correctly and find the electron transfer cross section by computer simulations. Numerical solutions of the problem of transition of a classical electron between two Coulomb cores as a result of collision of a highly excited atom with an ion is the subject of this paper. Along with the cross section of resonant charge exchange, computer simulation of this problem allows analyzing other parameters of electron evolution including the change in the electron angular momentum and its binding energy. We analyze collision of a Rydberg atom with an ion by computer simulation of an excited classical electron.

2. CHARACTER OF ELECTRON MOTION IN THE COURSE OF CHARGE EXCHANGE

The classical transition of an excited electron between two Coulomb centers proceeds when the distance R between colliding particles is less than the critical

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distance R_0 at which the barrier separating the fields of ions disappears. Because the barrier is symmetric with respect to the ion positions, its maximum is at the middle point between the ions. The barrier is decreased compared to the continuum-spectrum boundary due to the electron–ion interactions, equal to $4e^2/R$ at a distance R between the nuclei (we take the ion charge to be equal to the electron charge e). But we have different results for the critical distance depending on the character of change of the ion fields [4]. Indeed, in the adiabatic limit, the electron potential energy is given by

$$U = -\frac{1}{r_1} - \frac{1}{r_2},$$

where r_1 and r_2 are the electron distances from the corresponding nucleus, R is the distance between the nuclei, and we use the atomic units $e^2 = m_e = \hbar = 1$. At large distances between the nuclei, this field is split between two regions of action of each nucleus, and these regions are separated by a barrier. This barrier disappears at the distance R_0 between the nuclei determined by the condition

$$U(r_1 = r_2 = R_0/2) = \varepsilon, \tag{1}$$

where ε is the electron energy. In the adiabatic limit, at a distance R between the nuclei, we have

$$\varepsilon = -J - \frac{1}{R}, \tag{2}$$

where

$$J = \gamma^2/2$$

is the atom ionization potential. The barrier vanishes at

$$R_0 = 3/J = 6/\gamma^2.$$

Accordingly, the cross section of resonant charge exchange in this limit, which corresponds to low collision velocities $v \ll \gamma$, is

$$\sigma_{ad} = \frac{\pi R_0^2}{2} = \frac{18\pi}{\gamma^4} = \frac{9\pi}{2J^2}. \tag{3a}$$

In the diabatic limit, the electron energy is $\varepsilon = -J$, and condition (1) implies that

$$R_0 = 4/J.$$

This gives the cross section of barrier disappearance in the diabatic limit as

$$\sigma_{diab} = \frac{\pi R_0^2}{2} = \frac{32\pi}{\gamma^4} = \frac{8\pi}{J^2}, \tag{3b}$$

which corresponds to high collision velocities $v \gg \gamma$. This formula describes the diabatic way of collisions, such that the second ion does not change the electron energy in the field of the first ion in the course of collision. Thus, the adiabatic and diabatic ways in which atomic particles approach each other lead to different cross sections of the electron transfer.

3. COMPUTER SIMULATION OF THE TRANSITION OF A CLASSICAL ELECTRON BETWEEN TWO COULOMB CENTERS

In considering the problem of motion of a classical electron in the field of two moving Coulomb centers, we take the electron momentum to be zero or almost zero. It is then convenient to choose the boundary condition that the electron velocity is zero or almost zero, and the electron distance from the parent Coulomb center is

$$r_0 = e^2/J.$$

In this problem, the electron motion is described by the Newton equations

$$m\frac{d^2x_i}{dt^2} = -\frac{\partial U}{\partial x_i}, \quad x_i \equiv x, y, z,$$

$$U = -\frac{e^2}{r} - \frac{e^2}{|\mathbf{r} - \boldsymbol{\rho} - \mathbf{v}t|}, \tag{4}$$

where

$$r = \sqrt{x^2 + y^2 + z^2}$$

is the distance of the electron from the first Coulomb center (where the electron is located at the beginning), $\boldsymbol{\rho}$ is the impact parameter of collision of two Coulomb centers, and $\mathbf{v}$ is the collision velocity. Under these assumptions, the cores are moving along straight trajectories. Taking the direction of $\boldsymbol{\rho}$ along the x axis and the direction of $\mathbf{v}$ along the y axis, we obtain the set of Newton equations in the form

$$\begin{aligned} \frac{d^2x}{dt^2} &= \frac{x}{r^3} + \frac{x-\rho}{r_2^3}, \\ \frac{d^2y}{dt^2} &= \frac{y}{r^3} + \frac{y+vt}{r_2^3}, \\ \frac{d^2z}{dt^2} &= \frac{z}{r^3} + \frac{z}{r_2^3}, \end{aligned} \tag{5}$$

where

$$r_2 = \sqrt{(x-\rho)^2 + (y-vt)^2 + z^2}$$

is the electron distance from the second atomic core, and we introduce the reduced distance

$$r \to r/r_0, \quad \rho \to \rho/r_0,$$

the reduced velocity

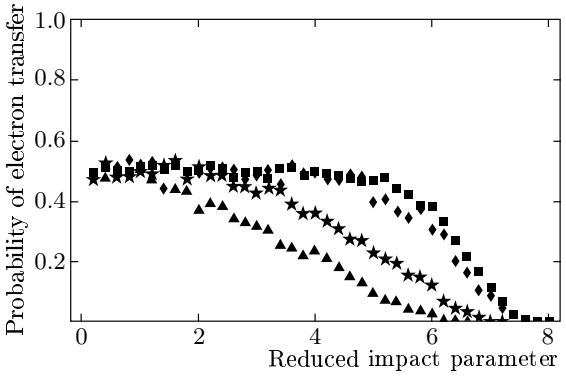

Fig. 1. The probability of electron transfer between two Coulomb centers versus the impact parameter of collision of Coulomb centers at given velocities according to computer simulations. $v = 0.01v_0$ (■), $0.02v_0$ (⧫), $0.05v_0$ (⋆), $0.1v_0$ (▲), $v_0 = e^2\gamma/\hbar$

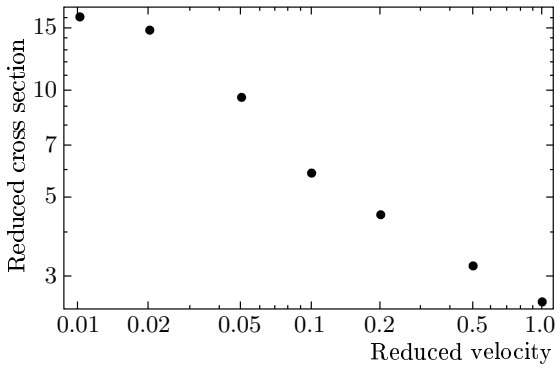

Fig. 2. The reduced cross sections of resonant charge exchange for a highly excited atom, given in units a_0^2/γ^4 (a_0 is the Bohr radius), versus the collision velocity expressed in $e^2\gamma/\hbar$. The cross sections of the over-barrier electron transfer follow from computer simulations for a classical electron in the field of two Coulomb centers

$$v \to v/v_0,$$

and the reduced time

$$t \to t/t_0,$$

where

$$v_0 = \sqrt{2J/m_e}, \quad t_0 = r_0/v_0.$$

Within the computer simulation framework, we solve system (5) of Newton equations under different initial conditions for a given impact parameter of collision, which gives the probability for the electron to transfer to the second core after the collision and the probability to change the momentum and binding energy at a given impact parameter of the collision. From this probability, we find the cross section of resonant charge exchange at the given collision velocities, and dispersions of the electron binding energy and angular momentum. Figure 1 shows the probability $W(\rho, v)$ of the electron transition into the field of another core as a function of the impact parameter of collision at some collision velocities. Each dot results from averaging over 500 initial conditions that correspond to a random electron location on the sphere of the radius $r_0 = e^2/J$ centered at the first Coulomb center, where J is the electron binding energy at the beginning. This boundary condition corresponds to zero electron velocity at the beginning. Figure 2 shows the velocity dependence for the cross section of resonant charge exchange involving a highly excited atom with over-barrier electron transitions taken into account.

Computer simulation of a classical electron in the field of two Coulomb centers exhibits large fluctuations

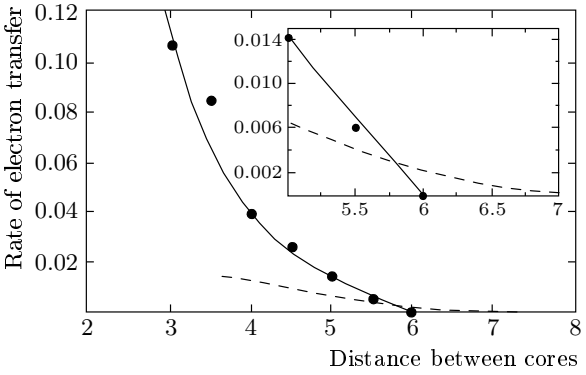

Fig. 3. The rate of electron transfer between two Coulomb centers for a fixed distance between the centers. Dots are the rates of the over-barrier electron transition due to computer simulation, the solid line approximates these results by the dependence $\nu(R) \approx a(R_0^2 - R^2)\exp[b(R_0^2 - R^2)^3]$ in accordance with formula (13), the dashed line gives the rate of the tunnel electron transition in accordance with (25) for $n = 1/\gamma = 4$. The reduced rate is expressed in units $\hbar^3\gamma^3/m_e e^4$ and the reduced distance is given in units a_0/γ^2

of electron parameters at small distances between the cores due to their motion. To eliminate the effect of small distances between the cores on the electron parameters, we formulate this problem differently and, fixing the distance between the cores, determine some electron parameters. We let $\nu(R)$ denote the average rate of electron transition between the cores at a given distance R between the cores, which allows determin-

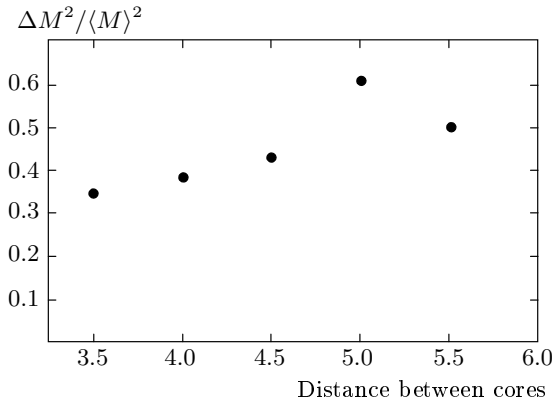

Fig. 4. The relative fluctuation of the electron momentum $\Delta M^2/\langle M^2\rangle$ at a typical time $1/\nu$ of the electron transition between Coulomb centers at a fixed distance R between them according to computer simulations

ing the probability of electron transfer in slow collisions. Figure 3 contains this value for a classical electron, i.e., with over-barrier transitions taken into account. Figure 4 shows the fluctuation of the electron momentum with respect to the initial Coulomb center during a typical transition time $1/\nu$. This demonstrates a remarkable mixing of states of a classical electron in the course of electron transfer.

Based on the rate $\nu(R)$ of the electron transfer between two Coulomb cores, we have the following balance equations for the probabilities $P_1(t)$ and $P_2(t)$ of the electron location at time t in the field of the first and the second core:

$$\begin{aligned} \frac{dP_1}{dt} &= -\nu(P_1 - P_2), \\ \frac{dP_2}{dt} &= -\nu(P_2 - P_1). \end{aligned} \tag{6}$$

The solutions of these equations under the initial conditions

$$P_1(t = -\infty) = 1, \quad P_2(t = -\infty) = 0$$

(with $P_1 + P_2 = 1$) are given by

$$\begin{aligned} P_1(t) &= \frac{1}{2} + \frac{1}{2}\exp\left(-2\int\limits_{-\infty}^{t}\nu(t')\,dt'\right), \\ P_2(t) &= \frac{1}{2} - \frac{1}{2}\exp\left(-2\int\limits_{-\infty}^{t}\nu(t')\,dt'\right). \end{aligned} \tag{7a}$$

If the transition probability after the collision is small, it is given by the formula

$$P_2(\infty) = 1 - P_1(\infty) = \zeta(\rho) = \int\limits_{-\infty}^{\infty}\nu(t)\,dt. \tag{7b}$$

Within the framework of the classical model (we assume free relative motion of nuclei, i.e., $R^2 = \rho^2 + v^2t^2$), it follows from Eq. (7a) that the probability $W(\rho, v)$ of the above-barrier electron transition at a given impact parameter ρ of collision is given by

$$W(\rho, v) = P_2(\infty) = \frac{1}{2} - \frac{1}{2}\exp\left(-\frac{2}{v}\int\limits_{\rho}^{R_0}\nu(R)\frac{RdR}{\sqrt{R^2 - \rho^2}}\right). \tag{8}$$

From this, we find the cross section σ of resonant charge exchange under the assumption of a sharp dependence $\zeta(\rho)$, given by

$$\zeta(\rho) = \zeta(\rho_0)\exp[-\alpha(\rho - \rho_0)]$$

in a narrow range of ρ. Under these conditions, we evaluate the cross section of resonant charge exchange as

$$\sigma = \int\limits_0^{\infty} W(\rho, v)\cdot 2\pi\rho d\rho = \int\limits_0^{\infty}(1 - \exp[-2\zeta(\rho)])\,\pi\rho\,d\rho. \tag{9}$$

Applying the general method in [5, 6] for evaluating the cross section to this expression, we divide integral (9) into two parts,

$$\sigma = \int\limits_0^{\rho_1}(1 - \exp[-2\zeta(\rho)])\,\pi\rho d\rho + \int\limits_{\rho_1}^{\infty}(1 - \exp[-2\zeta(\rho)])\,\pi\rho\,d\rho,$$

and take ρ_1 such that, on the one hand, $\zeta(\rho_1) \gg 1$ and, on the other hand, the exponential dependence

$$\zeta(\rho) = \zeta(\rho_1)\exp[-\alpha(\rho - \rho_1)]$$

near ρ_1 is valid for $\zeta(\rho) \ll 1$. Then the integral for the cross section reduces to the form [5, 7]

$$\sigma = \frac{\pi\rho_1^2}{2} + \pi\rho_1 \int\limits_0^{\zeta_1} (1 - \exp(-2\zeta))\,\frac{d\zeta}{\alpha\zeta} = \\ = \pi\rho_1 \left(\rho_1 + \frac{C + \ln\zeta_1}{\alpha}\right) = \frac{\pi\rho_0^2}{2}, \qquad (10) \\ \zeta(\rho_0) = \frac{e^{-C}}{2} = 0.28,$$

where $\zeta_1 = \zeta(\rho_1)$, $C = 0.577$ is the Euler constant, and we use the expansion for $\zeta_1 \gg 1$. Equation (10) gives an asymptotic expression for the classical cross section of resonant charge exchange.

The classical rate of electron transfer to the field of the other core becomes zero when the barrier separating the cores vanishes, i.e., $\nu(R_0) = 0$. Below, we use computer simulations to find the dependence $\nu(R)$ near R_0, where the electron transfer rate is relatively small, and compare it with the dependence obtained on the basis of a simple and transparent model [8] in the adiabatic and diabatic limits. In this model, the electron transitions between two cores are considered a result of the flux of a classical electron through the cross section in the middle between the nuclei, where the classical electron may be located. This cross section, through which a classical electron can transfer between the cores, is equal to $\pi(R_0^2 - R^2)/4$ at a given distance R between the nuclei, and the electron flux through this cross section is $N_e v_e/4$, where N_e is the average electron density near the separation plane if the electron is located in the field of the first nucleus, and v_e is its velocity in the separation plane. Hence, within the framework of this model, we have

$$\nu(R) = \int\limits_0^{\sqrt{R_0^2 - R^2}} \frac{N_e v_e}{4} \cdot 2\pi b\, db, \qquad (11)$$

where b is the distance from the axis joining the nuclei in the symmetry plane that separates the effects of fields of different cores.

In the classical case, we have $N \sim 1/v_e$, which gives the rate of electron transfer in the case where the hole radius for the classical electron transition between the cores is small as

$$\nu(R) = a(R_0^2 - R^2), \quad a = 1.2 \cdot 10^{-3}. \qquad (12)$$

We find the factor a from the results of computer simulation in the limit of small collision energies, but the range of validity of approximation (12) is narrow. We use the approximation

$$\nu(R) = a(R_0^2 - R^2)\exp\left[b(R_0^2 - R^2)^3\right], \qquad (13)$$

and computer simulation gives $b = 6.2 \cdot 10^{-5}$. From this, we can find the transition probability in accordance with Eq. (8) and the classical cross section of electron transfer in accordance with Eq. (9) if we assume that $W(\rho, v) = 1/2$ for small impact parameters of collisions, where approximation (13) is violated.

We note a similarity law for the transition of a classical electron with respect to the parameter γ (the ionization potential is $J = \gamma^2/2$). The similarity law gives

$$R \sim 1/\gamma^2, \quad v \sim \gamma, \quad \sigma \sim 1/\gamma^4, \quad t \sim 1/\gamma^3, \quad \nu \sim \gamma^3,$$

and this was used in Figs. 1 and 2. Correspondingly, the electron transfer probability can be taken as $W(\rho\gamma^2, v/\gamma)$. We note that the parameter $1/\gamma$ is analogous to the principal quantum number for the hydrogen atom.

We also give the limit expressions for the cross section of resonant charge exchange if this process results from a flux of the classical electron through the classically available cross section that separates the two Coulomb cores [8]. In the limit cases of small and large collision velocities v, this model gives the following expressions for the cross section of electron transfer:

$$\sigma = \begin{cases} \dfrac{18}{\gamma^4}\left[1 - 0.8\left(\dfrac{v}{\gamma}\right)^{2/5}\right], & v \ll \gamma, \\ \dfrac{12}{v\gamma^5}, & v \gg \gamma. \end{cases} \qquad (14)$$

Here, all the parameters are expressed in atomic units.

We note that the analysis of this problem can be based on the traditional classical method [9] using classical trajectories for colliding particles. In particular, this approach was used for calculating the charge exchange in collisions of hydrogen atoms with multicharged ions [10, 11]. In spite of the analogy of this process to the process under consideration, the classical description of the hydrogen atom in the ground state is problematic. This does not allow comparing the results of different processes. The difficulties in the considered problem of collision of a highly excited atom and an ion are related to parameters of the interaction of colliding particles at different distances between them, which are known correctly only at large distances. This fact compels us to construct another scheme of evaluation of the cross section of resonant charge exchange, different from the standard classical

scheme [9]. Indeed, although information about the interaction parameters at low distances between colliding particles is not correct, the average probability of resonant charge exchange at low impact parameters is 1/2. This allows us to determine the cross section of resonant charge exchange in accordance with Eq. (10), because the cross section is determined by large distances between colliding particles, where the electron transfer rate is evaluated correctly.

4. SEMICLASSICAL ELECTRON IN THE FIELDS OF TWO COULOMB CENTERS

We now analyze the electron transfer between two Coulomb centers from another standpoint, considering a highly excited electron as a semiclassical object. If the centers are motionless, we restrict ourselves by the adiabatic limit and determine corrections due to additional interactions of the electron with Coulomb centers. This allows us to find the criterion for the validity of approximation (3) with only the Coulomb interaction of the electron with the second center. The Schrödinger equation for an electron in the field of two Coulomb centers is separated in elliptic coordinates [12, 13], and the electron state is characterized by the elliptic quantum numbers n, n_1, n_2, and m. Ignoring additional interactions, we have the electron energy

$$E_0 = -\frac{1}{2n^2} - \frac{1}{R}. \tag{15}$$

Formula (15) is similar to formula (3) if the principal quantum number is $n = 1/\gamma$, and the ionization potential of a highly excited atom is $J = 1/2n^2$. Equation (15) holds at large distances between the Coulomb centers when the interaction of the electron with the second Coulomb center is reduced to their Coulomb interaction. We represent the electron energy at large distances R between the centers in the form of an expansion over a small parameter of the order of $1/R$, and then represent the electron energy as

$$E = E_0 + \Delta E. \tag{16}$$

We take $n \gg 1$ for a highly excited electron, assume the electron momentum projection on the molecular axis to be $m = 0$ in accordance with the above evaluations, and assume $n_1 \gg n_2$ for simplicity. Under these conditions, we have [14]

$$\Delta E = -\frac{5n^4}{R^3} + \frac{7n^6}{R^4}. \tag{17}$$

We see that the small parameter of this expansion is proportional to n^2/R.

From this, we can find that the expansion is valid at some distances between the Coulomb centers below $R_0 = 6n^2$, at which the barrier that separates the fields of two Coulomb centers acting on the electron vanishes. Although formally applying the above expansion at distances $R < R_0$ is not valid, we can use this expansion in some range of R where $E_0 \gg \Delta E$. Indeed, at $R = R_0 = 6n^2$, the ratio of terms in Eq. (16) is

$$\frac{|\Delta E|}{|E_0|} = 0.027.$$

For $R = 4n^2$, when a classical electron can freely transfer between the two centers, we have

$$\frac{|\Delta E|}{|E_0|} = 0.034.$$

For $R = 3n^2$, the above formula gives

$$\frac{|\Delta E|}{|E_0|} = 0.059,$$

and for $R_0 = 2n^2$, we obtain the ratio of terms in Eq. (16) as

$$\frac{|\Delta E|}{|E_0|} = 0.19.$$

Thus, we use the Coulomb interaction only for an excited electron that transfers between fields of two cores, and this interaction is described by Eqs. (3) and (15) for the electron energy. Of course, this holds for not small distances between the Coulomb centers, but these formulas can be used in a range of distances between the Coulomb centers where a classical electron can transfer between the Coulomb centers freely. One can be sure that the above approximation for a classical electron is valid for distances between the nuclei $R > 2n^2$.

Another problem is the number of eigenstates that are present in a real state of a highly excited electron transferred between two colliding Coulomb centers. We first suppose that the electron is in a state with quantum numbers n, l, m. Assuming the conservation of the electron energy, i.e., of the principal quantum number n, we then find the rate of electron transition to neighboring states of the electron momentum. In particular, the cross section of collision of a highly excited atom with an ion for the transition $l \to l \pm 1$, averaged over the electron momentum projection on the impact parameter direction, is [4]

$$\sigma_{l\to l\pm1} = 6\pi \frac{n^4}{v_a^2} \frac{l+1}{2l+1} \ln \frac{v_a^2 n}{\Delta_l}, \tag{18}$$

where $\Delta_l \ll 1$ is the quantum defect for this state and v_a is the collision velocity. We see that this cross section

significantly exceeds the cross section of classical electron transfer, i.e., such transitions proceed effectively in the range of distances $R \sim R_0$. This means that the states of different electron momenta are effectively mixed in the field of a given Coulomb center in the course of collision. We note that during this collision, the electron momentum projection onto the direction perpendicular to the motion plane is conserved just as in the classical case. The principal quantum number is conserved essentially due to the adiabatic character of the electron energy variation in slow collisions (excluding small distances between centers where the electron reflects many times from the moving cores). But other quantum numbers are mixed for a highly excited electron because of the interaction with the moving Coulomb centers. Therefore, a real electron state at a given time is a mixture of many eigenstates of the electron located in the field of two Coulomb centers, and using elliptic and spherical electron coordinates is equivalent to the quantum analysis of this problem. Below, we therefore use a simpler case of spherical coordinates for a transferring electron.

We note one more peculiarity of this resonant charge exchange process that follows from the above analysis. Because the electron transfer cross section is less than the cross section (18) of transition between states with neighboring electron momenta, the splitting of excited levels can be neglected at collision velocities when the Massey parameter is small. This is true for not small collision velocities

$$v_a \gg \delta_l/n^2,$$

where δ_l is the quantum defect for a given excited state.

5. TRANSITION OF A SEMICLASSICAL ELECTRON

A certain contribution to the cross section of the electron transfer process involving a highly excited atom follows from the distances where the classical electron transition is impossible. Therefore, we now consider the problem of electron transfer from another standpoint, based on the principles of quantum mechanics. Taking the transferring electron in the s-state in the Coulomb field of two slowly moving cores, we assume that the exchange interaction is small in comparison with the energy of transition to a neighboring electron state. We can then neglect the transitions to other electron states, and the resonant charge exchange results from the interference of even and odd electron states. Indeed, in this case, the electron wave function is

$$\Psi = \frac{1}{\sqrt{2}}\psi_g \exp\left(-i\int\limits_{-\infty}^{t}\varepsilon_g dt'\right) + \frac{1}{\sqrt{2}}\psi_u \exp\left(-i\int\limits_{-\infty}^{t}\varepsilon_u dt'\right), \quad (19)$$

where ψ_g and ψ_u are the even and odd electron wave functions and ε_g and ε_u are the energies of these states. These values depend on the distance R between the nuclei as a parameter, and the state symmetry refers to the electron reflection with respect to the plane that passes through the middle of the axis joining the nuclei and bisects it. From this, we obtain the probability of charge exchange at a given impact parameter of collision as [15]

$$W = |\langle\psi_2 \mid \Psi(t=\infty)\rangle|^2 = \sin^2\int\limits_{-\infty}^{\infty}\frac{\Delta}{2}dt, \quad (20)$$

where the exchange interaction potential is

$$\Delta = \varepsilon_g - \varepsilon_u.$$

It follows that the rate of the electron transition between two cores is now given by

$$\nu = \frac{\Delta}{2}, \quad (21)$$

where we use the atomic units, as previously.

We note that in the classical case, transition probability (7) averaged over initial electron positions varies monotonically from 0 to 1/2; this is in contrast to this case of one electron state in a highly excited atom, where the transition probability oscillates between 0 and 1. Indeed, we consider the case where the initial electron state includes a mixture of many eigenstates. Taking the electron wave function in the atom in the form

$$\Psi = \sum_i c_j\psi_j$$

and assuming the absence of transitions between these states, we obtain the transition probability as

$$W(\rho) = \sum_i |c_j|^2 \sin^2\int\limits_{-\infty}^{\infty}\frac{\Delta_j}{2}dt = \sum_i |c_j|^2 \sin^2\zeta_j(\rho), \quad (22)$$

where the parameters $\Delta_j(R)$ and

$$\zeta_j(\rho) = \frac{1}{2}\int\limits_{-\infty}^{\infty} \Delta_j dt$$

correspond to a given electron state. It follows that averaging over states leads to a monotonic variation of the transition probability from 0 to 1/2, similarly to Eq. (7) for a classical electron.

Nevertheless, we have a different character of transition in the quantum and classical cases. Indeed, in the quantum case, we operate with the amplitudes of electron location in the field of the first (a_{1j}) and the second (a_{2j}) cores, and the Schrödinger equation for these amplitudes has the form [6]

$$\begin{aligned} ia_{1j} &= \frac{\Delta_j}{2} a_{2j}, \\ ia_{2j} &= \frac{\Delta_j}{2} a_{1j} \end{aligned} \tag{23}$$

if we neglect the transitions between electron states with different j. Therefore, introducing the transition rate averaged over electron states in the field of the first core, we can see that the dependences in (22) and (7b) are different when the transition probability is small. This difference follows from the different character of the quantum and classical mechanics because the first deals with amplitudes and the second with probabilities. In finding the electron transfer cross section, we assume a sharp dependence $\zeta_j(\rho)$, which allows using the asymptotic theory [5] with the cross section

$$\sigma = \frac{\pi R_0^2}{2}, \quad \zeta(R_0) = \frac{e^{-C}}{2} = 0.28. \tag{24}$$

We note that in spite of the difference between the dependences in (7) and (20) for the resonant charge exchange probabilities on the classical and quantum numbers, the cross sections of this process are expressed through the electron transfer rate by the same formulas in accordance with Eqs. (10) and (24).

Analyzing the electron transfer from the quantum standpoint, we use a simple model in which a highly excited s-electron is located in the field of two moving Coulomb centers. In this case, the rate of electron transition between two cores is determined by the ion–atom exchange interaction potential, and below we find it both in the case where a classical electron can pass to the region of another core and in the case where this transition has the tunnel character. Placing a highly excited electron in the s-state, when its wave is isotropic with respect to angles, we obtain the following general expression for the exchange interaction potential [15]:

$$\Delta(R) = \pi R \psi^2\left(\frac{R}{2}\right), \quad R > R_0. \tag{25a}$$

Here, $\psi(r)$ is the total wave function of the s-electron located in the field of two single-charged cores. This function is taken at the midpoint between the nuclei. This exchange interaction gives the rate of the electron transition from one core to the other as

$$\nu(R) = \Delta(R)/2,$$

which accounts for both over-barrier and tunnel electron transitions. If the classical transition of an electron between the fields of two cores is possible, i.e., $R < R_0$, the tunnel transition makes a certain contribution to the electron transfer rate, given by

$$\nu_{tun} = \frac{\Delta(R_0)}{2} = \frac{\pi}{2} R_0 \psi^2\left(\frac{R_0}{2}\right), \quad R < R_0. \tag{25b}$$

Thus, mixing of excited states in the course of collision of a highly excited atom and ion leads to Firsov formula (25) for the rate of tunnel electron transition, although this formula initially describes the transition between two atomic s-states of a quantum system [15].

We now compare this with the rate obtained for a classical model [8], where the electron transfer is considered as a flux through the symmetry plane located in the middle between the cores and bisecting it. Then the electron flux is $N_e v_e/4$, where N_e is the electron number density and v_e is the electron velocity. Because $N_e \sim 1/v_e$ in the classical case, the electron flux is independent of the cross section point in the classically available region. Hence, the rate of transfer of a classical electron is

$$\nu_{cl}(R) = \frac{N_e v_e}{4}\,\frac{\pi(R_0^2 - R^2)}{4}. \tag{26}$$

At the midpoint of the molecular axis, we have $R_0 - R \ll R_0$, then

$$N_e = \psi^2\left(\frac{R}{2}\right), \quad v_e = \sqrt{2\left(\frac{4}{R} - \frac{4}{R_0}\right)}.$$

This gives the rate of transfer of a classical electron between the cores as

$$\nu_{cl}(R) = \frac{\pi}{4\sqrt{2}} \psi^2\left(\frac{R}{2}\right)(R_0^2 - R^2)\sqrt{\frac{R_0 - R}{R R_0}}. \tag{27}$$

This leads to the contribution of over-barrier transitions to the total electron transfer rate given by

$$\frac{2\nu_{cl}(R)}{\Delta(R)} = \frac{\sqrt{2}(R_0 + R)}{4\sqrt{R_0}}\left(\frac{R_0 - R}{R}\right)^{3/2} = \sqrt{\frac{R_0}{2}}\epsilon^{3/2}, \tag{28}$$

$$\epsilon = \frac{R_0 - R}{R_0} \ll 1.$$

In accordance with the definition, the ratio $(R_0 - R)/R$ is small,

$$\frac{R_0 - R}{R} \ll 1,$$

and we use it as a small parameter. We then find that the contribution of the classical transfer dominates when $R < R_0$, and these distances are not sufficiently short.

We can estimate the contribution to the electron transfer rate from general considerations. Indeed, the γ dependence for the classical rate of electron transition is

$$\nu_{cl}(R) \propto \gamma^3,$$

while the tunnel rate is

$$\nu_{tun}(R) \propto \gamma^4 \quad (R \sim 1/\gamma^2).$$

Hence, for a highly excited electron ($\gamma \ll 1$), the rate of the over-barrier transition exceeds the rate for the tunnel transition in the range where the classical electron transfer is permitted ($R < R_0$), excluding a range near the critical distance.

Using the assumption about the isotropy of the electron wave function (in particular, in order to pass from the three-dimensional to the one-dimensional case), we obtain the following semiclassical expressions for the electron wave function (see, e.g., [16]):

$$\psi = \frac{C}{r\sqrt{p}} \cos\left(\int_0^r p dr - \frac{\pi}{4}\right) \tag{29a}$$

in the region of classical motion and

$$\psi = \frac{C}{2r\sqrt{|p|}} \exp\left(-\int_0^r |p|\, dr\right) \tag{29b}$$

in the region where location of a classical electron is forbidden. Here, C is a normalization factor, and in the adiabatic case of ion–atom collisions, the electron momentum is equal to

$$p = \sqrt{2(\varepsilon - U)}, \quad \varepsilon = -\frac{\gamma^2}{2} - \frac{1}{R}, \qquad U = -\frac{1}{r_1} - \frac{1}{r_2}, \tag{30}$$

where R is the distance between the nuclei, and r_1 and r_2 are the distances between the electron and the first and the second nuclei. In the limit of large separations,

$$R\gamma^2 \gg 1,$$

Eqs. (25) give the general expressions for the wave function of a classical electron with zero momentum [4, 17]. Above, we used the form of the Schrödinger equation for the radial wave function, which is similar to the one-dimensional Schrödinger equation if the radial wave function is multiplied by r.

To obtain the normalization factor C, we find the asymptotic expression for the radial wave function, which has the form

$$\psi(r) = Ar^{1/\gamma - 1} e^{-r\gamma}, \; r\gamma^2 \gg 1, \tag{31a}$$

where

$$A = \frac{\gamma^{3/2}\,(2\gamma)^{1/\gamma}}{\Gamma(1/\gamma)} \tag{31b}$$

in the case where an excited electron is located in the Coulomb field of a core. Evaluating wave function (29b) in the limit $r\gamma^2 \gg 1$ and accounting for $|p| = \gamma$ in this limit ($\gamma = 1/n$), we obtain

$$\begin{aligned}\psi(r) &= \frac{C}{2r\sqrt{|p|}} \exp\left(-\int_0^r |p|\, dr\right) = \\ &= \frac{C}{2r\sqrt{\gamma}} \exp\left(-\int_{r_0}^r \sqrt{\gamma^2 - \frac{2}{r}} dr\right) = \\ &= Cr^{1/\gamma - 1} e^{-r\gamma} e^{1/2\gamma} \sqrt{\gamma} (2\gamma^2)^{1/\gamma - 1}. \end{aligned} \tag{32}$$

Comparing this expression with Eq. (31a), we find

$$\begin{aligned} C &= \frac{A}{\sqrt{\gamma}} e^{-1/2\gamma} (2\gamma^2)^{1 - 1/\gamma} = \\ &= 2e^{-1/2\gamma} \gamma^{5/2 - 1/\gamma} \Gamma^{-1}\left(\frac{1}{\gamma}\right). \end{aligned} \tag{33}$$

The Table contains the values of the coefficients A and C for integer values of $n = 1/\gamma$.

We first consider the over-barrier electron transition, where, averaging over the phase in formula (26a) in accordance with Eqs. (32) and (33), we have

$$\nu = \frac{\pi C^2}{R\sqrt{\dfrac{6}{R} - \gamma^2}}, \quad C^2 = \frac{1}{2\pi}\left[\int d\cos\theta \int_0^{[r_0, R/2]} \frac{dr}{\sqrt{\dfrac{2}{r} + \dfrac{2}{\sqrt{r^2 + R^2 - 2Rr\cos\theta}} - \dfrac{2}{R} - \gamma^2}}\right]^{-1}. \tag{34}$$

Coefficients A and C

$n = 1/\gamma$	A	C
1	2	$\frac{2}{\sqrt{e}}$
2	$\frac{1}{2\sqrt{2}}$	$\frac{1}{e}$
3	$\frac{4}{81\sqrt{3}}$	$\frac{1}{e^{3/2}}$
4	$\frac{1}{768}$	$\frac{4}{3e^2}$

In this expression, we assume γ to be a small parameter, $\gamma \ll 1$, and use Eq. (29a) for the electron wave function. The turning point r_0 at a given polar angle θ with respect to the axis is determined by the condition $p = 0$, which gives the equation

$$\frac{2}{r_0} + \frac{2}{\sqrt{r_0^2 + R^2 - 2Rr_0\cos\theta}} = \frac{2}{R} + \gamma^2. \qquad (35)$$

A typical atom size is

$$r \sim 1/\gamma^2,$$

and therefore

$$C^2 \sim r \sim 1/\gamma^2$$

and

$$\nu \sim 1/\gamma.$$

In Fig. 3, we present the semiclassical electron transfer rate $\nu(R)$ in comparison with that of the classical model.

6. TRANSITION OF AN EXCITED ELECTRON BETWEEN TWO COULOMB CENTERS

We have considered two models for transition of a highly excited electron between two colliding Coulomb centers. In the first model, an excited electron is moving in a classically available region. According to subsequent estimations, this consideration is valid for distances between centers $R > 2n^2$. In this distance range, the classical model describes electron evolution correctly, allowing us to find the cross section of the resonant charge process, if this cross section is averaged over initial conditions. Although the classical model leads to an error at small distances between the nuclei, this is not important for resonant charge exchange because the electron transfer probability at strong interaction is equal to one half. We note that the classical model does not account for tunnel transitions, which can make a large contribution to the cross section.

The other model for resonant charge exchange is based on the quantum character of electron transition and therefore accounts for tunnel electron transitions. But in this case, we use a simple expression to model the electron wave function, which does not allow us to follow the evolution of the electron wave function near each core. In other words, the time variation of the wave function packet for the electron is not taken into account in this approach.

Nevertheless, we can use the advantages of each model by matching the electron transfer rates as a function of the distance between the cores. We assume that the semiclassical model gives a correct dependence of the electron transfer rate on the separation R. We then match this dependence with that given by the classical model in the range of separations with over-barrier transitions where the classical model is correct.

7. CONCLUSIONS

In considering the resonant charge exchange process with transition of a highly excited electron, we use two models for the transferred electron, the classical and semiclassical ones. The classical model describes the electron behavior in a classically available region and allows determining the cross section of over-barrier electron transfer. The semiclassical model assumes the absence of transitions between electron states when the electron is located in the field of one core, but simultaneously accounts for over-barrier and tunnel electron transitions. Correction of the semiclassical model based on the classical model in a classically available region of electron location allows determining the electron transfer probability in a wide range of impact parameters and separately finding the contributions of the over-barrier and tunnel electron transition to the cross section of resonant charge exchange. Both models are not correct at small distances between the Coulomb cores where the fields of both cores are mixed. But this is not essential for evaluation of the electron transfer cross section because the probability of resonant charge exchange is equal to 1/2 for collisions with such impact parameters.

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