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THE CHARACTER OF RESONANT CHARGE EXCHANGE INVOLVING HIGHLY EXCITED ATOMS

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We study the process of resonant charge exchange involving excited helium atoms with the principal quantum number $n = 5$ colliding with the helium ion in the ground state in the collision energy range from thermal up to 10 eV. This information may be important for the analysis of planet atmospheres containing helium, in particular, for Jupiter's atmosphere, but our basic interest is the transition from the quantum to classical description of this process, where, due to large cross sections, evaluations of the cross sections are possible. For chosen process, quantum theory allows determining the cross section as a result of a tunnel electron transition, while classical theory accounts for over-barrier electron transitions. The classical theory additionally requires effective transitions between states with close energies. The analysis of these transitions for helium with $n = 5$ shows that electron momenta and their projections are mixed for a part of the states, while for other states, the mixing is absent. A simple criterion to separate such states is given. In addition, the main contribution to the cross section of resonant charge exchange follows from tunnel electron transitions. As a result, the quantum theory is better for calculating the cross sections of resonant charge exchange than the classical one and also allows finding the partial cross sections of resonant charge exchange, while the classical approach gives the cross section of resonant charge exchange in a simple manner with the accuracy of 20 %.

1. INTRODUCTION

The process of resonant charge exchange involving highly excited atoms is important for a weakly ionized nonequilibrium gas and influences transport phenomena in such a plasma. In analyzing this process, we are guided by Jupiter's atmosphere where nonequilibrium helium plasma with excited helium atoms is formed under the action of solar radiation, and highly excited atoms influence the transport properties of this plasma because of the low gaseous temperature [1–4]. For definiteness, in the analysis of the resonant charge exchange process with the participation of highly excited atoms, we are guided by processes involving excited helium atoms with the principal quantum number $n = 5$.

There are two methods to evaluate the cross section of resonant charge exchange. In the classical limit, this process is considered as an over-barrier electron transition from one charged core to another. The quantum theory is based on the ion–atom exchange interaction potential that characterizes the rate of electron transition between two cores as a result of overlapping of electron wave functions centered on different cores. In the quantum case, we are based on the asymptotic theory that represents the ion–atom exchange interaction potential and the cross section of resonance charge exchange as the result of an expansion of these quantities over a small parameter, which is a reciprocal value of the large distance between the cores that determines the cross section.

For electron transfer involving highly excited atoms, one can expect that the classical theory holds true in contrast to the asymptotic theory [5–7], which is not applicable to highly excited atoms. But we can show that the criteria of both classical and asymptotic theories are valid simultaneously in a wide range of parameters, and we use them below for the helium-ion–atom

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collisions in the range of collision energies 0.1–10 eV and atom excitations with the principal electron quantum number $n = 5$. But the quantum and classical theories are related to different physical situations. Namely, the classical theory in its simple version considers an electron with averaged parameters, while the quantum theory corresponds to certain quantum numbers of the electron. The question is what occurs in reality and what is the rate of transitions between energetically close states in the course of the resonant charge exchange process.

The goal of this paper is to study in detail the possibilities of using simple versions of classical and quantum theories for the resonant charge exchange process and the criteria of these approaches. In this analysis, we are guided by highly excited helium atoms with $n = 5$.

2. EXCHANGE INTERACTION OF AN EXCITED ATOM WITH AN ION

We construct the wave functions of an excited electron in the helium atom for the principal quantum number $n = 5$ and the exchange interaction potential for this atom with a parent ion. Because an excited electron is located mostly in the spatial region where the Coulomb field of the atomic core acts on it, we can use the wave functions of the hydrogen atom for this electron. The radial wave function of an electron in the hydrogen atom with the principal quantum number $n = 5$ has the form [8, 9]

$$\psi^H_{n=5,\ell=0}(r) = \frac{2}{25\sqrt{5}}\frac{1}{1875}\times \\ \times\left(9375 - 7500r + 1500r^2 - 100r^3 + 2r^4\right)\exp\left(-\frac{r}{5}\right), \tag{2.1}$$

$$\psi^H_{n=5,\ell=1}(r) = \frac{1}{25\sqrt{30}}\frac{4r}{1875}\times \\ \times\left(3750 - 1125r + 90r^2 - 2r^3\right)\exp\left(-\frac{r}{5}\right), \tag{2.2}$$

$$\psi^H_{n=5,\ell=2}(r) = \frac{1}{75\sqrt{70}}\frac{4r^2}{625}\left(525 - 70r + 2r^2\right)\times \\ \times\exp\left(-\frac{r}{5}\right), \tag{2.3}$$

$$\psi^H_{n=5,\ell=3}(r) = \frac{1}{75\sqrt{70}}\frac{2r^3}{125}\left(8 - \frac{2r}{5}\right)\times \\ \times\exp\left(-\frac{r}{5}\right), \tag{2.4}$$

$$\psi^H_{n=5,\ell=4}(r) = \frac{1}{225\sqrt{70}}\frac{4r^4}{625}\exp\left(-\frac{r}{5}\right), \tag{2.5}$$

where the distance r between the electron and the Coulomb center is given in atomic units (a_0), and all these wave functions are normalized by the relation

$$\int\limits_0^\infty r^2\psi^2(r)\,dr = 1.$$

Using these wave functions, we can construct the exchange interaction potential $\Delta(R)$ of the ion and excited atom. Along with the principal quantum number $n = 5$, the electron states in the field of the Coulomb center are characterized by the electron orbital momentum l, its projection m onto a given direction, the atom spin, and its projection onto this direction. We first consider the stationary problem where nuclei are motionless and restrict ourselves to the case $m = 0$. We also first ignore the influence of the electron spin on the symmetry of molecular wave functions and subsequently on the exchange interaction potential. Under these conditions, the exchange interaction potential has the form [10]

$$\Delta(R) = \frac{R}{4}\left|\psi_{mol}\left(\frac{R}{2}\right)\right|^2. \tag{2.6}$$

We also use the atomic units for the interaction potential. Expressing the molecular wave functions ψ_{mol} of the electron through its atomic wave functions $\psi_{n=5}(r)$, i. e., taking the action of the second Coulomb center into account, we obtain [7, 9]

$$\Delta(R) = \frac{R}{4}\left(\frac{4}{e}\right)^{1/\gamma}\left|\psi_{n=5}\left(\frac{R}{2}\right)\right|^2. \tag{2.7}$$

Since in this case $\gamma = 0.2$, from (2.7) we obtain

$$\Delta(R) = 1.725R\left|\psi_{n=5}\left(\frac{R}{2}\right)\right|^2. \tag{2.8}$$

Table 1 gives the values $R_{max} > 45$ at which the exchange interaction potential $\Delta(R)$ has the last maximum as a function of the ion–atom distance, the exchange interaction potential $\Delta(R_{max})$, and the distance $R_2 > R_{max}$ such that

$$\Delta(R_2) = \frac{\Delta(R_{max})}{2}.$$

The parameter R_2 characterizes the decrease in the exchange interaction potential after the last maximum. If the cross section of resonant charge exchange is determined by ion–atom distances $R > R_{max}$, this transition has the tunnel character.

Table 1

l	R_{max}, a_0	$\Delta(R_{max})$, cm^{-1}	R_2, a_0
0	77.6	868	95.9
1	75	891	93.8
2	70.7	950	89.2
3	62.4	1080	81.1
4	45	1596	65.0

3. CLASSICAL THEORY OF RESONANT CHARGE EXCHANGE

We analyze the resonant charge exchange process from the classical standpoint for a transferring electron. We consider the resonant exchange process involving highly excited atoms at low collision velocities compared with a typical energy of the bound excited electron in its orbit. Then the significant contribution to the cross section of resonant charge exchange follows from over-barrier electron transition. Then electron motion has a classical character and the electron transition from the region of action of one core to that of the other occurs when the barrier separating fields of the action of these cores disappears. The Hamiltonian of the interacting electron and the ion has the form

$$\widehat{H} = \frac{\widehat{p}^2}{2m_e} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R},$$

where $\widehat{p}$ is the operator of the electron momentum, m_e is the electron mass, e is the electron and ion charge, r_1 and r_2 are distances of the electron from the first and second ion, and R is a distance between ions. We note two possibilities for transition of a classical electron between two Coulombs wells, adiabatic and diabatic ones [11], depending on the ion participation in the energy balance. In the adiabatic case, ions exchange by energy of electrons in the course of the electron transition, whereas in the diabatic case, this transition is fast and the transferring electron does not draw ions in an energy exchange.

In the adiabatic case, the barrier separating the region of action of the first and second ion disappears at the distance between ions $R = R_0$, where

$$\frac{3e^2}{R_0} = J,$$

and J is the ionization potential of an excited atom. Below, we use the atomic units and set $J = \gamma^2/2$, whence $R_0 = 6/\gamma^2$, and the classical cross section of resonant charge exchange in the limit of low collision velocities is [12, 13]

$$\sigma_{cl} = \sigma_0 = \frac{1}{2}\pi R_0^2 = \frac{9\pi}{2J^2} = \frac{18\pi}{\gamma^4} = 18\pi n^4, \qquad (3.1)$$

where n is the principal quantum number for the excited electron.

In the diabatic case where the collision is fast and the ion–electron equilibrium is not fulfilled, the separation R_0 of the barrier disappearence follows from the relation

$$\frac{4e^2}{R_0} = J,$$

and the classical cross section of electron transfer is given by

$$\sigma_{cl} = \frac{1}{2}\pi R_0^2 = \frac{32\pi}{\gamma^4} = 32\pi n^4. \qquad (3.2)$$

It is simple to extend this result to the collision of a multicharge ion of a charge Z if the excited electron is located in the field of another multicharge ion of the same charge. Instead of formula (3.2), replacing the interaction electron–ion parameter e^2 by Ze^2, we then obtain

$$\sigma_{cl} = \frac{\pi}{2}R_0^2 = \frac{8\pi Z^2 e^4}{J^2} = 32\pi Z^2 n^4 \qquad (3.3)$$

in the diabatic limit.

If the collision energy increases, the transferring electron cannot overcome the barrier along some trajectories, and the cross section of resonant charge exchange decreases with an increase in the collision velocity v. In the framework of statistical physics, the classical cross section in the adiabatic limit has the form [14]

$$\sigma_{cl} = \sigma_0 \left[1 - 0.8\left(\frac{v}{\gamma}\right)^{2/5}\right], \quad v \ll \gamma, \qquad (3.4)$$

which is confirmed by evaluations using the method of molecular dynamics [15]. In the limit of large collision velocities, the statistical method of averaging over electron trajectories gives [15]

$$\sigma_{cl} = \frac{12\pi}{v\gamma^3}, \quad v \gg \gamma. \qquad (3.5)$$

Combining formulas (3.1) and (3.5), we obtain the classical cross section of resonant charge exchange based on the computer simulation of this process [15]

$$\sigma_{cl} = \frac{18\pi}{\gamma^4}\left(1 - \frac{3v}{2\gamma}\right)^{-1}. \qquad (3.6)$$

Below, we use this expression for evaluation of the cross section of resonant charge exchange.

4. RESONANT CHARGE EXCHANGE WITH TUNNEL ELECTRON TRANSITION

We now consider the tunnel electron transition if a potential barrier separates the action of two Coulomb centers. Due to the symmetry of the problem, the states of a bound electron are separated into even (g) and odd (u) ones, such that the corresponding electron wave functions preserve or reverse their sign as a result of electron reflection with respect to the symmetry plane that is perpendicular to the axis joining the cores and bisects this axis [9]. If electron states are degenerate, the probability P of electron transition from the region of action of the first core to that of the second core is expressed in terms of the exchange interaction potential

$$\Delta(R) = \varepsilon_g(R) - \varepsilon_u(R)$$

(where $\varepsilon_g(R)$ and $\varepsilon_u(R)$ are the energies of the even and odd electron states at a distance R between cores) as [10]

$$P = \sin^2 \int\limits_{-\infty}^{\infty} \frac{\Delta(R)}{2}\, dt, \tag{4.1}$$

and the classical motion of nuclei is characterized by a certain trajectory $R(t)$. We assume here that resonant charge exchange is not entangled with other processes in this collision process, such as rotation of electron momenta and transitions between different spin states. Under this assumption, which is connected with the relative narrowness of the transition region, we can simply generalize to the case of degenerate levels [11].

For the resonant charge exchange process involving atoms in the ground and weakly excited states, the asymptotic theory [5, 7] is applicable that represents the cross section of this process as an expansion in the small parameter $1/R_0\gamma$ (the cross section is $\sigma_{ex} = \pi R_0^2/2$). The asymptotic theory is violated for highly excited atoms, but the method for evaluating the probability of the tunnel electron transition can be used in evaluating the resonant charge exchange cross section with participation of highly excited atoms. Assuming the angle of rotation of the molecular axis during the electron transition from one core to another to be small due to a sharp dependence of the ion–atom exchange interaction potential on the distance between them, we can then separate transitions with different directions of the orbital electron momentum, and then average over this direction. Below, we do this for resonant charge exchange involving excited helium atoms with $n = 5$.

The asymptotic theory of resonant charge exchange [5, 7] is used under the condition that the second core acts on the wave function of the electron whose wave function is centered on the first core, at distances r from the core where the asymptotic expression for the atomic wave function holds true (i. e., in the region where the electron binding energy is large compared with the Coulomb interaction potential of this electron with the core). This condition is expressed as the criterion

$$r\gamma^2 \gg 1.$$

Representing the resonant charge exchange cross section as

$$\sigma_{ex} = \frac{\pi R_0^2}{2},$$

we have the asymptotic theory applicability criterion in the form

$$\frac{1}{\alpha} = \frac{R_0\gamma^2}{2} \gg 1, \tag{4.2}$$

and α is the small parameter of the asymptotic theory. The first two terms of the expansion in this small parameter are typically used in the calculated cross section of resonant charge exchange [7, 16, 17].

If a valence electron with an orbital momentum l_e and its projection μ onto the molecular axis is located in the field of two structureless cores, the exchange interaction potential $\Delta_{l_e\mu}$ is given by [6, 7, 11]

$$\Delta_{l,\mu}(R) = A^2 R^{2/\gamma-1-|\mu|} e^{-R\gamma-1/\gamma} \times \\ \times \frac{(2l+1)(l+|\mu|)!}{(l-|\mu|)!\,|\mu|!(\gamma)^{|\mu|}}, \tag{4.3}$$

where R is the distance between the nuclei, and γ and A are the parameters of the asymptotic wave function of the valence electron, such that the radial wave function of this electron in an atom at a large distance r from the nucleus is given by

$$\psi(r) = A r^{1/\gamma-1}\exp(-r\gamma), \quad r\gamma^2 \gg 1. \tag{4.4}$$

We calculate the resonant charge exchange cross section based on the asymptotic formula in the two-state approximation for the electron transition with $m = 0$, which has the form [5, 7, 10]

$$\sigma_{res} = \frac{\pi R_0^2}{2}, \\ \frac{\Delta_{l,\mu}(R_0)}{v}\sqrt{\frac{\pi R_0}{2\gamma}} = \frac{e^{-C}}{2} = 0.28. \tag{4.5}$$

We can extend the asymptotic theory of resonant charge exchange to the case of the tunnel transition of a highly excited electron. Indeed, we assume that the transition occurs in a region of ion–atom distances R where the exchange interaction potential varies sharply with R. Instead of formula (4.5), we then obtain the cross section of resonant charge exchange as

$$\sigma_{res} = \frac{\pi R_0^2}{2}, \\ \frac{\Delta_{l,\mu}(R_0)}{v}\sqrt{\frac{\pi R_0}{2\alpha}} = \frac{e^{-C}}{2} = 0.28, \\ \alpha = -\frac{d\ln\Delta_{l,\mu}(R_0)}{dR_0}. \tag{4.6}$$

We use this formula in what follows to evaluate the cross section of resonant charge exchange involving a highly excited atom. We note that the difference between the cross sections evaluated on the basis of formulas (4.5) and (4.6) is small in reality, when $R_0 > R_{max}$. Indeed, in this case,

$$\alpha \equiv -\frac{d\ln\Delta_{l,\mu}(R_0)}{dR_0} \approx \gamma\left(1 - \frac{2}{R_0\gamma^2}\right) \approx \\ \approx \gamma\frac{(R_0 - R_{max})}{R_0}, \tag{4.7}$$

and because R_0 is mostly determined by an exponential dependence of the ion–atom exchange interaction potential on the distance between them, this variation of the value in the radicand is not essential. Using formula (4.6), we drop criterion (4.2), but require a sharp decrease of the ion–atom exchange interaction potential $\Delta_{l,\mu}(R)$ with a decreasing ion–atom distance R,

$$\Delta_{\ell,\mu}(R) \propto \exp(-\alpha R).$$

5. RESONANT CHARGE EXCHANGE INVOLVING EXCITED HELIUM ATOMS

In the foregoing, we have considered two versions of resonant charge exchange involving excited atoms. In the first, classical version, an over-barrier electron transfer occurs, and the behavior of the valence electron is described by the laws of classical mechanics. In the second version, the cross section of resonant charge exchange is determined by tunnel electron transitions from one core to another, and the electron quantum numbers are conserved in the course of this transition. In Table 2, we give the cross sections of resonant charge exchange for the tunnel electron transition according to formula (4.6) for the collision energy $E = 1eV$ in the laboratory frame of reference and for the electron momentum projection $\mu = 0$. For comparison, the classical cross sections for an over-barrier transition are given in Table 2. We note that the collision velocity is $v = 6.6\cdot 10^{-3}$ in this case, i. e., $v \ll \gamma \approx 0.2$, which allows using formula (3.4) for the classical cross section given in Table 2. It follows that the quantum and classical cross sections are comparable. We note that characteristic distances R_0 for the electron transition in the quantum and classical cases are almost identical, but correspond to the different nature of the process. It is essential that in the classical case, we use a certain assumption for averaging over the electron momentum during collision, and hence the coincidence of the classical and quantum cross sections does not contradict the nature of this transition. Moreover, the criterion of the validity of a tunnel transition, $R_0 > R_{max}$, is satisfied. Based on the obtained data, we can expect that the accuracy of the classical theory for highly excited atoms is approximately 20 %.

In Table 2, the electron binding energies in the helium atom with $n = 5$ are expressed in cm^{-1}. The quantum cross section of resonant charge exchange

$$\sigma_{tun} = \frac{\pi R_0^2}{2}$$

at the collision energy of 1 eV in the laboratory frame of reference for a state with the projection $\mu = 0$ of the momentum of the excited electron onto the impact parameter vector are evaluated based on formula (4.6), $\Delta(R_0)$ is the ion–atom interaction potential for this collision energy, and

$$\sigma_{cl} = \frac{\pi R_{cl}^2}{2}$$

is the classical cross section evaluated by formula (3.4) at the collision energy 1 eV in the laboratory frame. The cross sections σ_{tun} and σ_{cl} are expressed in 10^{-14} cm^2.

Table 3 contains the resonant charge exchange cross sections for states of the excited electron with any momentum projection onto the impact parameter of collision. We note that if the states with the total electron spin $S = 0$ and $S = 1$ are separated, i. e., the energy difference for atoms in these states is greater than the exchange interaction potential $\Delta(R_0) = 0.3$–0.5 cm^{-1}, the total spin is conserved in the course of resonant charge exchange. In such cases, it is necessary to multiply the ion–atom exchange interaction potential in formula (4.5) by the respective factor 1/4 or 3/4 for states with the total spin $S = 0$ and $S = 1$.

The tunnel cross sections σ_{tun} of resonant charge exchange are given in 10^{-14} cm^2 at an indicated collision energy in the laboratory frame of reference. The ion–atom exchange interaction potential is evaluated

Table 2

Electron state	State	Energy, cm^{-1}	γ	σ_{tun}	R_0, a_0	$\Delta(R_0)$, cm^{-1}	σ_{cl}	R_{cl}, a_0
$1s5s$	5^3S	4963.8	0.213	75	131	0.5	58	132
$1s5s$	5^1S	4647.3	0.206	75	132	0.4	66	141
$1s5p$	5^3P	4510.1	0.203	97	148	0.4	69	146
$1s5d$	5^3D	4393.6	0.200	108	157	0.3	74	150
$1s5d$	5^1D	4392.5	0.200	109	157	0.3	74	150
$1s5f$	5^3F	4389.7	0.200	109	157	0.3	74	150
$1s5f$	5^1F	4389.7	0.200	109	157	0.3	74	150
$1s5g$	5^3G	4389.2	0.200	109	157	0.3	74	150
$1s5g$	5^1G	4389.2	0.200	109	157	0.3	74	150
$1s5p$	5^1P	4368.3	0.200	93	145	0.3	74	150

Table 3

Electron state	m	σ_{tun}, $E = 0.1$ eV	σ_{tun}, $E = 1$ eV	σ_{tun}, $E = 10$ eV
$1s5s$ 5^3S	0	85	75	66
$1s5s$ 5^1S	0	86	76	66
$1s5p$ 5^3P	0	109	97	87
$1s5p$ 5^3P	1	83	74	64
$1s5d$ $5^{1,3}D$	0	117	105	94
$1s5d$ $5^{1,3}D$	1	101	90	80
$1s5d$ $5^{1,3}D$	2	78	68	60
$1s5f$ $5^{1,3}F$	0	106	95	84
$1s5f$ $5^{1,3}F$	1	98	87	77
$1s5f$ $5^{1,3}F$	2	82	73	64
$1s5f$ $5^{1,3}F$	3	63	54	47
$1s5g$ $5^{1,3}G$	0	88	77	67
$1s5g$ $5^{1,3}G$	1	85	75	65
$1s5g$ $5^{1,3}G$	2	75	66	58
$1s5g$ $5^{1,3}G$	3	63	54	47
$1s5g$ $5^{1,3}G$	4	46	40	33
$1s5p$ 5^1P	0	104	93	82
$1s5p$ 5^1P	1	79	69	59

based on formula (4.3), and the exchange interaction potential is connected with the resonant charge exchange cross section by formula (4.6).

We consider collisions of an excited helium atom with its ion in the ground state at collision velocities below a typical electron velocity on the electron orbit for an excited state of the helium atom. Then the analysis of the processes in such a collision reduces to finding the behavior of the electron terms of the quasimolecule consisting of the colliding particles and motionless nuclei. In the simplest case with one electron state for the transferring electron in each atomic core, the electron transfer probability is determined by the splitting of the electron term into even and odd parts with respect to reflection in the symmetry plane. The quantum theory of resonant charge exchange [5, 6] then holds true because it is based on the fact that the electron transfer proceeds at large distances between colliding particles compared with the atom size. The theory uses the fact that the parameter $1/\alpha R_0$ is small, where $\pi R_0^2/2$ is the resonant charge exchange cross section. The basis of the quantum theory is the tunnel character of electron transition, and this is violated for high excitation. In the classical version, the charge exchange process involving an excited electron state can be represented as a classical electron transition between two cores [12–15]. Below, we consider these two types of electron transitions as the limit cases for electron transfer in the resonant charge process involving excited states.

We note one more peculiarity of the case where an excited state partakes in the resonant charge exchange process. Quasimolecular levels with different quantum numbers become then closer to one another, and hence the resonant charge process involves processes such as transitions between states with different orbital moments of electrons and different momentum projections [11], and we account for these transitions in describing classical behavior of an excited bound electron.

Electron transfer involving an excited atom state includes two simultaneous processes, charge exchange for an electron in the ground state of the helium atom and transition between two cores for an excited electron. Hence, the cross section of excitation transfer is close to the cross section of resonant charge exchange involving the helium ion and atom in the ground states. The change of the momentum and the momentum projection of an excited electron are the subject of investigation. Simultaneously, we consider these transitions for an excited electron without transfer of excitation (i. e., without resonant charge exchange for the helium atom and ion in the ground state). It is clear that this cross section significantly exceeds the excitation transfer cross section.

We consider the resonant charge exchange process in slow collisions from another standpoint. In the course of interaction, the colliding ion and atom form a quasimolecule whose parameters vary slowly during the collision process. In this treatment, the electron transfer results from the interference of electron wave functions for the even and odd states, but the character of this interference depends on electron quantum numbers. Averaging over these states depends on the rate of transitions between states with different electron quantum numbers, such as the electron momentum and its projection onto the molecular axis, and the total atom spin. In this treatment, we assume these rates to be small compared with the rate of electron transfer between cores.

6. TRANSITIONS BETWEEN EXCITED STATES IN ION–ATOM COLLISIONS

We analyze the possibility of transitions between electron states in the course of collision between an ion and an excited atom. In the first place, such transitions are possible under the action of the electric field of a moving ion, and hence the operator of ion–atom interaction corresponds to an expansion of the interaction potential in the small separation R,

$$V = \frac{1}{|\mathbf{R}-\mathbf{r}|} - \frac{1}{R} = \frac{\mathbf{r}\cdot\mathbf{R}}{R^3}, \tag{6.1}$$

where $\mathbf{r}$ is the electron coordinate and $\mathbf{R}$ is the vector connecting the nuclei. We give the matrix elements that determine these transitions between excited electron states with the same principal quantum number n [8]:

$$\langle nlm|z|n,l+1,m\rangle = \frac{3}{2}n\sqrt{n^2-(l+1)^2}\times \times\sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}}, \tag{6.2}$$

$$\langle nlm|z|n,l-1,m\rangle = \frac{3}{2}n\sqrt{n^2-l^2}\times \times\sqrt{\frac{l^2-m^2}{(2l+1)(2l-1)}}, \tag{6.3}$$

$$\langle nlm|x+iy|n',l+1,m+1\rangle = \frac{3}{2}n\sqrt{n^2-(l+1)^2}\times \times\sqrt{\frac{(l+m+2)(l+m+1)}{(2l+3)(2l+1)}}, \tag{6.4}$$

$$\langle nlm|x-iy|n,l+1,m-1\rangle = -\frac{3}{2}n\sqrt{n^2-(l+1)^2}\times \times\sqrt{\frac{(l-m+2)(l-m+1)}{(2l+3)(2l+1)}}, \tag{6.5}$$

$$\langle nlm|x+iy|n,l-1,m+1\rangle = \frac{3}{2}n\sqrt{n^2-l^2}\times \times\sqrt{\frac{(l-m)(l-m-1)}{(2l+1)(2l-1)}}, \tag{6.6}$$

$$\langle nlm|x-iy|n,l-1,m-1\rangle = \frac{3}{2}n\sqrt{n^2-l^2}\times \times\sqrt{\frac{(l+m)(l+m-1)}{(2l+1)(2l-1)}}. \tag{6.7}$$

We now determine the amplitude of transitions between two highly excited states with the principal quantum number $n = 5$ in the framework of the perturbation theory. For simplicity, we now restrict ourself to transitions with the conservation of the momentum projection m onto the impact parameter of collision ρ. In the first approximation of the perturbation theory, the transition amplitude c_{ik} between states i and k is then given by

$$c_{ik} = \int_{-\infty}^{\infty} \exp(i\Delta\varepsilon t) V_{ik}\, dt, \tag{6.8}$$

where V_{ik} is the matrix element between transition states for the interaction operator given by formula (6.1) and $\Delta\varepsilon$ is the energy difference for transition states. Taking the distance R between colliding particles to be given by

$$R^2 = \rho^2 + v^2t^2,$$

where v is the collision velocity and t is time, we reduce formula (6.8) in the new variable

Table 4

Transition	$\Delta\varepsilon$, cm^{-1}	R_0, a_0	z_{ik}	ξ	c
$5^3S \to 5^3P$	453.7	140	21	91	150
$5^1S \to 5^1P$	279	149	21	60	141
$5^3P \to 5^3D$	16.5	153	12	3.6	81
$5^1P \to 5^1D$	21.4	158	12	4.8	79
$5^3D \to 5^3F$	3.9	157	8.8	0.88	55
$5^1D \to 5^1F$	2.8	157	8.8	0.63	55
$5F \to 5G$	0.5	157	5.7	0.1	5.7

Table 5

Initial electron state	σ_{tun}, $E = 0.1$ eV	σ_{tun}, $E = 1$ eV	σ_{tun}, $E = 10$ eV
$1s5s$ 5^3S	85	76	66
$1s5s$ 5^1S	86	76	66
$1s5p$ 5^3P	92	82	72
$1s5p$ 5^1P	87	77	67
$1s5d$, $1s5f$, $1s5g$ $5^{1,3}D$, $5^{1,3}F$, $5^{1,3}G$	83	76	67

$$x = vt/\rho$$

to the form

$$c_{ik} = \frac{z_{ik}}{\rho v} \int\limits_{-\infty}^{\infty} \exp(i\xi x) \frac{dx}{1+x^2}, \quad \xi = \frac{\Delta\varepsilon\rho}{v}, \tag{6.9}$$

where z_{ik} is the matrix element given by formula (6.2) for the projection of the electron coordinate $\mathbf{r}$ onto the impact parameter of the collision. In Table 4, we give the values of this matrix element for $n = 5$ and $m = 0$. It then follows that formula (6.2) takes the form

$$z_{ik} = \frac{15}{2}\sqrt{25-(l+1)^2}\sqrt{\frac{(l+1)}{(2l+1)(2l+3)}}.$$

We evaluate the integral in (6.9) by the standard method by means of displacing the integration contour into the complex plane of x and expressing the integral through the residue of the integrand. We obtain

$$c_{ik} = c\exp(-\xi), \quad c = \frac{\pi z_{ik}}{\rho v}. \tag{6.10}$$

Table 4 contains parameters of some transitions between states with the principal quantum number $n = 5$. The transition energy $\Delta\varepsilon$ is taken from Table 2, the impact parameter of collision is $\rho = R_0$, where R_0 determines the resonant charge exchange cross section at the collision energy 1 eV in the laboratory frame, and the values of R_0 are taken from Table 2. The matrix element z_{ik} is evaluated by formula (6.2) for states with $m = 0$. The parameter c is given by formula (6.10), and the parameter ξ is given by formula (6.9).

Although the process under consideration is characterized by a large number of transitions and we restrict ourself in Table 4 to transitions with $m = 0$, these data lead to simple conclusions. We can divide the states and transitions between highly excited states into two groups. If the electron is located in the beginning in the states $5s$ or $5p$, the transitions are adiabatically weak because of a large value of the parameter ξ, which is practically the Massey parameter [18]. The mixing of states occurs for other states, and it is necessary to use the mean value of the transition rate $\Delta(R)$ for these states. Table 5 gives the cross sections of resonant charge exchange obtained in this way.

In Table 5, the quantum cross sections σ_{tun} of resonant charge exchange are given in 10^{-14} cm^2 at the indicated collision energy in the laboratory frame. The ion–atom exchange interaction potential is evaluated by formula (2.8), and the exchange interaction potential is related to the resonance charge exchange cross section by formula (4.6).

We note that in calculating the cross section of resonant charge exchange with the transition of an excited electron, we used the one-electron approximation and assumed the cores to be structureless. In this assumption, we keep in mind that states with different core structures are close in energy. Because this assumption is violated for some electron states, we find corrections to the ion–atom exchange interaction potential. The electron states of an excited electron in the helium atom are characterized by the total spin of the inner and excited electrons, which can be zero or one. To account for this, we represent the ion–atom exchange interaction potential in the general form (see, e, g., [7])

$$\Delta(R) = 2\langle\psi_1|\widehat{H}|\psi_2\rangle - 2\langle\psi_1|\widehat{H}|\psi_2\rangle\langle\psi_1|\psi_2\rangle, \tag{6.11}$$

where $\widehat{H}$ is the Hamiltonian of the electron system and ψ_1 and ψ_2 are the respective wave functions of all the electrons if the excited (transferring) electron is centered on the first or second core. Because these wave functions are the product of the spin and coordinate wave functions, the general structure of the exchange interaction potential is

$$\Delta(R) = p_{sp}\Delta_{coor}(R), \tag{6.12}$$

where the factor p_{sp} is determined by the correlation of electron spins and the factor Δ_{coor} is independent of spins and in this case is related to structureless cores, as it was used above. In other words, formula (6.12) accounts for the correlation of total spins of the cores and the transferring electron, and p_{sp} is the probability that the excited electron forms the same spin with the second core as it had with the first core. Evidently, this factor is $p_{sp} = 1/4$ for states of an excited helium atom with the total spin $S = 0$ (singlet states), and $p_{sp} = 3/4$ for atom states with the total spin $S = 1$ (triplet states). This factor is taken into account in calculations of the cross sections in Table 5.

7. SEMICLASSICAL AND CLASSICAL THEORY OF RESONANT CHARGE EXCHANGE

The above analysis allows understanding why the classical approach to the resonant charge exchange process involving a highly excited electron can be used. Based on the classical theory of the resonant charge exchange process involving a highly excited electron, we average the cross section over all quantum numbers of this electron for states with a given quantum number. In reality, this corresponds to an average over the quantum numbers l, m, and S, where l is the orbital electron moment, m is its projection onto a fixed axis, and S is the atom total spin. Moreover, we usually restrict ourself to over-barrier transitions in the classical approach. In this form, the classical approach is rough, but it allows estimating the cross section in a simple way.

Guided by resonant charge exchange involving the excited helium atom with $n = 5$, we can formulate a rigorous method for evaluating the cross sections of resonant charge exchange for certain excited atoms and their ions. The comparison of the data in Table 1 and in Tables 2 and 3 shows that the quantum theory is applicable in evaluating these cross sections, but the correct averaging over some quantum numbers is required because of effective transitions between these states in the course of collisions. These transitions are induced by the interaction of the ion Coulomb field with the dipole moment of the excited atom and mix states with close energies if the energy gap for these states does not exceed a certain value. Transitions into other states have a small probability because of a high Massey parameter [18] for these transitions.

This analysis gives a simple recipe to divide the states of excited atoms into groups such that effective transitions occur inside each group, whereas transitions from one group to another one have small probability. Such a division for the resonant charge exchange process with participation of the helium ion and atom with $n = 5$ is given in Table 5. Although this relates to the collision energy 1 eV, this division of states into groups depends weakly on the collision energy because the energy gap between groups is sufficiently large, i. e., the Massey criterion for transitions between groups of states is much greater than unity. Next, the asymptotic theory for resonant charge exchange is applicable inside each group, which follows from the comparison of the data in Table 1 and Table 5. This means that in collisions of a highly excited helium atom and its ion, the main contribution to the resonant charge exchange cross section is made by the tunnel transition of the excited electron. Averaging over states inside one group is made over the momentum projection of the excited electron or over states with a high orbital moment l of the electron and correspondingly over states with close energies.

8. CONCLUSION

We usually treat an atomic system as a classical one based on the Heisenberg principle, if the difference of neighboring energy levels is small on the scale of times under consideration. This allows using classical laws in describing this system. But this criterion is not sufficient for the classical description of this atomic system because mixing of states with close energies is required for the classical description. In addition, we note that the apparatus of quantum mechanics is developed deeper than that of classical mechanics, and it is sometimes convenient to use semiclassical methods of quantum mechanics in the case where the classical criterion holds true.

The analysis of the resonant charge exchange process involving highly excited atoms from this standpoint gives some experience in understanding the transition from the laws of quantum mechanics to classical laws for atomic systems. On the one hand, transitions in this process proceed at large distances between colliding particles, where perturbation theory methods can be used. On the other hand, criteria of the classical character of electron motion are fulfilled. Based on the analysis in this paper, we conclude, first, that the semiclassical description of an electron is valid along with its classical description. Second, mixing of electron levels occurs for a part of states only, i. e., the classical approach holds true only for a part of electron states.

The semiclassical approach of quantum mechanics in the form of the asymptotic theory of resonant charge exchange allows analyzing this process deeper. This procedure consists in separating the electron states that are not mixed in the course of the charge exchange process and in averaging the transition rate for electron transfer between atomic cores for the electron states that are mixing in the course of ion–atom collision.

Therefore, in analyzing the process of resonant charge exchange involving highly excited electron, we can expect its classical description to be valid. In the framework of a general approach [12], it is then necessary to construct the potential energy surface for a transferring electron; the charge exchange process must result in an over-barrier transition between two potential wells. But the potential energy surface for the transferring electron depends on the electron momentum, and hence there are different potential energy surfaces, and the choice among them is ambiguous. In reality, the potential energy surface is taken with zero electron momentum [12–14], but this restricts the accuracy of the classical approach. The problem of the choice of the appropriate potential energy surface can be resolved by using the classical approach with statistical averaging [15] where all electron trajectories are accounted for and the transition cross section results from averaging over these trajectories. This approach requires choosing between the adiabatic or diabatic character of the electron interaction with ions in the course of electron motion. Assuming that the classical description of the process is applicable, we can then find the average electron transition cross section at a given collision velocity rather roughly.

The experience with the analysis of charge exchange processes involving highly excited atoms shows that the classical criterion is fulfilled partially. First, the classical approach requires the mixing of all electron states with a given energy, which is the case for a part of these states. Second, along with over-barrier transitions, tunnel transitions give a contribution to the cross section. These transitions can be taken into account if we drop the assumption of the asymptotic theory of resonant charge exchange [7, 11] that the distance of the tunnel transition greatly exceeds the atom size. We note that this remark about the validity of the classical approach for the charge exchange process has a principal character. As regards classical cross sections of resonant charge exchange within the simple analysis in Sec. 3, they can be used as estimates, and their accuracy is better than 20 %.

The above analysis allows formulating a rigorous approach to this problem. We divide the electron states of a given electron energy into several groups such that the Massey criterion is small for transitions inside one group of states. The electron transition proceeds for each group independently and is characterized by a certain transition cross section for each group. But as can be seen from Table 5, the cross sections for different states coincide within the accuracy of 10 %.

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