Transitions between highly excited states of an atom when a neutral particle moves near its core

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Transitions are investigated between highly excited states of an atom, accompanied by a change of principal quantum number and caused by a collision between a neutral particle and an atomic residue (core). Such transitions of a Rydberg electron are due to the action exerted on it by inertial forces when the core moves with acceleration, and are also caused by interaction with the dipole moment due to the redistribution of the density of the inner electrons in the course of the particle collision. The state of the inner electrons does not change in the transitions. The mechanism considered is most effective when the potential of the interaction between the neutral particle and the atomic core of the highly excited atom has a deep well and a large value of the lower vibrational quantum. This situation is realized, for example, in relaxation of Rydberg states of hydrogen H(n) in collisions with helium atoms He[1s]. It is shown that the cross sections and rates of the \( n \rightarrow n' \) transitions are determined in this case by the mechanism investigated in the paper, and not by scattering of a weakly bound electron by the neutral particle, as is the case for \( nl \rightarrow nl' \) transitions with change of only the orbital momentum.

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1. INTRODUCTION

Processes with participation of highly excited states of atoms play a decisive role in the relaxation of a dense low-temperature plasma and are of considerable interest in the physics of gas discharge, gas and flame lasers, astrophysics, and others (see, e.g., Refs. 1 and 2).

It is known that in a dense weakly ionized plasma the processes of excitation and de-excitation of Rydberg states of atoms take place in collisions not with electrons, but mainly with neutral particles. In such collisions, these processes can be the result of different mechanisms. Thus, in Ref. 3 (and later also in Ref. 4), in an investigation of ternary recombination of electrons and ions in a monatomic gas, the active interaction of a weakly bound electron with a neutral particle was considered in the model of classic elastic scattering of a slow electron by an atom. The rates of mixing of the Rydberg states of the atoms \( e^- \rightarrow e^- \) were calculated within the framework of this model in Refs. 4 and 5, under the assumption that the \( nl \) sublevels are uniformly populated within the given level \( n \).

Besides the transitions of a highly excited atom \( A(n) \), when a neutral particle \( B \) collides with a Rydberg electron \( e^- \), transitions are also possible which are due to collision of this particle with the atomic residue (core) \( A^+ \). These mechanisms of the transitions in the system \( (A^+, B, e^-) \) can be considered independently, because of the large radius of the orbit, \( r_e \rightarrow n^2 \) of the atom \( A(n) \). When the particle \( B \) passes near the core \( A^+ \), the transitions of the external electron of such a system can be due to interaction with the inner electrons of the quasimolecular ionic core \( BA^+ \) and lead to their excitation (ionization) or de-excitation. This mechanism is particularly effective in the case of a homonuclear system \( (H^+, A, e^-) \).

We consider here another mechanism of transitions between highly excited levels:

\[
A(n){+}B \rightarrow A(n'){+}B, \tag{1}
\]

which is realized when a neutral particle \( B \) passes near the core \( A^+ \), and is not accompanied by a change in the state of the inner electrons of the quasimolecular heteronuclear ion \( BA^+ \). The reaction (1) corresponds to direct exchange of the energy of a weakly bound electron with the kinetic energy \( E \) of the relative motion of the heavy particles \( A^+ \) and \( B \). i.e., it takes place within the limits of one electron term of the quasimolecular ion \( BA^+ \).

In such a mechanism, the transitions (1) can be due to two causes. The principal effect is the result of the inertial force acting on the outer electron of the atom \( A(n) \) as a result of acceleration of the Coulomb center \( A^+ \) upon collision with the neutral \( B \). The second effect is connected with the interaction of this electron with the dipole moment of the quasimolecular ion \( BA^+ \), due to displacement of its inner electrons relative to the nuclei \( A^+ \) and \( B \) in the course of their collision. However, as will be shown below (Sec. 2), both effects can be considered simultaneously within the framework of the dipole interaction that takes into account also the contribution of the positive Coulomb center \( A^+ \).

The corresponding preliminary analysis of the reaction (1) for the velocity region \( v_B = (2E/\mu)^{1/2} \Delta \Delta n/n^2 \) (\( \mu \) is the reduced mass of the heavy particles) was carried out in Ref. 9.

The noninertial mechanism proposed in Ref. 10 was investigated earlier for the mixing of Rydberg states with respect to the orbital momentum \( l \). In these studies it was established that collision of a neutral particle \( B \) with an ion \( A^+ \) does not make a substantial contribution to the transitions \( nl \rightarrow nl' \). Such transitions are due to the mechanism of direct scattering of the outer electron by the neutral \( B \), which is in fact the mechanism investigated in the over-
whelming majority of the recent theoretical and experimental studies of l-mixing (see Refs. 14–23 and the review). The analysis presented here leads to the following basic conclusion: for transitions with change $n \rightarrow n'$ of the principal quantum number there can occur a situation which is the inverse of l-mixing, i.e., the predominant contribution of the collisions of the neutrals with the core. This fact was established for the system $H(n + 1) = H(n')$ as a result of the comparison with calculations based on the competing mechanisms of elastic scattering of a Rydberg electron by a neutral particle.\textsuperscript{1} The latter mechanism leads only to establishment of an equilibrium distribution over the $l$-sublevels, which is in fact proposed from now on.

All the results were obtained by perturbation theory, thereby limiting the analysis by the condition $v_p < \Delta n/n^2$ (for thermal velocities of relative motion of heavy particles this yields $n \sim 30–40$). We have investigated the most interesting case, when the potential of the interaction of the atom B with the atomic core A* of a highly excited atom A(n) has a sufficiently deep well $E_n$. Three regions of principal quantum numbers are singled out, and in these regions the behavior of the cross sections and of the rate constants of the investigated $n \rightarrow n'$ transitions are qualitatively different: the adiabatic region, the "shakeup" region, and an intermediate region (see Figs. 2 and 3). It is shown that owing to the substantial decrease of the collision time of the heavy particles A* and B in the potential well, compared with the case of the repulsion ($i.e., r_c < \sqrt{n'}$), where $\omega$ is the lower vibrational quantum of the ion BA*\textsuperscript{1}, the adiabatic decrease of the cross sections $\sigma_{\omega\omega}$ sets in at sufficiently low values of $n$, for which $\omega_{\omega} > \omega_0$ or $\pi < 5$ for the system $H(n) = H(n')$. In the intermediate frequency region $\omega_{\omega} = \Delta n/n^2 \ll \omega_0/(5 \leq n \leq 10–15)$ the $n \rightarrow n'$ transitions which occur when a neutral particle B passes near the atomic core A* becomes non-adiabatic. The cross sections and the rate constants of these transitions do not decrease drastically (in case of the mechanism of Refs. 3–5, due to scattering of the Rydberg electron e\textsuperscript{−} by a neutral B, see Figs. 2 and 3), and it is just this which determines the effectiveness of the mechanism investigated here. This effect is explained by the contribution of the internuclear distances at which the relative velocity of the heavy particles A* and B increases substantially as a result of their acceleration in the potential well. To describe the behavior of the cross sections in the indicated frequency region, we construct in this paper a quasiclassical model based on the method of Fourier components.

It will be shown that the low-frequency region $\omega_{\omega} = \Delta n/n^2 \ll \omega_0/(\pi \leq n \leq 10–15)$ can be described by the simple "shakeup" model (see, e.g., Ref. 14, p. 180) of a Rydberg electron. It will be made clear that the transitions with such frequencies are due to the region of large internuclear distances $R_e < \omega_{\omega} < \omega_0$ (the capture impact parameter) on the right-hand branch of the term, where there is no acceleration of the particles A* and B in the potential well. We note that the previously obtained\textsuperscript{9} semiclassical formulae for the cross sections of noninertial\textsuperscript{10} transitions $n \rightarrow n'$ pertain only to the region of low frequencies. We emphasize also that the conclusion drawn in Ref. 10, that the semiclassical analysis is inapplicable (and the transitions described by this formula are inessential) is incorrect, inasmuch as it is valid in the region of applicability of the shakeup model already at velocities $v_p < \Delta n/n^2$.

For comparison, we also analyze the noninertial mechanism of transitions with change of only the orbital momentum $A(n) \rightarrow B(n') + B$. (2)

For this case the behavior of the cross sections as functions of $n$ is much simpler, since the entire region $v_p < 1/n^2$ considered by us by perturbation theory is the shakeup region. The results obtained in this case for $n \rightarrow n'$ transitions are in full agreement with the conclusions of the authors of Refs. 11–13 that the noninertial mechanism is ineffective for l-mixing.

2. FORMULATION OF PROBLEM. EQUATIONS FOR THE CROSS SECTIONS

We consider a system consisting of a neutral atom B, an atomic ion A*, and an electron e\textsuperscript{−}. The Rydberg-electron transitions (1) investigated here take place in the region of internuclear distances $R_{BA^*}$, the size of which is much smaller than the radius $r_c = n^2/\pi$ of its orbit. Therefore, the system (A*, Ba,e\textsuperscript{−}) has a small parameter $R_{BA^*} / n^2 \ll 1$ that makes it possible to calculate the cross sections of the reaction (1) by stationary perturbation theory in the continuous spectrum. Recognizing that the state of the electron shell of the quasimolecular ion BA*, considered in the Born-Oppenheimer approximation, is not changed in transitions of an outer electron, we represent the total Hamiltonian of this system (A*, Ba,e\textsuperscript{−}) in the form

\begin{equation}
\hat{H}(r, R) = -\frac{\mu_e}{2M} + \hat{U}(R), \quad \hat{U}(r) = \frac{\Delta}{2} - \frac{1}{r}
\end{equation}

(with the atomic system of units, $e = \hbar = m_e = 1$).

Expression (3) is written in the mass center of the particles A* and B, where $H_{BA^*}(R)$ is the Hamiltonian of the isolated ion BA* in the electronic ground state, $R$ is the radius vector joining the nuclei B and A*, $\mu$ is their reduced mass, $\mu_0$ and $M$ are the radial-momentum and angular-momentum operators, $U(R)$ is the electronic term, $\hat{H}(r)$ is the Hamiltonian of an outer electron in a Coulomb field, and $r$ is its radius vector.

The operator $\hat{P}(r, R)$ is the interaction energy of two subsystems e\textsuperscript{−} and BA*, and is determined principally by the long-range electron-dipole interaction:

\begin{equation}
\hat{P}(r, R) = -\frac{\mu_e}{2M} \frac{\mu}{\mu_0} \frac{\mathbf{D} (R)}{\mathbf{D}^\ast (R) R} \cdot \mathbf{r}.
\end{equation}

Here $\mathbf{D}(R) = \mathbf{D}^\ast (R) + \mathbf{D}^\ast (R)$ is the dipole moment of the ion BA* relative to the mass center of the particles A* and B. The linear part $\mathbf{D}(R) = R_{BA^*}$ corresponds to the contribution made to $\mathbf{D}(R)$ by the positive Coulomb center A* (the radius vector and its mass $M_e$ is the mass of the nucleus A*). With the aid of the Ehrenfest theorem we have $\tau = r^2/2 + \mu_0 \mathbf{D}(R)$, and the interaction (4) can be rewritten in the form $\hat{P} = \mathbf{D} \cdot \hat{r}$, and it is just such
an interaction which occurs as a result of the inertial force acting on the outer electron in the noninertial coordinate system connected with the Coulomb center $A^+$ (Ref. 10). The nonlinear part of the dipole moment $D^{(3)}(R)$, however, is the result just as in the case of neutral molecules of displacement (polarization at $R > 1$ a.u.) of the inner electrons relative to the nuclei $A^+$ and $B$ in the quasimolecular ion BA$^+$.

We shall regard the operator $\hat{P}(r,R)(d)$ as a perturbation in the Hamiltonian (3). We shall be interested in the transition to the nuclei $A^+$ and $B$ in the excitation (de-excitation) cross section and summed over the final $(l'\text{ and } m')$ orbital and magnetic quantum numbers of the Rydberg electron. If the atom $B$ and the ion $A^+$ have in the initial state $(l,m)$ an energy $E = q^2/2\mu$ and a wave vector $\mathbf{q} = \mathbf{q}_0 + \mathbf{q}_1$, while in the final state ($l'$) their wave vector lies in the interval $[\mathbf{q}_0' + \mathbf{q}_1']$, by normalizing the initial wave function $\psi_{l,m}(\mathbf{r},0)$ and the final wave function $\psi_{l',m'}(\mathbf{r},0)$ of the motion of the nuclei to unity flux of the incident particles, and the final wave function $\psi_{l',m'}(\mathbf{r},0)$ to a $\delta$ function of $\mathbf{q} - \mathbf{q}'$ we have for the electron differential excitation (de-excitation) cross section

$$
\sigma_{\text{ex}}(\mathbf{q},\mathbf{q}') = \frac{\mu^2}{4\pi^2} \sum_{\nu,m} \left| \langle \psi_{l,m} | \mathbf{D}_{l,m}^{\text{r}} | \psi_{l',m'} \rangle \right|^2 \delta(\mathbf{q} - \mathbf{q}') \delta(q - q')
$$

(5)

The wave functions $\psi_{l,m}(\mathbf{r},0)$ and $\psi_{l',m'}(\mathbf{r},0)$ of the continuous spectrum of the heavy particles $A^+$ and $B$ constitute a superposition of a plane and diverging or converging spherical waves as $R \to \infty$ (see, e.g., Ref. 24). The functions $|nlm\rangle$ and $|n'l'm'\rangle$ are the Coulomb functions of a Rydberg electron with initial energy $E_\nu = -1/2\mu q^2$ and final energy $E_\nu - 1/2\mu q^2$. Integrating the result (5) over all the values of the wave number $dq$ and all the possible directions $dO_{\nu}$ of the particles $A^+$ and $B$ in the final state, and averaging over the directions $dO_{\nu}$ in the initial state, we obtain for the total cross section $\sigma_{\text{ex}}(\mathbf{q})$, after a number of transformations:

$$
\sigma_{\text{ex}}(\mathbf{q}) = 4q^2 \frac{\mu^2}{q'} \sum_{\nu,m} \left| \frac{1}{R} \mathbf{D}_{l,m}^{\text{r}} |nlm\rangle \langle n'l'm'\rangle \right|^2 \delta(\mathbf{q} - \mathbf{q}')
$$

(6)

The radial part of the wave function of the relative motion of the nuclei $A^+$ and $B$ (normalization of a $\delta$ function of the wave number $q = 2\mu E^{1/2}$, and $\psi_{l,m} = \psi_{l,m}(0,\mathbf{r})$ is its angular part ($l$ and $J$, are the quantum numbers of the orbital momentum of the nuclei and of its projection). Summing further over the projections of the angular momenta $J$ and $J'$ (the selection rule $J' = J \pm 1$ and changing from the wave function $\psi_{l,m}(\mathbf{r})$ to the function $\psi_{l,m}(R)$ normalized to $\delta(2\mu E - E')$, we obtain for the total cross section $\sigma_{\text{ex}}(E)$ for excitation (de-excitation) of a Rydberg atom $A(n)$ by collision with a neutral particle. Ultimately we obtain

$$
\sigma_{\text{ex}}(E) = \frac{\mu^2}{3\pi} \sum_{n,m} \left| \frac{g(n,m)}{n'^2} \right|^2 (J+1) \left| \langle j_{l+m}^{(l)} | J_{l,m}^{(l)} \rangle \right|^2 \delta(2\mu E - E')
$$

(7)

In the derivation of this equation we used also the Ehrenfest theorem for the matrix elements of a transition in a Coulomb field (Ref. 24), and the Kramers results (for the sum of the oscillator strengths over the possible degenerate states $|lm\rangle$ and $|l'm'\rangle$)

$$
\left\{ \sum_{n,m,l,m'} \left| \langle nlm | \mathbf{E}_{l,m}^{(l)} | l'm' \rangle \right|^2 \right\} = \frac{2}{\pi} \frac{g(n,m)}{n'^2}
$$

(7a)

The quantity $g(n,m)$ of (6) and (7a) is that Gaunt factor, which yields the difference between the exact quantum-mechanical result (7a) and the Kramers results ($g(n,m) = 1$). $D^{(3)}(R)$ denotes the radial matrix element of the dipole moment of the BA$^+$ over the nuclear wave functions of the continuous spectrum:

$$
D^{(3)}(R) = \frac{1}{\pi} \int \psi_{l,m}^{(l)}(R) \psi_{l',m'}^{(l')}(R) \mathbf{r} \cdot d\mathbf{r}
$$

(7b)

It must be emphasized that expression (6) is obtained by using a coordinate system with origin at the mass center of the colliding particles $A^+$ and $B$ in the valid quantum-number region $dn/n < E_\nu$, for which the effects of the recentering of the wave functions of the Rydberg electron are insignificant. On the other hand when the transitions (1) are considered in the region $dn/n > E_\nu$, the question of recentering does not arise at all, since the problem is solved (see Sec. 4) in a coordinate frame connected with the Coulomb center $A^+$.

### 3. HEAVY-PARTICLE TRANSITION-MATRIX ELEMENTS

The investigated transitions (1) proceed most effectively when the potential of the interaction of the atom $B$ with the ion $A^+$ has a sufficiently deep well $E_\nu$. For the low-temperature plasma case of interest to us, the energies $E$ and $E'$ of the colliding particles $A^+$ and $B$ will be assumed small compared with $E_\nu$. This allows us to calculate the matrix elements of the dipole moment (7b) in a quasiclassical approximation by the Fourier-component method. In this paper we investigate free-free transitions of the particles $A^+$ and $B$. Of considerable interest, however, are also free-bound and bound-free transitions, with participation of a molecular ion BA$^+$, on high vibrational-rotational energy levels $|E_{l,m}\rangle$. We consider all these cases by a single procedure:
Here $A$, $A_1$, and $A_2$ are the normalization constants of the initial and final states of the quasimolecular or molecular ion $BA^+$, with $A_1 = 2E_0/\mu^{1/2}$ and $A_2 = 2T^{1/2}$ for the continuous and discrete spectra ($T_{\omega}$ is the period of the vibrational-rotational motion), $t(R)$ is the time of motion from the lower vibrational quantum of the ion $BA^+$ ion and specifies thus the limit of the adiabatic $\omega \tau_{\omega}^{-1}$ and nonadiabatic $\omega \tau_{\omega}^{-1}$ regions of the transitions.

In the adiabatic region $\omega \tau_{\omega}^{-1}$ the result (9a) for the matrix elements $D_{\omega}$ of the transition in a potential with a well at energies $E_i, E_j, E_k$ can be obtained by integrating the Fourier components (8a) in the complex $t$ (or $R$) plane by a method proposed by Landau (see, e.g., Ref. 31, Russian pp. 149-155 and 187-191). To this end, we represent the integral of motion $t(R)$ in the form

$$t(R) = i\tau_{\omega} - \frac{1}{\omega (R - R_0)} \exp(-\omega \tau_{\omega}),$$

where $\tau_{\omega}$ is the collision time defined in (9b). Inasmuch as at high frequencies $\omega \tau_{\omega}^{-1}$ the main contribution to the integrals (8a) is made by complex values of $R$, for which $U(R)$ is large for a Morse potential, $t(R)$ takes the following form (with $\exp \omega \tau_{\omega}$):

$$t(R) = i\tau_{\omega} - \frac{1}{\omega (R - R_0)} \exp(-\omega \tau_{\omega}).$$

Determining $R$ from this and substituting the result in (8a) we obtain with allowance for relation (10b) for the slow variation of $D(R)$ in the region $a S R \leq R_s$

$$D_{\omega}(R) = \frac{A_1 A_2}{4} \frac{\exp(-\omega \tau_{\omega})}{\omega (R - R_0)} \int_{-i\tau_{\omega}}^{i\tau_{\omega}} \exp(i \omega \tau_{\omega}) dt.$$
\[ d(w) = -\chi w (w - \chi) \frac{d\delta}{dw} \left\{ \frac{R_0}{r_0} - \frac{R_0}{r_{\infty}} \right\} \]

\[ \chi \frac{d\delta}{dr} \left\{ \frac{d\delta}{dr} \right\} = -\Delta R_0 \]

\[ \chi = (2(k+1)/3)^{1/3} (k/3)^{(k+1)} \Gamma(1+(k+1)) \]

with \( \gamma \to \infty \) as \( k \to \infty \), and \( T_0 = 3d R_0 / r_{\infty} - R_0 / r_{\infty} \).

At frequencies \( w \geq T_0 \), the transition takes place on the repulsion branch of the term in the vicinity of the bottom of the well (interunuclear distances \( \tilde{R} \rightarrow R \), make no contribution to the integral (8a) because of the rapid oscillations of the integrand). In the region \( w \sim T_0 \), however, the transitions are due to the right-hand branch of the attraction of the term, where the use of the Morse potential and of the approximations (10) and (13) of the term and of the characteristic dimension of the term near this point. The interunuclear distance \( R_{\infty} \) corresponds to the time of motion of the particles \( A^+ \) and \( B \), equal to \( w^{-1} \), i.e., it is determined from the condition \( d(w) = 0 \).

\[ \tilde{R}(R) = \int \frac{dr}{w} = \frac{1}{w} \]

The region of large distances \( R_0 \rightarrow R_{\infty} \) makes no contribution to the transition, for in this case \( R_{\infty} \rightarrow 1 \) and the integrand (8a) oscillates rapidly. The region of small distances is also inessential for transitions with frequencies \( w \leq T_0 \), since the decrease of the velocity and the increase of the characteristic dimension \( \Delta R_0 \) cause the time of passage of the right branch of the term near the point \( R_{\infty} \rightarrow R_0 \), to be much longer than the time of motion along the repulsion branch and near the bottom of the well.

We consider now the frequency region \( T_0 \sim \omega \ll T_0 \), where

\[ T_0 = \frac{2\Delta R_0}{r_{\infty}} \sim \frac{\Delta R_0}{\Delta R_{\infty}} \frac{E_{\infty}}{E_R} \sqrt{\frac{\gamma}{\gamma - 1}} \]

is the time \( T_0 = t \) of motion of the particles \( A^+ \) and \( B \) to the point \( R = b \), determined from the condition \( U(R) = E_i \Delta R_0 = U(b) - \Delta R_0 U(R) \) (the characteristic dimension of the term at this point). In the case of a discrete spectrum \( E_i = E_{\infty} \) (the point \( b \) coincides with the right-hand turning point \( b = b_0 \) of the potential \( U(r) \). In accordance with the discussion above, the transitions with frequencies in the region \( \omega \ll T_0 \) are caused by the region of interunuclear distances beyond the inflection point on the right-hand attraction branch \( R_{\infty} \sim \omega \), where it suffices to use simple approximations of the term and of the dipole moment \( D(R) = D(R) + D(R) \) :
transition frequencies \( v_n \equiv e \omega_n E_0 \). For the case of interest to us, that of transitions in the quasimolecular ion \( \text{He}\text{H}^+ \), the function \( d(\omega) \) is calculated in the frequency region \( 0.01 \text{ eV} < \omega < 0.6 \text{ eV} \) with the aid of (12a) and (16a) on the basis of data\(^\text{39}\) on the term and on the dipole moment of the electron ground state (see Fig. 1).

The quasiclassical Fourier-component method employed here is valid under the following conditions:

\[
\mu \left( R_0 \right) \Delta R_0 \gg 1, \quad \frac{1}{\mu} \mu \left( R_0 \right) = \left[ U \left( R_0 \right) \right] > E, \quad \left| E \right|, \quad \omega, \quad \alpha, \quad \nu,
\]

where \( \mu \left( R_0 \right) \) is the relative velocity of the heavy particles \( A^+ \) and \( B \) at the point \( R_0 \). The second of these conditions is equivalent to the inequality \( R_0 \geq \tilde{b} \), which in fact limits the foregoing analysis to a region of not too low frequencies \( \omega \ll v_n \). At low frequencies \( \omega \ll v_n \), Eq. (9a) is not valid, since the main contribution to the transition is made by the remote section of the term \( R_0 \ll \tilde{b} \), where \( \left| U \left( R_0 \right) \right| \ll E \). For these frequencies, the transitions \( \left( 1 \right) \) of a Rydberg electron will be considered in the shakeup model in Sec. 4.

4. TRANSITIONS BETWEEN RYDBERG STATES OF AN ATOM

In the frequency region \( v_n \equiv e \omega_n E_0 \), the transitions \( \left( 1 \right) \) of a highly excited electron will be considered on the basis of the quasiclassical formulas of Sec. 3. For the investigated \( n \rightarrow n' \) transitions the only important collisions of the heavy atoms \( A^+ \) and \( B \) are those in which they are captured into the region of short distances with subsequent reflection from the repulsion branch of the potential. At energies \( E \ll E_0 \), the capture of the particles \( A^+ \) and \( B \) takes place at larger distances \( R_0 \ll \tilde{b} \), on the right-hand branch of the term \( \left( 12 \right) \), so that the corresponding cross sections

\[
\sigma_{n \rightarrow n'} \left( E \right) = v \frac{n^2}{v^2 - 2} \left( \frac{v}{2} \right)^{2n} \left( \frac{2 \pi}{2E} \right)^{2n} \chi_{n}^{2n} \chi_{n'}^{2n'} \left( 15 \right)
\]

exceed significantly the gaskinetic cross sections. At \( \rho \ll \rho_{\text{max}} \left( E \right) \) the values of the matrix elements of the transition are drastically decreased. This is due to the substantial increase of the particle collision time \( \tau_{\rho} \ll \rho_{\text{max}} \left( E \right) \), as the reflection takes place at \( \rho \ll \rho_{\text{max}} \) no longer from the repulsion branch of the term, but from the centrifugal barrier. Accordingly the matrix elements \( D_{f} \left( \rho \ll \rho_{\text{max}} \right) \) undergo an adiabatic decrease for all the considered frequencies \( \omega \ll v_n \ll \rho_{\text{max}} \left( E \right) \).

At \( \rho \ll \rho_{\text{max}} \), the matrix elements \( D_{f} \left( \rho \right) \) can be regarded in the zeroth approximation as independent of \( \rho \) in the frequency range \( v_n \equiv e \omega_n E_0 \) i.e., \( D_{f} \left( \rho \ll \rho_{\text{max}} \right) = D_{f} \left( \rho = 0 \right) \). Indeed, for each value of \( \omega \) we can separate a range of variation of the orbital angular momentum \( 0 \leq J \leq J_{\text{max}} \left( \omega \right) \), in which the characteristics of the effective potential

\[
U(J) = U \left( J \right) + \left( J + 1 \right) \left( J + 1 \right) \frac{\mu}{2 R^2}
\]

coincide with the corresponding characteristics of the term \( U \left( R \right) \) in the transition region (i.e., at \( R = R_{\text{c}} \)). The value of \( J_{\text{max}} \left( \omega \right) \) is determined from the condition \( \left| U \left( R_{\text{c}} \right) \right| = J_{\text{max}} \left( \omega \right) / 2 p R_{\text{c}} \), meaning

\[
J_{\text{max}} \left( \omega \right) = \left\{ \begin{array}{ll} v_n E_0 \left( R_{\text{c}} \right) \left( \frac{\pi}{2} \right)^{2n} \left( \frac{2 \pi}{2E} \right)^{2n} \chi_{n}^{2n} \chi_{n'}^{2n'} \left( 15 \right) & \text{if } \omega \ll v_n \ll \rho_{\text{max}} \left( E \right) \end{array} \right.
\]

with \( J_{\text{max}} \left( \omega \right) = \rho_{\text{max}} \left( E \right) \left( R_{\text{c}} \right) > 1 \) in the region of the quasiclassical approach. Comparison of \( J_{\text{max}} \) and \( J_{\text{max}} \equiv \rho_{\text{max}} \left( E \right) \) [see (15)] shows that \( J_{\text{max}} \left( \omega \right) \ll J_{\text{max}} \equiv \rho_{\text{max}} \left( E \right) \) in the case \( E > E_0 \) and \( \omega > v_n \) of interest to us.

These arguments concerning the behavior of \( D_{f} \left( \rho \right) \) permit summation over \( J \) in the quantum-mechanical expression (6) (or integration over the impact parameter \( p = J / \rho \) with the aid of the following formula:

\[
\frac{1}{\rho^2} \int \left[ \left( J + 1 \right) \left( J + 1 \right) \frac{1}{2E} D^{(2E)} \left( J \right) + J \left( J + 1 \right) \right] dJ dE
\]

where (16a) and (16b) refer respectively to the cases \( E > E_0 \) and \( E < E_0 \). Then, using (7b) and (9a), we arrive at the following expressions for the total cross sections for excitation \( n \rightarrow n' \) and de-excitation \( n' \rightarrow n \) of the Rydberg states of the atom

\[
\sigma_{n \rightarrow n'} \left( E \right) = \frac{2}{n^2} \frac{E - E_0}{E_{\text{max}}} \sigma_{n \rightarrow n'} \left( E = E_{\text{max}} \right)
\]

\[
\sigma_{n' \rightarrow n} \left( E \right) = \frac{2}{n^2} \frac{E - E_0}{E_{\text{max}}} \sigma_{n' \rightarrow n} \left( E = E_{\text{max}} \right)
\]

\[
\frac{v_n}{n^2} \left( 15 \right) \left( \frac{\pi}{2} \right)^{2n} \left( \frac{2 \pi}{2E} \right)^{2n} \chi_{n}^{2n} \chi_{n'}^{2n'} \left( 15 \right)
\]

\[
\frac{v_n}{n^2} \left( 15 \right) \left( \frac{\pi}{2} \right)^{2n} \left( \frac{2 \pi}{2E} \right)^{2n} \chi_{n}^{2n} \chi_{n'}^{2n'} \left( 15 \right)
\]
The region of applicability of (17) (see the conditions in the parentheses) is certainly justified, since the corresponding transition probabilities are small: \( \sigma_{\text{mix}} \ll \sigma_{\text{coll}} \). Averaging expressions (17) over the Maxwellian distribution of the heavy particles we obtain for the rate constants for de-excitation \( \{k_{\text{mix}}(T)\} \) and excitation \( \{k_{\text{exc}}(T)\} \) of an atom \( A(n) \) by the neutrals \( B \), respectively

\[
\begin{align*}
\frac{k_{\text{mix}}(T)}{v_{\text{E}/M_\ast}} & = \frac{1}{n^2} \exp \left( -\frac{u_{\text{m}}}{T} \right) k_{\text{mix}}(T), \\
\frac{k_{\text{exc}}(T)}{v_{\text{E}/M_\ast}} & = \frac{1}{n^2} \exp \left( -\frac{u_{\text{m}}}{T} \right) k_{\text{exc}}(T).
\end{align*}
\]

(18)

We consider now the opposite limiting case of small frequencies \( \omega_{\text{m}} \) of the Rydberg electron

\[
\omega_{\text{m}} = \frac{1}{n^2} \sum \left( \frac{\ln(m|e^{-ni\Phi^m}|^2)}{n^2} \right),
\]

where \( \Phi = \Phi' - \Phi''/\mu M_\ast \) is the change of the velocity of the atomic core \( A^+ \) in collision with \( B \), and \( \Phi' \) and \( \Phi'' \) are the relative velocities of the nuclei before and after the impact. The second equation in (19) holds only for \( \mu \text{v}/\mu M_\ast \ll 4\pi \rho \), when it suffices to retain the first term of the expansion of the exponential \( \exp(-n\Phi) \), which is equivalent to the condition for the applicability of perturbation theory. Calculating next the sum in (19) (Ref. 26, pp. 423 of Russ. transl.), integrating the probabilities \( u_{\text{m}}(\rho) \) over the impact parameters, we obtain ultimately for the total cross section \( \sigma_{\text{m}}(E) \) of the \( n\rightarrow n' \) transition

\[
\sigma_{\text{m}}(E) = \frac{4}{3\pi^3} \left( \frac{\mu^2}{M_\ast} \right) \frac{u_{\text{m}}^2}{n^2} \sigma_{\text{coll}}(E),
\]

\[
\sigma_{\text{mix}}(E) = \frac{\sigma_{\text{m}}(E)}{2} \left[ 1 - \cos \Theta \left( \rho' \right) \right] 2\pi \rho dp.
\]

(20)

Here \( \sigma_{\text{m}} \) is the transport cross section for the scattering of particles \( A^+ \) and \( B \), and coincides practically with the capture cross section (15). From this we obtain for the corresponding rate constant in the case of Maxwellian distribution of heavy particles

\[
k_{\text{mix}}(T) = \left( 2/\pi \right) \Gamma \left( 3/2 \right) v_{\text{E}/M_\ast} \sigma_{\text{mix}}(T),
\]

(21)

where Eqs. (20) and (21) pertain equally well to the case of de-excitation and excitation of a Rydberg electron.

Let us explain the physical meaning of the obtained formulas using as an example the transitions (1) between neighboring Rydberg levels, \( n-n' \), of the atom \( A(n) \). For greater clarity we take into account only the fundamental noninertial effect [the first term in (4)] and neglect completely the dipole interaction connected with the redistribution of the electron density in the quasimolecular ion \( BA^+ \).

For the system \( \text{He}(n) + \text{He}(1s) \) the contribution of the second effect to the total cross section (17) turns out to be maximal at sufficiently low levels \( n \sim 5 \) [where \( \omega \sim \tau_1^{-1} \) and \( \tau_1 \sim \tau_2^{-1} \) and amounts to approximately 30% of the cross section for the noninertional transition. With increasing \( n \), the role of the noninertional mechanism becomes even greater because of the decrease of \( D''(R) \) at \( R \sim R_1 \). This enables us to write Eqs. (17) and (20) in the following unified form for the entire considered region \( \omega < 1/n^4 \)

\[
\sigma_{\text{mix}}(E) = \left( \mu/\mu M_\ast \right) \sigma_{\text{coll}}(E) n^2 u_{\text{m}},
\]

\[
(2\pi \rho)(\rho') \sim n^{-2} \sigma_{\text{mix}}(E) \rho R \exp(-2\mu R/R_1). \]

It follows therefore that the cross sections \( \sigma_{\text{mix}} \) are proportional to the quantity \( n^2(R) \), and in the shakeup region (where the main contribution to the transition is made by large distances \( R \sim \rho \)), the \( \sigma_{\text{mix}} \) decreases with increasing \( n \) like \( n^2 \).

In the opposite limiting case \( \omega \sim \tau_1^{-1} \) the transitions take place in the region of internuclear distances \( R_1 \sim \rho \), in which the relative velocity \( \rho \) of the particles \( A^+ \) and \( B \) increases considerably with increasing \( n \) owing to their acceleration in the potential well of the interatomic interaction, and reaches value \( \rho \sim n^{-1} \), which in the velocity \( \rho \) causes the cross sections to change little with decreasing principal quantum number in the frequency region \( \omega^{-1} \sim \omega \tau_1^{-1} \) [see Fig. 2]. The decrease of the cross section sets in only at \( n \sim 10^{-1/3} \), i.e., in the adiabatic region of frequencies \( \omega \sim \tau_1^{-1} \), with \( \sigma_{\text{mix}} \sim n \sim 10^{-1/3} \) change rapidly [see Eqs. (17) and (20)] with increasing \( n \).

To compare the results on the cross sections of the transitions with change of the principal (1) and orbital (2) quantum numbers of the Rydberg electron, we present a formula for the total I-mixing cross section. In the case when the \( n \rightarrow n' \) transitions in the \( A(n) \) atom are due to collisions of the neutral particle \( B \) with the core \( A \), the total I-mixing cross section \( \sigma_{\text{mix}}(E) \) will be determined with the aid of the shakeup model, just as in the derivation of Eq. (20). Using the expression for the sum \( \sum_{n\rightarrow n'} \left( \frac{\text{nl} |n' \pi m' \rangle}{|n \pi m \rangle} \right)^2 \) (Ref. 26, pp. 399 and 413 of Russ. transl.), we have

\[
\sum_{n\rightarrow n'} \left( \frac{\text{nl} |n' \pi m' \rangle}{|n \pi m \rangle} \right)^2 = \left( \frac{\text{nl} |\pi m \rangle}{|n \rangle} \right)^2 \sum_{n\rightarrow n'} \left( \frac{\text{nl} |\pi m \rangle}{|n \rangle} \right)^2.
\]

This enables us to write Eqs. (17) and (20) in the following unified form for the entire considered region \( \omega < 1/n^4 \)
curves 4 and 5 of the transitions of Ref. 22 and to the calculation of Ref. 15 for the quenching of the \( n \) levels of \( \text{H}(n) = 1 \) by helium atoms.

\[
a_{n}(E) = \frac{2}{3} \left( \frac{\mu\nu}{M_j} \right)^{1/3} \int_{1-\cos E(\phi)}^{1} \left( \ln(1+q) \right)^{1/2} \frac{1}{2l+1} \sum_{m'} (n,n\ell',l') a_{n'}(E),
\]

The result (22) coincides with a formula obtained earlier\(^{13}\) as a particular case of the general solution of the problem of \( l \)-mixing on account of the noninertial mechanism, and is valid for all values of \( n \) in the range 4 \( \leq n \leq 10 \) (i.e., for 4 \( \leq n \leq 30 \) in the case of the system \( \text{H}(n\ell) + \text{He}(1\ell) \) at thermal collision velocities).

5. DISCUSSION OF RESULTS

We discuss the results of concrete calculations of the cross sections and rate constants of the transitions (1) and (2), performed in the energy (temperature) range 0.02 \( \leq E \leq 0.4 \) eV for the case of collision of highly excited hydrogen \( \text{H}(n\ell) \) [or \( \text{H}(n) \)] with helium atoms \( \text{He}(1\ell) \).

1. From the calculation (see Fig. 2) of the cross sections for the de-excitation \( n \rightarrow n + 1 \) [Eqs. (17), (20)] and quenching of the \( n \ell \) levels (22) we draw the following conclusion: in the quantum number region \( n \approx 10^{-15} \), the noninertial transitions with change of the principal quantum number \( n \rightarrow n' \) are much more effective than those with change of only the orbital momentum \( (nl \rightarrow nl') \). In the shakedown region \( n \approx 10^{-15} \), i.e., at \( 10^{-15} \leq n \leq 30 \) or \( 10^{-15} \leq n \leq 40 \), however, these transitions are approximately equally probable. In all the considered regions \( n \approx 10^{-15} \) (i.e., \( n \leq 30 \)–40), the quenching of the \( n \ell \) levels or the establishment of equilibrium over the \( l \) sublevels is due to a mechanism that is more effective for \( l \)-mixing, namely direct collision of the Rydberg electron with the neutral particle. The corresponding cross sections (see, e.g., the experimental data of Ref. 22 shown in Fig. 2, as well as the calculations of Refs. 14–21) exceed by more than two orders of magnitude the cross sections for both the transition \( n \rightarrow n' \) and \( n\ell \rightarrow n\ell' \), owing to the noninertial mechanism.

2. Of basic interest is the comparison, shown in Fig. 3, of the rates of de-excitation of the \( n \)-levels \( k_{n \rightarrow n'}(T) \), calculated from Eqs. (18) and (21), with the corresponding rates \( k'_{n \rightarrow n'}(T) \) due to the elastic mechanism, calculated in Refs. 4 and 5. This comparison points to predominance of the mechanism investigated here for the transitions \( n \rightarrow n' \) in the region \( n \approx 10^{-15} \) and also at \( n \geq 20 \)–25. The effectiveness of the noninertial mechanism at \( n \geq 20 \)–25 is attributed to the fact that its limiting cross sections (at \( n \rightarrow n \ell \approx 10^{-15} \)) turn out to be of the order of the transport cross section for the scattering of the \( \text{H}^+ \) ion by the atom \( \text{He}(1\ell) \) [\( \sigma_{\text{He}}^{\text{el}} = 60 \AA^2 \) at \( E = 300 \text{ K} \)]. At the same time, for the elastic mechanism\(^{5}\) the cross sections of the \( n \rightarrow n' \) transitions are expressed in terms of the transport cross section for the scattering of a slow electron by a helium atom [\( \sigma_{\text{He}}^{\text{el}} = 5 \AA^2 \)], which is more than 10 times smaller. At \( n \approx 10 \)–15 the \( n \rightarrow n' \) transitions produced in the hydrogen atom \( \text{H}(n) \) by collision of the atom \( \text{He} \) with the proton \( \text{H}^+ \) are highly effective both because \( \sigma_{\text{He}}^{\text{el}} \) is large and because the relative velocity of the
heavy particles increases substantially when they move in the region \( R < R_{\text{break}} \).

3. It can be seen from Fig. 4 that collision quenching total rate \( K_n = \sum_{a} \sigma_{na} \omega_{na} n(\text{H}_n) \) of the levels of hydrogen \( \text{H}(n) \) with \( n \geq 6 \) greatly exceeds their radiative decay \( \lambda_n = \sum_{a} \omega_{na} n(\text{H}_n) \) even and helium densities \( n(\text{H}_n) > 10^{17} \) cm\(^{-3} \). This makes possible measurement of the cross sections and rates of the transitions \( (n \rightarrow n') \) with decreasing principal quantum number of a Rydberg electron in a weakly ionized plasma of \( \text{H}_2 \) and \( \text{He} \). These measurements can be performed, e.g., on the basis of the dependence of the radiation intensity of the highly excited levels of the hydrogen atoms \( \text{H}(n) \) produced in such a plasma on the pressure of the buffer gas (helium). Experiments of this type on \( n \rightarrow n' \) transitions are undoubtedly of interest for the study of the relaxation of a dense low-temperature plasma.

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"The noninertial mechanism of transitions between Rydberg states of an atom was discussed also in Refs. 25. As shown in Refs. 10–13, however, the analysis there is in error. The author of Refs. 25 arrives at the incorrect conclusion that the maximum cross sections of the noninertial transitions \( n \rightarrow n' \) and \( \alpha \rightarrow \alpha' \) are determined not by the transport cross section \( \sigma_{\alpha,\alpha'} \) but by the elastic cross section \( \sigma_{\alpha,\alpha} \) for scattering of the neutral particle \( \alpha \) by the atomic core \( \alpha' \). At thermal collision energies, however, \( \sigma_{\alpha,\alpha'} \ll \sigma_{\alpha,\alpha} \), so that the result of Eq. (25) greatly overestimates the cross sections for noninertial transitions.

"The particles \( \alpha \) and \( \beta \) go through such transitions in reactions analogous to \( (n \rightarrow n') \) in their mechanism, but with formation or decay of molecular ion \( \alpha \beta \) (associative ionization), with excitation of vibrational level by electron impact, etc.

"Equation (9a) with the function \( d(\omega) = \omega 
\) (see [Eq. (12a)]) is the quasi-

"We note that the condition for the validity of Eq. (17) can be written in a more useful form: \( a_s E_{\alpha,\alpha'} \omega_{\alpha,\alpha} \) if it is recognized that the characteristic dimension \( A_\alpha = \sqrt{\frac{\omega_{\alpha,\alpha}}{\omega_{\alpha,\alpha}}} \) is of the order of one atomic unit (at thermal velocities of the collision of the particles \( \alpha' \) and \( \beta \)).