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

V. S. Lebedev and V. S. Marchenko

P. N. Lebedev Physics Institute, USSR Academy of Sciences
(Submitted 31 May 1982)
Zh. Eksp. Teor. Fiz. **84**, 1623–1637 (May 1983)

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($1s^2$). It is shown that the cross sections and rates of the $n \to n'$ 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 $nl \to nl'$ transitions with change of only the orbital momentum.

PACS numbers: 34.50.Hc, 34.20.Be, 31.50. + w

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 $n \to n'$ 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, $r_n \sim n^2$ 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^-).[6–8]

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

$$A(n)+B \rightleftarrows A(n')+B, \tag{1}$$

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 mechansim, the transitions (1) can be due to two causes. The principal effect is the result of the inertia 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 $v_E = (2E/\mu)^{1/2} \ll \Delta n/n^3$. ($\mu$ is the reduced mass of the heavy particles) was carried out in Ref. 9.

The noninertial mechanism proposed in Ref. 10 was investigated earlier[11–13] 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 core A^+ does not make a substantial contribution to the transitions $nl \to nl'$. 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-

 0038-5646/83/050946-09$04.00

whelming majority of the recent theoretical and experimental studies of l-mixing (see Refs. 14–23 and the review[1]).

The analysis presented here leads to the following basic conclusion: for transitions with change $n \to n'$ 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 $H(n) + He(1s^2)$ as a result of the comparison with calculations[4,5] based on the competing mechanism of elastic scattering of a Rydberg electron by a neutral particle.[3] 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 $v_E \ll (\Delta n/n)^2$ (for thermal velocities of relative motion of heavy particles this yields $n \lesssim 30$–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_0. 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 $n \to n'$ 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 with the well, compared with the case of the repulsion (i.e., $\tau_a \sim \omega_e^{-1}$, where ω_e is the lower vibrational quantum of the ion BA^+), the adiabatic decrease of the cross sections $\sigma_{nn'}$ sets in at sufficiently low values of n, for which $\omega_{nn'} \gg \omega_e$ or $n \lesssim 5$ for the system $H(n) + He(1s^2)$. In the intermediate frequency region $v_E \ll \omega_{nn'} = \Delta n/n^3 \ll \omega_e (5 \lesssim n \lesssim 10$–$15)$ the $n \to n'$ transitions which occur when a neutral particle B passes near the atomic core A^+ becomes nonadiabatic. The cross sections and the rate constants of these transitions do not decrease drastically (as in the case of the mechanism of Refs. 3–5, due to scattering of the Rydberg electron e^- by a neutral B, see Figs. 2 and 3), and it is 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 $\omega_{nn'} = \Delta n/n^3 \ll v_E (n \gg 10$–$15)$ can be described by the simple "shakeup" model (see, e.g., Ref. 24, 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 $R_e \ll \rho_{cap} \lesssim R_\omega \ll n^2$ (ρ_{cap}—is 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[10] semiclassical formula for the cross sections of noninertial[1)] transitions $n \to n'$ pertains 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 $v_E \gg \mu^{-1}$.

For comparison, we analyze also the noninertial mechanism of transitions with change of only the orbital momentum:

$$A(nl) + B \to A(nl') + B. \tag{2}$$

For this case the behavior of the cross sections as functions of n is much simpler, since the entire region $v_E \ll 1/n^2$ considered by us by perturbation theory is the shakeup region. The results obtained in this case for $nl \to nl'$ 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^-. 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 $r_n \sim n^2$ of its orbit. Therefore, the system (A^+, B, e^-) 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^+, B, e^-) in the form

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{H}_{BA^+}(\mathbf{R}) + \hat{H}_e(\mathbf{r}) + \hat{V}(\mathbf{r}, \mathbf{R}), \tag{3}$$

$$\hat{H}_{BA^+}(\mathbf{R}) = \frac{\hat{p}_R^2}{2\mu} + \frac{\hat{M}^2}{2\mu R^2} + U(R), \qquad \hat{H}_e(\mathbf{r}) = -\frac{\Delta_\mathbf{r}}{2} - \frac{1}{r}$$

(we use here 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 $H_{BA^+}(\mathbf{R})$ is the Hamiltonian of the isolated ion BA^+ in the electronic ground state, $\mathbf{R}$ is the radius vector joining the nuclei B and A^+, μ is their reduced mass, $\hat{p}_R$ and $\hat{M}$ are the radial-momentum and angular-momentum operators, $U(R)$ is the electronic term, $\hat{H}_e(\mathbf{r})$ is the Hamiltonian of an outer electron in a Coulomb field, and $\mathbf{r}$ is its radius vector. The operator $\hat{V}(\mathbf{r}, \mathbf{R})$ is the interaction energy of two subsystems e^- and BA^+, and is determined principally by the long-range electron-dipole interaction:

$$\hat{V}(\mathbf{r}, \mathbf{R}) = -\frac{\mathbf{D}\mathbf{r}}{r^3} = -\frac{\mu}{M_{A^+}}\frac{\mathbf{R}\mathbf{r}}{r^3} - \frac{\mathbf{D}^{nl}(R)\mathbf{r}}{r^3}. \tag{4}$$

Here $\mathbf{D}(R) = \mathbf{D}^l(R) + \mathbf{D}^{nl}(R)$ is the dipole moment of the ion BA^+ relative to the mass center of the particles A^+ and B. The linear part $\mathbf{D}^l(R) = \mathbf{R}_{A^+}$ corresponds to the contribution made to $\mathbf{D}(R)$ by the positive Coulomb center A^+ ($\mathbf{R}_{A^+} = \mu\mathbf{R}/M_{A^+}$ is the radius vector and M_{A^+} is the mass of the nucleus A^+). With the aid of the Ehrenfest theorem we have $\mathbf{r} = \mathbf{r}/r^3, \mu\mathbf{R} = -\nabla_\mathbf{R} U$, and the interaction (4) can be rewritten in the form $\hat{V} = \ddot{\mathbf{R}}_{A^+}\mathbf{r}$. 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 $\mathbf{D}^{nl}(R)$, however, is the result (just as in the case of neutral molecules) of displacement (polarization at $R \gg 1$ a.u.) of the inner electrons relative to the nuclei A^+ and B in the quasimolecular ion BA^+.

We shall regard the operator $\hat{V}(\mathbf{r},\mathbf{R})$ (4) as a perturbation in the Hamiltonian (3). We shall be interested in the transition $n \to n'$(1) cross sections averaged over the initial (l and m) and summed over the final (l' and m') orbital and magnetic quantum numbers of the Rydberg electron. If the atom B and the ion A^+ have in the initial state $|i\rangle$ an energy $E = q^2/2\mu$ and a wave vector $\mathbf{q} = (q,\vartheta_q,\varphi_q)$, while in the final state $|f\rangle$ their wave vector lies in the interval $(\mathbf{q}',\mathbf{q}' + d\mathbf{q}')$, by normalizing the initial wave function $(\mu/q)^{1/2}\Psi_q{}^+(\mathbf{R})$ of the motion of the nuclei to unity flux of the incident particles, and the final wave function $(2\pi)^{-3/2}\Psi_q - (\mathbf{R})$ to a δ function of $\mathbf{q} - \mathbf{q}'$ we have for the electron differential excitation (de-excitation) cross section

$$d\sigma_{nn'}(\mathbf{q},\mathbf{q}') = \frac{\mu}{4\pi^2 q n^2}\sum_{lm,l'm'}\left|\langle\Psi_q{}^+|\left\langle nlm\left|\frac{\mathbf{Dr}}{r^3}\right|n'l'm'\right\rangle|\Psi_{q'}{}^-\rangle\right|^2 \times\delta(E+\varepsilon_n-\varepsilon_{n'}-E')\,q'^2\,dq'\,dO_{\mathbf{q}'}. \quad (5)$$

The wave functions $\Psi_q{}^+(\mathbf{R})$ and $\Psi_q{}^-(\mathbf{R})$ 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 $\varepsilon_n = -1/2n^2$ and final energy $\varepsilon_{n'} = -1/2n'^2$.

Intergrating the result (5) over all the values of the wave numbers dq' and all the possible directions $dO_{q'}$ of the particles A^+ and B in the final state, and averaging over the directions dO_q in the initial state, we obtain for the total cross section $\sigma_{nn'}(q)$, after a number of transformations:

$$\sigma_{nn'}(q) = 4\pi^3\frac{\mu^2}{q^3q'}\sum_{lm,l'm'}\sum_{JJ_z,J'J_z'}\left|\left\langle\frac{1}{R}\chi_{qJ}|\langle JJ_z|\langle nlm|\right.\right. \times\frac{\mathbf{Dr}}{r^3}|n'l'm'\rangle|J'J_z'\rangle|\left.\left.\frac{1}{R}\chi_{q'J'}\right\rangle\right|^2$$

where

$$\left|\frac{1}{R}\chi_{qJ}(R)\right\rangle$$

is the radial part of the wave function of the relative motion of the nuclei A^+ and B (normalization of a δ function of the wave number $q = (2\mu E)^{1/2}$, and $|JJ_z\rangle = Y_{JJz}(\theta,\Phi)$ is its angular part (J and J_z 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_z and J_z' (the selection rule $J' = J \pm 1$) and changing from the wave fucntion $\chi_{qJ}(R)$ to the function $\chi_{EJ}(R)$ normalized to $\delta(E - E')$, we obtain for the total cross section $\sigma_{nn'}(E)$ for excitation (de-excitation) of a Rydberg atom A(n) by collision with a neutral particle. Ultimately we obtain

$$\sigma_{nn'}(E) = \frac{8\pi^2}{3\sqrt{3}}\frac{g(n,n')}{n^5n'^3}\frac{1}{q^2}\sum_J[(J+1)|D_{EE'}^{(J,J+1)}|^2 + J|D_{EE'}^{(J,J-1)}|^2]. \quad (6)$$

In the derivation of this equation we used also the Ehrenfest theorem for the matrix elements of a transition in a Coulomb field

$$(\mathbf{r}/r^3)_{nlm}^{n'l'm'} = \omega_{nn'}^2\mathbf{r}_{nlm}^{n'l'm'} \quad (\omega_{nn'} = \varepsilon_n - \varepsilon_{n'} = E' - E)$$

and the known Kramers relation for the sum of the oscillator strengths over the possible degenerate states lm and $l'm'$ (see, e.g., Ref. 26, p. 423 of Russian translation):

$$\sum_{lm,l'm'}\left|\langle nlm|\frac{\mathbf{r}}{r^3}|n'l'm'\rangle\right|^2 = \omega_{nn'}^4\sum_{lm,l'm'}\left|\langle nlm|\mathbf{r}|n'l'm'\rangle\right|^2 = \frac{2}{\pi\sqrt{3}}\frac{g(n,n')}{n^3n'^3}. \quad (7a)$$

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

$$D_{EE'}^{(J,J')} = \left\langle\frac{1}{R}\chi_{EJ}|D(R)|\frac{1}{R}\chi_{E'J'}\right\rangle = \int_0^\infty\chi_{EJ}(R)\,D(R)\,\chi_{E'J'}(R)\,dR. \quad (7b)$$

It must be emphasized that expression (6) obtained by using a coordinate system with origin at the mass center of the colliding particles A^+ and B is valid in the quantum-number region $\Delta n/n^3 \gg v_E$, 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 $\Delta n/n^3 \ll v_E$, 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_0. 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_0. This allows us to calculate the matrix elements of the dipole moment (7a) 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,[2)] with participation of a molecular ion BA^+, on high vibrational-rotational energy levels ($|E_{vJ}| \ll E_0$). We consider all these cases by a single procedure:

$$D_{if}=\frac{A_iA_f}{4}\int_{-\infty}^{+\infty}D[R(t)]e^{i\omega t}\,dt$$

$$=-\frac{A_iA_f}{2\omega}\int_a^{\infty}\frac{dD(R)}{dR}\sin[\omega t(R)]\,dR, \tag{8a}$$

$$t(R)=\left(\frac{\mu}{2}\right)^{1/2}\int_a^R\frac{dR'}{[E-U(R')]^{1/2}}. \tag{8b}$$

Here A_i and A_f are the normalization constants of the initial $|i\rangle$ and final $|f\rangle$ states of the quasimolecular or molecular ion BA^+, with $A_E=(2/\pi)^{1/2}$ and $A_{vJ}=2/T_{vJ}^{1/2}$ for the continuous and discrete spectra (T_{vJ} is the period of the vibrational-rotational motion), $t(R)$ is the time of motion from the left turning point a to the point R in the electron term $U(R)$ of the ion BA^+. When calculating the matrix elements (8a) we shall make use of the procedure used in Ref. 27 to consider radiative transitions of an atom and an ion in a single electron term.

In the case of arbitrary collisions of heavy particles A^+ and B or in the absence of rotational excitation of a bound ion BA^+ the matrix elements $D_{if}^{(J=0)}$ between states close to the dissociation boundary ($E,|E_v|\ll E_0$), can be represented in the form

$$D_{if}^{(J=0)}(\omega)=\frac{\pi}{2}A_iA_f d(\omega)\frac{1}{\omega}\exp(-\omega\tau_a), \tag{9a}$$

$$\tau_a=\left(\frac{\mu}{2}\right)^{1/2}\int_0^a\frac{dR}{[U(R)-E]^{1/2}}. \tag{9b}$$

The type of the transition is taken into account in (9a) with the aid of the normalization constants A_i and A_f. The quantity τ_a is the time of collision of the particles A^+ and B. For a Morse potential, in the approximation in which the dipole moment varies slowly in the vicinity of the bottom of the well $R=R_e$,

$$U(R)=E_0\left[\exp\left(-2\alpha\frac{R-R_e}{R_e}\right)-2\exp\left(-\alpha\frac{R-R_e}{R_e}\right)\right] \tag{10a}$$

$$D(R)=D_e+(dD/dR)_{R_e}(R-R_e). \tag{10b}$$

Formula (9a) can be obtained in a wide range of frequencies $\tau_b^{-1}\ll\omega\ll E_0$ (τ_b is defined below) by directly calculating the Fourier components (8a) in the limit $E,|E_v|\ll E_0$, using the exact expression for the integral of motion[27]:

$$t(R)= \tag{11a}$$

$$=\begin{cases}\dfrac{R_e}{\alpha v_0}\dfrac{1}{|\beta|^{1/2}}\left\{\dfrac{\pi}{2}-\operatorname{arctg}\left[\dfrac{1-|\beta|\pm[1+u(R)]^{1/2}}{|\beta|^{1/2}[-|\beta|-u(R)]^{1/2}}\right]\right\}(\beta<0),\\ \dfrac{R_e}{\alpha v_0}\dfrac{1}{\beta^{1/2}}\ln\left\{\dfrac{1+\beta\pm[1+u(R)]^{1/2}+\beta^{1/2}[\beta-u(R)]^{1/2}}{1\pm[1+u(R)]^{1/2}(1+\beta)^{1/2}}\right\}(\beta>0).\end{cases} \tag{11b}$$

Here $u(R)=U(R)/E_0$, $\beta=E/E_0$, $v_0=(2E_0/\mu)^{1/2}$; the plus sign pertains to motion along the repulsion branch $a\leqslant R\leqslant R_e$, and the minus sign corresponds to the attraction region $R\geqslant R_e$. The function $d(\omega)$ and the collision time τ_a are determined in the zeroth approximation in the parameter $|E|/E_0\ll 1$ by the following expressions[3)]:

$$d(\omega)=\frac{dD}{dR}\Big|_{R_e}\frac{R_e}{\alpha}=\left(\frac{dD^l}{dR}+\frac{dD^{nl}}{dR}\Big|_{R_e}\right)\cdot 3\Delta R_a, \tag{12a}$$

$$\tau_a=\omega_e^{-1}=\frac{R_e}{\alpha(2E_0/\mu)^{1/2}}=\frac{3\Delta R_a}{v_0}. \tag{12b}$$

The collision time τ_a is determined by the characteristic dimension $\Delta R_a=U'(a)/U''(a)$ of the variation of the term in the left-hand turning point $a=R_0$ [where $U(R_0)=0$] and by the rate v_0 of the acceleration of the heavy particles in the potential well. The reciprocal quantity τ_a^{-1} coincides with the value ω_e of the lower vibrational quantum of the BA^+ ion and specifies thus the limit of the adiabatic $\omega\gg\tau_a^{-1}$ and nonadiabatic $\omega\lesssim\tau_a^{-1}$ regions of the transitions.

In the adiabatic region $\omega\gg\tau_a^{-1}$ the result (9a) for the matrix elements D_{if} of the transition in a potential with a well at energies $E,|E_v|\ll E_0$, 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

$$t(R)=i\tau_a-i\left(\frac{\mu}{2}\right)^{1/2}\int_0^R\frac{dR'}{[U(R')-E]^{1/2}},$$

where τ_a is the collision time defined in (9b). Inasmuch as at high frequencies $\omega\tau_a\gg 1$ the main contribution to the integral (8a) is made by complex values of R, for which $U(R)\gg|E|$, for a Morse potential, $t(R)$ takes the following form (with $\exp\alpha\gg 1$):

$$t(R)=i\tau_a-i\frac{R_e}{\alpha v_0}\exp(-\alpha)\left[\exp\left(\alpha\frac{R}{R_e}\right)-1\right].$$

Determining $R(t)$ 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 $a\lesssim R\lesssim R_*$

$$D_{if}^{(J=0)}=\frac{A_iA_f}{4}\frac{dD}{dR}\Big|_{R_e}\frac{R_e}{\alpha}\frac{1}{i\omega}\int_{-\infty}^{+\infty}\frac{e^{i\omega t}\,dt}{t-i\tau_a}.$$

Calculation of this integral by the stationary-phase method (the oscillating exponential $\exp i\omega t$ is transformed into a damped $\exp(-\omega z)$ along the line $z=\operatorname{Im}t$ of the contour enclosing the point $i\tau_a$) leads to Eq. (9a) in which the quantities $d(\omega)$ and τ_a are defined by expressions (12a) and (12b).

A similar analysis for the Lennard-Jones potential

$$U(R)=4E_0\left[\left(\frac{R_0}{R}\right)^{2k}-\left(\frac{R_0}{R}\right)^{k}\right]$$

also leads to Eq. (9a), in which the function $d(\omega)$ is of the form

$$d(\omega)=\gamma_k(\omega\tau_a)^{-1/(k+1)}\frac{dD}{dR}\Big|_{R_\omega}\frac{R_0}{k}=\gamma_k(\omega\tau_a)^{-1/(k+1)}$$

$$\times\left(\frac{dD^l}{dR}+\frac{dD^{nl}}{dR}\Big|_{R_\omega}\right)\cdot 3\Delta R_a,$$

$$\gamma_k=[2(k+1)/k]^{1/(k+1)}(k/\pi)\sin(\pi/(k+1))\Gamma(1+1/(k+1))$$

with $\gamma_k\to 1$ as $k\to\infty$, and $\tau_a=3\Delta R_a/v_0\approx/R_0\ /kv_0$.

At frequencies $\omega\gtrsim\tau_a^{-1}$ the transition takes place on the repulsion branch of the term in the vicinity of the bottom of the well (internuclear distances $R\gg R_e$ make no contribution to the integral (8a) because of the rapid oscillations of the integrand). In the region $\omega\ll\tau_a^{-1}$, 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 approximation (10b) with slow variation of the dipole moment are not valid. Expression (12a) thus becomes generally speaking inapplicable. However, an analytic calculation can be carried out by recognizing that the main contribution to D_{if} is made by the vicinity of a certain point R_ω of the order of the characteristic dimension of the term near this point. The internuclear distance R_ω corresponds to the time of motion of the particles A^+ and B, equal to ω^{-1}, i.e., it is determined from the condition[4)]

$$t(R_\omega)=\int_a^{R_\omega}\frac{dR}{v(R)}=\frac{1}{\omega}.$$

The region of large distances $R\gg R_\omega$ makes no contribution to the transition, for in this case $\omega t(R_\omega)\gg 1$ and the integrand of (8a) oscillates rapidly. The region of small distances is also inessential for transitions with frequencies $\omega\ll\tau_a^{-1}$, since the decrease of the velocity and the increase of the characteristic dimension ΔR_ω cause the time of passage of the right branch of the term near the point $R_\omega\gg R_e$ 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 $\tau_{\tilde b}^{-1}\ll\omega\ll\tau_a^{-1}$, where

$$\tau_{\tilde b}\approx\frac{2\Delta R_{\tilde b}}{v_E}\sim\tau_a\frac{\Delta R_{\tilde b}}{\Delta R_a}\left(\frac{E_0}{|E|}\right)^{1/2}\gg\tau_a$$

is the time [$\tau_{\tilde b}=t(\tilde b)$, see (8b)] of motion of the particles A^+ and B to the point $R=b$, determined from the condition $|U(\tilde b)|=E$,($\Delta R_{\tilde b}=U'(\tilde b)/U''(\tilde b)$ is the characteristic dimension of the term at this point). In the case of a discrete spectrum ($E\equiv E_v<0$) the point $\tilde b$ coincides with the right-hand turning point $\tilde b=b_c$ of the potential $U(r)$. In accordance with the discussion above, the transitions with frequencies in the region $\tau_{\tilde b}^{-1}\ll\omega\ll\tau_a^{-1}$ are caused by the region of internuclear distances beyond the inflection point on the right-hand attraction branch $R_*\ll\omega\ll\tilde b$, where it suffices to use simple approximations of the term and of the dipole moment [$D(R)=D^l(R)+D^{nl}(R)$]:

$$U(R)=-C_vR^{-v},\quad dD^l/dR=p,\quad dD^{nl}(R)/dR=A_\lambda R^{-\lambda}.\quad (13)$$

When calculating the integral of motion (8b) for the power-law approximations employed here we recognize that at the indicated distances $|U(R)|$ greatly exceeds the energies of the considered states of the discrete $|E_v|$ and continues (E) spectra of the BA^+ ion. Therefore the relative velocity of the heavy particles can be set equal to $v(R)=(2|U(R)|/\mu)^{1/2}$ and calculation of $t(R)$ in (8b) leads to

$$t(R)=x_cR^{(v+2)/2},\qquad R(t)=(t/x_c)^{2/(v+2)};$$

$$x_c=[2/(v+2)]\,(\mu/2C_v)^{1/2}.$$

Substituting this expression in (8a) for the matrix element D_{ij}, we obtain

$$D_{if}^{(J=0)}=\frac{A_iA_f}{\omega}\frac{(\omega x_c)^{-2/(v+2)}}{v+2}\left[p\int_{\omega t_*}^{\omega t_{\tilde b}}y^{2/(v+2)-1}\sin y\,dy\right.$$

$$\left.+A_\lambda(\omega x_c)^{2\lambda/(v+2)}\int_{\omega t_*}^{\omega t_{\tilde b}}y^{2(1-\lambda)/(v+2)}\sin y\,dy\right].$$

By virtue of the inequality $\tau_b\gg\tau_a$ in the considered frequency region $\tau_{\tilde b}^{-1}\ll\omega\ll\tau_a^{-1}$ in the considered frequency region $\tau_{\tilde b}^{-1}\ll\omega\ll\tau_a^{-1}$, the upper limit $\omega t_{\tilde b}\gg 1$ can be set equal to infinity, and the lower $\omega t_*\ll 1$ to zero ($t_*\equiv t(R_*)$ is the time of motion of the particles from the left turning point $a=R_0$ to the inflection point R_*), after which the integrals in this formula can be easily calculated. As a result we obtain for the matrix element of the transition, formula (9a) in which $d(\omega)$ is given by

$$d(\omega)=\left(\xi_v\frac{dD^l}{dR}+\zeta_{v,\lambda}\frac{dD^{nl}}{dR}\Big|_{R_\omega}\right)\Delta R_\omega,\qquad R_\omega=(\omega x_c)^{-2/(v+2)},\qquad (14a)$$

where $\Delta R_\omega=R_\omega/(v+1)$, and the coefficients ξ_v and $\zeta_{v,\lambda}$ are respectively

$$\xi_v=\frac{v+1}{\pi}\sin\left(\frac{\pi}{v+2}\right)\Gamma\left(1+\frac{2}{v+2}\right),$$

$$\zeta_{v,\lambda}=\frac{2(v+1)}{\pi(v+2)}\Gamma\left[\frac{2(\lambda-1)}{v+2}\right]\sin\left[\frac{\pi(\lambda-1)}{v+2}\right].\qquad (14b)$$

The first term in (12a) or (14a) describes in accordance with (4) the contribution made to $d(\omega)$ by a positive Coulomb center, i.e., $dD^l/dR=p=\mu/M_A^*$ (with $\xi_v\to 1$ as $v\to\infty$), the second gives the contribution of the nonlinear component of the dipole moment of the BA^+ ion. The constant $\zeta_{v,\lambda}$ is determined by the ratio λ/v of the characteristic dimensions of the changes of $U(R)$ and $D^{nl}(R)$ on the right-hand branch (with $\zeta_{v,\lambda}\to 1$ as $\lambda/v\to 0$).

It follows from (12a) and (14a) that the quantity $d(\omega)$ is determined by the increment of the dipole moment over the characteristic dimension $\Delta R_\omega=U'(R_\omega)/U''(R_\omega)$ of the term in the vicinity of the point R_ω, which makes the main contribution to the transition. These expressions go over continuously into one another (at $\omega\lesssim\tau_a^{-1}$), if the corresponding approximations (10) and (13) of ther term and of the dipole moment are matched in the distance range $R_*\lesssim R_\omega$ on the right-hand attraction branch. Thus, Eq. (9a) describes in unified fashion the entire considered range of

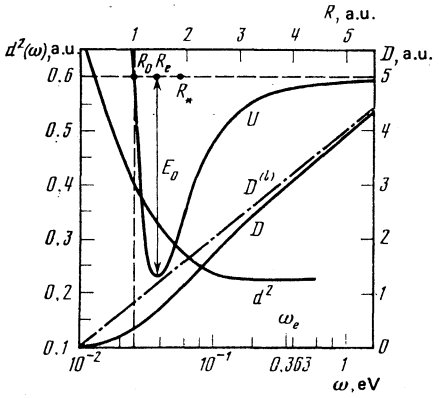

FIG. 1. Forms of the term $U(R)$, of the dipole moment $D(R)$, and of the function $d^2(\omega)$ for the ion $HeH^+(X\,^1\Sigma^+)$. The function $d^2(\omega)$ was calculated using the following approximations for $U(R)$, $D(R)$:0.1 eV$\leqslant\omega\leqslant$0.6 eV (1 a.u.$\leqslant R_\omega\leqslant$2.5 a.u.) is the Morse potential with parameters$dD/dR = \langle dD/dR\rangle = 0.84$ a.u. [see Eq. (12a)]; 0.01 eV$\leqslant\omega\leqslant$0.1 eV (2.5 a.u.$\leqslant R_\omega\leqslant$5.5 a.u.), $U(R)$ and $dD^{n'}/dR$ are power functions with parameters $\alpha = 2.3$, $E_0 = 1.85$ eV, $R_e = 1.4$ a.u. $C_\nu = 0.835$ a.u., $\nu = 3.8$ and $A_\lambda = 2.8$ a.u., $\lambda = 2.8$ while $dD^1/dR = \mu/M_H = 0.8$ a.u. ($\xi_\nu = 0.7$; $\zeta_{\nu,\lambda} = 1.7$ [see Eqs. (14a,b)]

transition frequencies $\tau_b^{-1} \ll \omega \ll E_0$. For the case of interest to us, that of transitions in the quasimolecular ion HeH^+, the function $d(\omega)$ is calculated in the frequency region 0.01 eV$\leqslant\omega\leqslant$0.6 eV with the aid of (12a) and (14a) on the basis of data[32] 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:

$$\mu v(R_\omega)\Delta R_\omega \gg 1, \quad {}^1/_2\mu v^2(R_\omega) = |U(R_\omega)| \gg E, \quad |E_v|, \quad \omega,$$

where $v(R_\omega)$ is the relative velocity of the heavy particles A^+ and B at the point R_ω. The second of these conditions is equivalent to the inequality $R_\omega \gtrsim \tilde{b}$, which in fact limits the foregoing analysis to a region of not too low frequencies $\omega \gg \tau_b^{-1}$. At low frequencies $\omega \lesssim \tau_b^{-1}$ Eq. (9a) is not valid, since the main contribution to the transition is made by the remote section of the term $R_\omega \gtrsim \tilde{b}$, where $|U(R_\omega| \lesssim E$. For these frequencies, the transitions (1) 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 $\tau_b^{-1} \ll \omega \ll E_0$, the transitions (1) of a highly excited electron will be considered on the basis of the quasiclassical formulas of Sec. 3. For the investigated $n \to n'$ 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 $R \sim \tilde{b}_E \gg R_e$ on the right-hand branch of the term (12), so that the corresponding cross sections

$$\sigma_{cap}(E) = \pi\rho_{cap}^2(E) = \pi\left(\frac{\nu}{\nu-2}\right)^{(\nu-2)/\nu}\left(\frac{\nu C_\nu}{2E}\right)^{2/\nu} \qquad (15)$$

exceed significantly the gaskinetic cross sections. At $\rho > \rho_{cap}(E)$ the values of the matrix elements of the transition are drastically decreased. This is due to the substantial increase of the particle collision time $\tau(\rho > \rho_{cap} \sim \rho/v_E \gg \tau_a(\rho \leqslant \rho_{cap}) \sim \omega_e^{-1}$, inasmuch as their reflection takes place at $\rho > \rho_{cap}$ no longer from the repulsion branch of the term, but from the centrifugal barrier. Accordingly the matrix elements $D_{if}(\rho > \rho_{cap}) \sim \exp(-\omega\rho/v_E)$ undergo an adiabatic decrease for all the considered frequencies $\omega > \tau_b^{-1} > v_E/\rho_{cap}$.

At $\rho \leqslant \rho_{cap}$ the matrix elements $D_{if}(\rho)$ can be regarded in the zeroth approximation as independent of ρ in the frequency range $\tau_b^{-1} \ll \omega \ll E_0$, i.e., $D_{if}(\rho \leqslant \rho_{cap}) = D_{if}(\rho = 0)$. Indeed, for each value of ω we can separate a range of variation of the orbital angular momentum $0 \leqslant J = q\rho \ll J_{max}(\omega)$, in which the characteristics of the effective potential

$$U^{(J)}(R) = U(R) + (J+{}^1/_2)^2/2\mu R^2$$

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

$$J_{max}(\omega) = \begin{cases} \sim (2\mu E_0)^{1/2} R_e \quad (\tau_a^{-1} \lesssim \omega \ll E_0), \\ (2\mu C_\nu)^{1/2} (\omega x_C)^{(\nu-2)/(\nu+2)} \sim (2\mu E_0)^{1/2} R_e (\omega\tau_a)^{(\nu-2)/(\nu+2)} \\ \quad (\tau_b^{-1} \ll \omega \ll \tau_a^{-1}), \end{cases}$$

with $J_{max}(\omega) = \mu v(R_\omega) R_\omega \gg 1$ in the region of the quasiclassical approach. Comparison of J_{max} and $J_{cap} = q\rho_{cap}$ [see (15)] shows that $J_{cap}(E) \ll J_{max}(\omega)$ in the case $E \ll E_0$ and $\omega > \tau_b^{-1}$ of interest to us.

These arguments concerning the behavior of $D_{if}(J)$ permit summation over J in the quantum-mechanical expression (6) (or integration over the impact parameters $\rho = J/q$) with the aid of the following formula:

$$\frac{\pi}{q^2}\sum_J [(J+1)|D_{EE'}^{(J,J+1)}|^2 + J|D_{EE'}^{(J,J-1)}|^2] \qquad (16a)$$

$$= \begin{cases} \int_0^\infty |D_{EE'}(\rho)|^2 \cdot 2\pi\rho\, d\rho = |D_{EE'}(\rho=0)|^2 \sigma_{cap}(E), \\ \frac{q'^2}{q^2}\int_0^\infty |D_{EE'}(\rho)|^2 \cdot 2\pi\rho\, d\rho = \frac{q'^2}{q^2}|D_{EE'}(\rho=0)|^2 \sigma_{cap}(E'), \end{cases} \qquad (16b)$$

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

$$\sigma_{n'n}(E') = \frac{n^2}{n'^2}\frac{E' - \omega_{nn'}}{E'}\sigma_{nn'}(E' - \omega_{nn'}) \qquad (17a)$$

$$\left(\frac{v_E}{2\Delta R_{\tilde{b}}} \ll \omega_{nn'} \ll E_0, \quad n^2 \gg \rho_{cap}(E)\right),$$

$$\sigma_{nn'}(E)=\frac{8\pi}{3\sqrt{3}}\frac{d^2(\omega_{nn'})}{n^5n'^3\omega^2_{nn'}}\exp(-2\omega_{nn'}\tau_a)\sigma_{cap}(E). \quad (17b)$$

We see therefore that the use of perturbation theory in the region of applicability of (17) (see the conditions in the parentheses)[5)] is certainly justified, since the corresponding transition probabilities are small: $\sigma_{nn'}\ll\sigma_{\text{cap}}$. Averaging expressions (17) over the Maxwellian distribution of the heavy particles we obtain for the rate constants for de-excitation $[k_{nn'}(t)]$ and excitation $[k_{n'n}(T)]$ of an atom A(n) by the neutrals B, respectively ($v_T=(2T/\mu)^{1/2}$ is the thermal velocity of the particles A^+ and B),

$$k_{nn'}(T)=\frac{2}{\sqrt{\pi}}\Gamma\left(2-\frac{2}{\nu}\right)v_T\sigma_{nn'}(T),$$
$$k_{n'n}(T)=\frac{n^2}{n'^2}\exp\left(-\frac{\omega_{nn'}}{T}\right)k_{nn'}(T). \quad (18)$$

We consider now the opposite limiting case of low frequencies $\omega_{nn'}\ll\tau_{\tilde b}^{-1}$, when the transitions take place at larger internuclear distances $R_\omega\gtrsim\tilde b_E\sim\rho_{\text{cap}}$ between the colliding particles A^+ and B. In this region it suffices to take into account only the non-inertial mechanism of the transition $n\to n'$, neglecting the small (at $R\gg R_e$) polarization increments to the linear parts of the dipole moment $D^l=\mu R/M_A^*$. The probabilities $w_{nn'}$ of such transitions in collisions of the particle B with the core A^+ of the atom A(n) can be calculated by virtue of the conditions $\omega_{nn'}\ll\tau_{\tilde b}^{-1}$ and $n^2\gg\rho_{\text{cap}}$ in the shakeup model (Ref. 24, Russ. p. 180) of the Rydberg electron

$$w_{nn'}=\frac{1}{n^2}\sum_{lm,l'm'}|\langle nlm|e^{-i\mathbf{vr}}|n'l'm'\rangle|^2$$
$$=\frac{\mu^2}{M_{A^+}^2}|\mathbf{v}_E-\mathbf{v}_E'|^2\frac{1}{3n^2}\sum_{lm,l'm'}|\langle nlm|\mathbf{r}|n'l'm'\rangle|^2, \quad (19)$$

where $\mathbf{v}=(\mathbf{v}_E'-\mathbf{v}_E)\mu/M_A^*$ is the change of the velocity of the atomic core A^+ in collision with B, and $\mathbf{v}_E$ and $\mathbf{v}_E'$ are the relative velocities of the nuclei before and after the impact. The second equation in (19) holds only for $\mu v_E/M_A^*\ll(\Delta n/n)^2$, when it suffices to retain the first term of the expansion of the exponential $\exp(-i\mathbf{v}\cdot\mathbf{r})$, which is equivalent to the condition for the applicability of perturbation theory. Calculating next the sum in (19) (Ref. 26, p. 423 of Russ. transl.), integrating the probabilities $w_{nn'}(\rho)$ over the impact parameters, we obtain ultimately for the total cross section $\sigma_{nn'}(E)$ of the $n\to n'$ transition.

$$\sigma_{nn'}(E)=\frac{4}{3\pi\sqrt{3}}\left(\frac{\mu v_E}{M_{A^+}}\right)^2\frac{1}{n^5n'^3\omega_{nn'}^4}\sigma_{tr}(E);$$
$$\omega_{nn'}\ll\frac{v_E}{2\Delta R_{\tilde b}},\quad \frac{\mu}{M_{A^+}}v_E\ll\left(\frac{\Delta n}{n}\right)^2,$$
$$\sigma_{tr}(E)=\int_0^\infty[1-\cos\vartheta(\rho)]\cdot2\pi\rho\,d\rho. \quad (20)$$

Here σ_{tr} 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

$$k_{nn'}(T)=(2/\sqrt{\pi})\Gamma(3-2/\nu)v_T\sigma_{nn'}(T), \quad (21)$$

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, $n\to n-1$, 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 H(n) + He($1s^2$) the contribution of the second effect to the total cross section (17) turns out to be maximal at sufficiently low levels $n\sim5$ (where $\omega\sim\tau_a^{-1}$ and $R_\omega\sim R_0-R_*$) and amounts to approximately 30% of the cross section for the noninertial transition. With increasing n, the role of the noninertial mechanism becomes even greater because of the decrease of $D^{nl}(R)$ at $R_\omega\gg R_e$. This enables us to write Eqs. (17) and (20) in the following unified form for the entire considered region $v_E\ll1/n^2$

$$\sigma_{n,n-1}(E)\approx{}^1/_4(\mu/M_{A^+})^2\sigma_{tr}(E)n^4v_E^2,$$
$$(2\Delta R_{\tilde b}/v_E)^{1/3}\ll n\ll(\mu v_E/M_{A^+})^{-1/3},$$
$$\sigma_{n,n-1}(E)\approx{}^1/_8\pi^2(\mu/M_{A^+})^2\sigma_{cap}(E)n^4v^2(R_\omega)\exp(-2\omega_{n,n-1}\tau_a),$$
$$\rho_{cap}^{1/2}\ll n\ll(2\Delta R_{\tilde b}/v_E)^{1/3}.$$

It follows therefore that the cross sections σ_{n-1} are proportional to the quantity $n^4v^2(R_\omega)$, and in the shakeup region (when the main contribution to the transition is made by large distances $R\gtrsim\tilde b_E$, where $v(R_\omega\sim v_E)$ they decrease with decreasing n like n^4. In the opposite limiting case $\omega\gg\tau_{\tilde b}^{-1}$ the transitions take place in the region of internuclear distances $a\ll R_\omega\ll\tilde b_E$, in which the relative velocity $v(R_\omega)$ of the particles A^+ and B increases considerably with increasing ω, owing to their acceleration in the potential well of the interaction, and reaches value $v_0\gg v_E$ at $\omega\sim\tau_a^{-1}$. This increase in the velocity $v(R_\omega)$ causes the cross sections to change little with decreasing principal quantum number in the frequency region $\tau_b^{l-1}\ll\omega\ll\tau_a^{-1}$ (see Fig. 2). The decrease of the cross section sets in only at $n\ll\tau_a^{-1/3}$, i.e., in the adiabatic region of frequencies $\omega\gg\tau_a^{-1}$, with $\sigma_{n,n-1}\sim\exp(-2\omega\tau_a)$. It is easy to see also that the cross section of the transitions $n\to n'$ between the Rydberg states with $\Delta n=|n-n'|\neq1$ decrease rapidly [see Eqs. (17) and (20)] with increasing Δn.

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 l-mixing cross section. In the case when the $nl\to nl'$ transitions in the A(nl) atom are due to collisions of the neutral particle B with the core A^+, the total l-mixing cross section $\sigma_{nl}(E)$ will be determined with the aid of the shakeup model, just as in the derivation of Eq.(20). Using the expression for the sum $\Sigma_{m,m'}|\langle nlm|\mathbf{r}|nl'm'\rangle|^2$ (Ref. 26, pp. 399 and 413 of Russ. transl.), we have

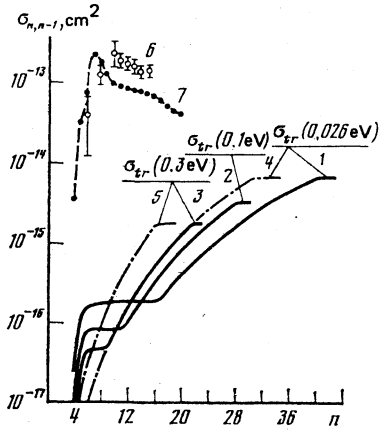

FIG. 2. Cross sections for de-excitation of Rydberg states of hydrogen in collisions with helium atoms $H(n) + He(1s^2) \to H(n-1) + He(1s^2)$ at various energies of the heavy particles. Curves 1, 2, and 3—cross sections for the transitions $\sigma_{n,n-1}(E)$ at $E = 0.026$, 0.1, and 0.3 eV, respectively; curves 4 and 5—cross sections $\sigma_{nl}(E)$ for orbital-momentum mixing at $l = 0$ for $E = 0.026$ and 0.3 eV; curves 6 and 7 correspond to the experimental data of Ref. 22 and to the calculation of Ref. 15 for the quenching of the nl levels of Na($n, l = 2$) by helium atoms.

$$\sigma_{nl}(E) = \frac{2}{3}\left(\frac{\mu v_E}{M_{A^+}}\right)^2 \int_0^\infty [1-\cos\vartheta(\rho)]$$
$$\times 2\pi\rho d\rho \frac{1}{2l+1}\sum_{l'\neq l}\sum_{m,m'} |\langle nlm|\mathbf{r}|nl'm'\rangle|^2$$
$$= \frac{3}{2}\left(\frac{\mu v_E}{M_{A^+}}\right)^2 n^2(n^2-l^2-l-1)\sigma_{tr}(E). \qquad (22)$$

The result (22) coincides with a fomula 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 $\rho_{cap}^{1/2} \ll n \ll (\mu v_E/M_A^+)^{-1/2}$ (i.e., for $4 \lesssim n \lesssim 30$ in the case of the system $H(nl) + He(1s^2)$ 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 $0.02 \lesssim E \lesssim 0.4$ eV for the case of collision of highly excited hydrogen H(n) [or H(nl)] with helium atoms He($1s^2$).

1. From the calculation (see Fig. 2) of the cross sections for the de-excitation $n \to n+1$ [Eqs. (17), (20)] and quenching of the nl levels (22) we draw the following conclusion: in the quantum number region $n \lesssim v_E^{-1/3}$, (i.e., at $n < 10$–15) the noninertial transitions with change of the principal quantum number $n \to n'$ are much more effective than those with change of only the orbital momentum ($nl \to nl'$). In the shakeup region $v_E^{-1} < n < v_E^{-1/2}$ (i.e., at $10 - 15 < n < 30$–40), however, these transitions are approximately equally probable. In all the considered regions $n < v_E^{-1/2}$ (i.e., $n < 30$–40) the quenching of the nl 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

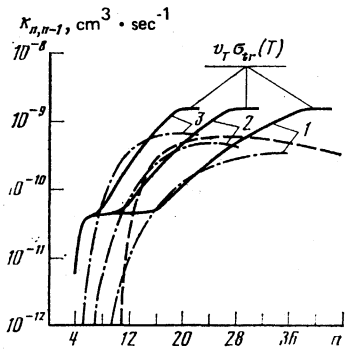

FIG. 3. Rates of de-excitation of Rydberg states $H(n-) + He(1s^2) \to H(n-1) + He(1s^2)$ at different temperatures. Curves 1, 2, and 3—rate constants $k_{n,n-1}(T)$ at $T = 250$, 1000, and 4000 K; the dash-dot curves show the corresponding rates $k^{el}_{n,n-1}(T)$ in elastic scattering of a weakly bound electron by helium atoms according to the data of Ref. 4; dashed curve—rate constant $k^{el}_{n,n-1}(T = 300\text{ K})$ calculated in Ref. 5.

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 $n \to n'$ and $nl \to nl'$, 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 $k_{n,n-1}(T)$, calculated from Eqs. (18) and (21), with the corresponding rates $k^{el}_{n,n-1}(T)$ due to the elastic mechanism, calculated in Refs. 4 and 5. This comparison points to predominance of the mechanism investigated here for the transitions $n \to n'$ in the region $n \lesssim 10$–15, and also at $n \gtrsim 20$–25. The effectiveness of the noninertial mechanism at $n \gtrsim 20$–25 is attributed to the fact that its limiting cross sections (at $n \to v_E^{-1/2}$) turn out to be of the order of the transport cross section for the scattering of the H^+ ion by the atom He($1s^2$) ($\sigma_{tr}^{H^+,He} = 60$ Å^2 at $E = 300$ K). At the same time, for the elastic mechanism[3–5] the cross sections of the $n \to n'$ transitions are expressed in terms of the transport cross section for the scattering of a slow electron by a helium atom ($\sigma_{tr}^{e^-,He} = 5$ Å^2), which is more than 10 times smaller. At $n \lesssim 10$–15 the $n \to n'$ transitions produced in the hydrogen atom H(n) by collision of the atom He with the proton H^+ are highly effective both because $\sigma_{tr}^{H^+,He}$ is large and because the relative velocity of the

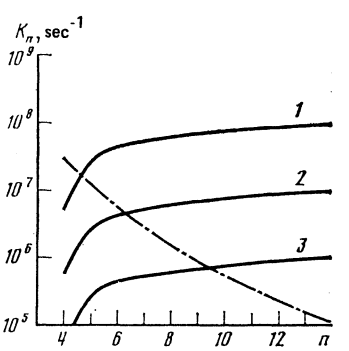

FIG. 4. Total rate $K_n = \Sigma_{\Delta n} k_{n,n\pm\Delta n} N_{He}$ of collision quenching of highly excited hydrogen levels by helium atoms He($1s^2$) at $T = 300$ K and at densities $N_{He} = 10^{18}$, 10^{17}, 10^{16} cm^{-3} (curves 1, 2, and 3, respectively). Dashed curve—total rate $A_n = \Sigma_{\Delta n} A_{n,n-\Delta n}$ of radiative decay of the level n.

heavy particles increases substantially when they move in the region $R \ll \rho_{cap}$.

3. It can be seen from Fig. 4 that collision quenching (total rate $K_n = \Sigma_{\Delta n} k_{n,n\pm\Delta n} N_{He}$) of the levels of hydrogen H(n) with $n \gtrsim 6$ greatly exceeds their radiative decay ($A_n = \Sigma_{\Delta n} A_{n,n-\Delta n}$) even and helium densities $N_{He} \gtrsim 10^{17}$ cm^{-3}. This makes possible measurement of the cross sections and rates of the transitions (1) with decreasing principal quantum number of a Rydberg electron in a weakly ionized plasma of H_2 and 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 H(n) produced in such a plasma on the pressure of the buffer gas (helium). Experiments of this type on $n \to n'$ transitions are undoubtedly of interest for the study of the relaxation of a dense low-temperature plasma.

The authors thank M. I. Chibisov and O. B. Firsov for a discussion of the results, as well as B. P. Kaulakis for copies of Refs. 13 and 21 prior to their publication.

[1)]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 $n \to n'$ and $nl \to nl'$ are determined not by the transport cross section $\sigma_{tr}(E)$ but by the elastic cross section σ_{el} for scattering of the neutral particle B by the atomic core A^+. At thermal collision energies, however, $\sigma_{el}(E) \gg \sigma_{tr}(E)$, so that the result of Eq. (25) greatly overestimates the cross sections for noninertial transitions.

[2)]The particles A^+ and B go through such transitions in reactions analogous to (1) in their mechanism, but with formation or decay of molecular ions (e.g., associative ionization), with excitation of virbational level by electron impact, etc.

[3)]Equation (9a) with the function $d(\omega) = \text{const}$ [see Eq. (12a)] is the quasiclassical limit (at $E, |E_v| \ll E_0$ and $\omega \gg \tau_b^{-1}$) of the exact quantum-mechanical expressions[28–30] for the matrix elements of the transition D_{if} in the Morse potential [see Eq. (10a)] in the linear-dipole-moment approximation.

[4)]We note that in a Morse potential the time $t(R)$ [see Eq. (11)] of motion to the bottom of the well is equal to the collision time, i.e., $R_\omega = R_e$ and $t(R_\omega) = \tau_a$ at $\omega = \omega_e$; for the frequency $\omega = \omega_e/\sqrt{3}$ we obtain $t(R_\omega) = \tau_a/\sqrt{3}$ and $R_\omega = R_*$, where $U(R_*) = -3E_0/4$ and $R_* = R_e(1 + \ln 2/\alpha)$ is the inflection point of the potential Eq. (10a). With further decrease of the frequency $\omega < \omega_e/\sqrt{3}$ the point R_ω shifts beyond the inflection point, $R_\omega > R_*$.

[5)]We note that the condition for the validity of Eqs. (17) can be written in a more lucid form: $v_E \ll \Delta n/n^3, v_0$, if it is recognized that the characteristic dimension $\Delta R_{\tilde{b}} = \tilde{b}_E/(\nu + 1)$ of the term on the right branch at the point $\tilde{b}_E = (C_\nu/E)^{1/\nu}$ is of the order of one atomic unit (at thermal velocities of the collision of the particles A^+ and B).

[1]B. M. Smirnov, Usp. Fiz. Nauk **131**, 577 (1980) [Sov. Phys. Usp. **23**, 450 (1980)].
[2]D. Kleppner, M. G. Littman, and M. L. Zimmerman, Scient. American **244** (5), 130–149 (1981).
[3]L. P. Pitaevskiĭ, Zh. Eksp. Teor. Fiz. **42**, 1326 (1962) [Sov. Phys. JETP **15**, 919 (1962)].
[4]D. R. Bates and S. P. Khare, Proc. Phys. Soc. **85**, 231 (1965).
[5]M. R. Flannery, Ann. Phys. (N.Y.) **61**, 465 (1970).
[6]V. A. Smirnov and A. A. Mikhaĭlov, Opt. Spetkrosk. **30**, 984 (1971).
[7]A. Z. Devdariani, A. N. Klyucharev, A. V. Lazarenko, and V. A. Sheverov, Pis'ma Zh. Tekh. Fiz. **4**, 1013 (1978) [Sov. Tech. Phys. Lett. **4**, 408 (1978)].
[8]R. K. Janev and A. A. Mikhajlov, Phys. Rev. A **20**, 1890 (1979).
[9]V. S. Lebedev, V. S. Marchenko, and S. I. Yakovlenko, Izv. AN SSSR ser. fiz. **45**, 2395 (1981).
[10]V. A. Smirnov, Opt. Spektrosk. **37**, 407 (1974).
[11]A. P. Hickman, J. Phys. B **14**, L419 (1981).
[12]M. Matsuzawa, *ibid.* L. 553.
[13]B. P. Kaulakis, Litovskiĭ fiz. sb. **22**, No. 1, 3 (1982).
[14]J. I. Gersten, Phys. Rev. A **14**, 1354 (1976).
[15]R. E. Olson, *ibid.* A **15**, 631 (1977).
[16]A. Omont, J. de Phys. **38**, 1343 (1977).
[17]J. Deroard and M. Lombardi, J. Phys. B **11**, 3875 (1978).
[18]A. P. Hickman, Phys. Rev. A **18**, 1339 (1978).
[19]M. Matsuzawa, J. Phys. B **12**, 3743 (1979).
[20]E. Prunele and J. Pascale, *ibid.* p. 2511.
[21]B. P. Kaulakis, Litovskii fiz.sb. **22**, No. 5, 20 (1982).
[22]T. F. Gallagher, S. A. Edelstein, and R. M. Hill, Phys. Rev. A **15**, 1945 (1977).
[23]M. Hugon, F. Gounand, P. R. Fournier, and J. Berlande, J. Phys. B **12**, 2707 (1979).
[24]L. D. Landau and E. M. Lifshitz, Quantum Mechanics, Nonrelativistic Theory, Pergamon, 1977.
[25]M. R. Flannery, J. Phys. B **13**, L657 (1980); Phys. Rev. A **22**, 2408 (1980).
[26]H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two-Electron Systems, Springer, 1958.
[27]V. S. Lebedev and V. S. Marchenko, FIAN Preprint No. 247, M. 1981; Khim. Fizika No. 12, 1589 (1982).
[28]H. S. Heaps and G. Herzberg, Zs. Phys. **133**, 48 (1952).
[29]J. A. Gallas, Phys. Rev. A **21**, 1829 (1980).
[30]V. A. Kochelap and Yu. A. Kukibnyi, Opt. Spetkrosk. **34**, 328 (1973).
[31]L. D. Landau, Collected Works, Vol. 1, Pergamon, 1965.
[32]H. H. Michels, J. Chem. Phys. **44**, 3834 (1966).

Translated by J. G. Adashko