Nonresonant collisional mixing of atomic Rydberg levels in the Fermi pseudopotential model

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A quasiclassical theory of inelastic transitions between atomic Rydberg states, accompanying the scattering of a neutral particle by the weakly-bound electron, is presented. The Fermi pseudopotential model is used to analyze n- and l-mixing processes, taking into account the change $\Delta\varepsilon$ in the energy of the highly-excited atom in these transitions. It is shown that the total cross sections for the $n\to n'$ and $nl\to n'$ elastic transitions with a large energy change $\Delta\varepsilon$ (for which $[\lambda_E = n\Delta\varepsilon/V_E \gg 1]$ where V_E is the relative velocity of the colliding atoms) falls rapidly with decreasing principal quantum number n, reaching a maximum for $(\lambda_E \approx 1)$, and tends to the quasielastic limit as $\Delta\varepsilon$ is reduced for large values of $n(\lambda_E \ll 1)$. General analytic expressions are obtained for the behavior of the cross sections and rate constants for the $n\to n'$ and $nl\to n'$ transitions throughout the range of validity of the model. It is shown that these expressions include previously published results on the quasielastic l-mixing of highly-excited states as special cases. Numerical calculations have been carried out of the cross sections for collisional quenching of Rydberg levels of atomic hydrogen and alkali metals in inert gases in the presence of the resonance defect, and the results are compared with existing experimental data. These results are used as a basis for a qualitative explanation of experimental data on the quenching of ns-states of Na and Rb atoms for which a substantial reduction is observed in the cross sections as compared with the quasielastic quenching of nd and nf levels.

I. INTRODUCTION

The development of methods for the selective excitation and detection of Rydberg states[1] has recently led to intensive studies of collisional quenching of highly-excited atoms by neutral particles (a review is given in Ref. 2). Until recently, the greater part of experimental and theoretical research has been directed toward the mixing of Rydberg states in the orbital angular momentum ($nl\to nl'$) in situations in which the resonance defect ($\Delta\varepsilon_{nl,nl'}$) is unimportant, so that one can speak of quasielastic l mixing.

The theory of this process is now essentially complete. It is based on the free-electron model proposed by Fermi[3] and subsequently developed in papers[4,5] on the broadening and shift of atomic Rydberg levels in a buffer gas. According to this model, the quasielastic $nl\to nl'$ transitions are due to the scattering of the incident neutral particle by the quasibound (quasifree) electron in the excited atom, and their interaction is described by the zero-range pseudopotential.[3] For the l-mixing process, the free electron model was implemented by quasielastic methods within the framework of perturbation theory,[6–8] the impulse approximation,[9–12] the strong coupling methods,[13–15] the Born approximation,[15] and the adiabatic description.[16] Existing theory[6–16] and the approximate formula constructed in Ref. 17 are, on the whole, in good agreement with experimental data on the quasielastic quenching of nd and nf levels of sodium[18–20] and nf levels of rubidium[21] in inert gases.

There is, however, a substantial group of experimental papers[22–28] on the quenching of atomic Rydberg nl levels of alkali metals with low values of the orbital angular momentum l (the s levels of sodium,[22,23] the p levels of potassium,[24] and the s, p, and d levels of rubidium[25–28]), which existing theory is unable to describe. This is due to the large quantum defect δ_l of these levels and, correspondingly, the substantial change in energy during collisional quenching. In this situation, quenching occurs preferentially with transition to the $n'l'$ state that is the closest in energy to the initial nl level (i.e., with mininum resonance defect ($\Delta\varepsilon_{nl,n'l'} = \varepsilon_{n'l'} - \varepsilon_{nl}$), so that, as a rule, it gives rise to a change not only in the orbital angular momentum l, but also in the principal quantum number n. The presence of the resonance defects $\Delta\varepsilon$ means that the quenching process can no longer be regarded as quasielastic.

There is practically no theory of nonresonant quenching of atomic Rydberg nl levels by inelastic $nl\to n'l'$ transitions. There is only a numerical calculation[12] of the cross sections for n and l mixing, which applies to the region where the energy defect is small, i.e., $\Delta\varepsilon < V_E/n$) where V_E is the relative velocity of the colliding atoms. For the quenching of ns levels of rudibium in helium, this calculation has demonstrated that, even when $\Delta\varepsilon$ is small, there may be an appreciable reduction in the cross sections for this process as compared with the quasielastic case ($\Delta\varepsilon = 0$). As far as large values of the energy defect are concerned ($\Delta\varepsilon \gtrsim V_E/n$), the very possibility of using the free-electron model in cross-section calculations in this essentially inelastic region has been in doubt (see Refs. 12 and 29).

The first calculations of the rate constants for inelastic transitions with a change in the principal quantum number ($n\to n'$) were reported in Refs. 30 and 31 for the case of a uniform distribution of atoms over degenerate l sublevels

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within each of the hydrogen-like levels n and n'. These calculations were performed by the semiclassical method, using the Pitaevskiĭ model,[32] originally put forward for the migration of a highly-excited electron over energy levels in the course of three-body recombination. The most general account of this is given in Ref. 31. However, analytic formulas for the behavior of cross sections and rate constants of inelastic $n \to n'$ transitions were not obtained in Refs. 30 and 31 (with the exception of the quasielastic region of high values of n for which it may be assumed that $(\Delta\varepsilon_{nn'} = 0)$. In the general case, the rate constants for $n \to n'$ transitions were therefore determined in these papers by numerical methods. moreover, there is a need for a more rigorous verification of the results of semiclassical theory.[30,31] There is therefore a need for an analytic examination of transitions with a change in the principal quantum number and for calculations of cross sections and rate constants for inelastic $nl \to n'$ transitions from a given selectively excited nl level to all the degenerate sublevels l' of another energy level n'. This latter case is of particular interest because it is amenable to direct comparison between theoretical results and the experimental data mentioned above [22–28] on nonresonant quenching of Rydberg nl levels with large quantum defect δ_l.

The development of a theory of nonresonant n and l mixing of Rydberg states in the free-electron model, using the impulse approximation, has encountered considerable difficulties that have arisen in the calculation of atomic form factors (see Refs. 12, 29, and 33). However, it will be shown below that this model can be used for inelastic transitions if we introduce the zero-range Fermi pseudopotential and the classical approximation to the wave functions of the Rydberg electron, and adopt a procedure similar to that used by Omont[6] for the quasielastic l-mixing process. This approach has enabled us to obtain general analytic formulas for the $n \to n'$ and $nl \to n'$ cross sections and rate constants, which contain explicitly the energy defect $\Delta\varepsilon$, the principal quantum number n, and the relative velocity V_E of the atoms. The essential point is that these formulas simultaneously describe the behavior of cross sections both in the usual quasielastic region $(\Delta\varepsilon \ll V_E/n)$ (where they become directly equivalent to the results reported in Ref. 6) and in the previously uninvestigated inelastic (nonresonant) region in which $(\Delta\varepsilon \gtrsim V_E/n)$. This brings out the physical parameter $(\lambda_E = n\Delta\varepsilon/V_E$, that characterizes the degree of inelasticity of collisional quenching. It is precisely this parameter that defines the quasielastic region $(\lambda_E \ll 1)$ in which the $n \to n'$ and $nl \to n'$ transition cross sections increase with decreasing principal quantum number $(\sigma \propto n^{-3})$ and the inelastic region $(\lambda_E \gg 1)$, in which the cross sections fall rapidly $(\sigma_{nn'} \propto n^7 \sigma_{nl,n'} \propto n^3)$. The inelastic transition cross sections reach their maximum for $\lambda_E \approx 1$.

We have used the formulas obtained above to calculate the cross sections and quenching-rate constants for highly-excited states of hydrogen H(n) and alkali metals Na(ns), Rb(ns) in the inert gases He and Ar. We have also developed an explanation for the observed[22–28] substantial reduction [by up to two orders of magnitude in the case of the system Na(ns) + Ar; see Fig. 4] in the collisional quenching cross sections of Rydberg nl states with large resonance defects $\Delta\varepsilon$, as compared with the quasielastic case $\Delta\varepsilon = 0$.

2. FORMULAS FOR INELASTIC TRANSITION PROBABILITIES

Collisional transitions between Rydberg levels $(nl \to n'l')$ in an atom A(nl), due to the scattering of an incident ground-state atom B by a weakly-bound electron e^- (Fermi mechanism), will now be described in terms of the zero-range pseudopotential (we shall use the atomic system of units in which $e = m_e = \hbar = 1$):

$$\hat{V}(\mathbf{r}, \mathbf{R}) = 2\pi L \delta(\mathbf{r} - \mathbf{R}), \tag{1}$$

where $\mathbf{r}$, $\mathbf{R}$ are the position vectors of the outer electron e^- and the atom B relative to the atomic residue (core) A^+, and L is the scattering length of a free electron on the same atom B.

In the classical description of the relative motion of the two heavy particles A^+ and B on a rectangular trajectory $\mathbf{R}(t) = \boldsymbol{\rho} + \mathbf{V}_E t$ (where $R^2(t) = \rho^2 + V_E^2 t^2$) with velocity $V_E = (2E/\mu)^{1/2}$ (E is the energy of relative motion and μ is the reduced mass) and impact parameter ρ, the probability of an $nl \to n'l'$ transition in first-order time-dependent perturbation theory[34] is given by

$$w_{nl,n'l'}(\rho) = \frac{1}{2l+1} \sum_{mm'} \left| \int_{-\infty}^{\infty} \langle nlm | \hat{V}[\mathbf{r}, \mathbf{R}(t)] | n'l'm' \rangle \times \exp(i\omega_{nl,n'l'} t)\, dt \right|^2. \tag{2}$$

The frequency $(\omega_{nl,n'l'} = \varepsilon_{n'l'} - \varepsilon_{nl})$ is determined by the change in the energy of the highly-excited atom in the course of the $nl \to n'l'$ transition under consideration. The matrix element of the perturbation (1) over the Coulomb wave functions

$$\Psi_{nlm} = R_{nl}(r)\, Y_{lm}(\theta_r, \varphi_r)$$

of the Rydberg electron with principal quantum number n, angular momentum quantum number l, and magnetic quantum number m, has the following form:

$$\langle nlm | \hat{V}[\mathbf{r}, \mathbf{R}(t)] | n'l'm' \rangle = 2\pi L \Psi^*_{nlm}[\mathbf{R}(t)]\, \Psi_{n'l'm'}[\mathbf{R}(t)]. \tag{3}$$

We shall use the quasiclassical approximation (see, for example, Ref. 34) for the radial wave functions of the highly-excited electron:

$$R_{nl}(r) = \left(\frac{2}{\pi n^3}\right)^{1/2} \frac{1}{r p_r^{1/2}} \cos\Phi_r, \quad \Phi_r = \int_{r_1}^{r} p_r\, dr - \frac{\pi}{4},$$
$$p_r = (2/r - 1/n^2 - \tilde{l}^2/r^2)^{1/2}, \quad r_{1,2} = n^2 \pm n(n^2 - \tilde{l}^2)^{1/2}, \tag{4}$$

where p_r is the electron momentum, Φ_r is the phase, $r_{1,2}$ are the turning points, and $\tilde{l} = l + \frac{1}{2}$. This enables us to assume that we are dealing with a purely hydrogen-like situation and to take into account the quantum defects δ_l and $\delta_{l'}$ of the initial (nl) and final $(n'l')$ levels. In the latter case, the value of n in (4) and all the subsequent formulas must be replaced with the effective quantum numbers $n_{\text{eff}} = n - \delta_l$.

In the coordinate system in which the core A^+ is at the origin, the Z axis is perpendicular to the plane of collision of particles A^+ and B, and the X axis lies along the vector ρ, the angles θ_r and φ_r at the point $\mathbf{r}=\mathbf{R}$ are given by

$$\theta_R=\pi/2, \quad \varphi_R=\operatorname{arctg}(V_E t/\rho),$$

so that the expression for the $nl\to n'l'$ transition probability can be written in the following form (see Ref. 6):

$$w_{nl,n'l'}(\rho)=\frac{16L^2}{n^3n'^3(2l+1)}\sum_{mm'}\left|Y_{lm}\left(\frac{\pi}{2},0\right)\right|^2 \times\left|Y_{l'm'}\left(\frac{\pi}{2},0\right)\right|^2\int_{-\infty}^{\infty}dt\int_{-\infty}^{\infty}dt'\exp[i\omega_{nl,n'l'}(t-t')] \times\exp[i(m-m')(\varphi_R-\varphi_{R'})]\frac{\cos\Phi_R\cos\Phi_{R'}\cos\Phi_{R'}'\cos\Phi_{R'}'}{R^2R'^2(p_Rp_{R'}p_R'p_{R'}')^{1/2}}. \tag{5}$$

If we use the quasiclassical expression for the spherical harmonics[35]:

$$\left|Y_{lm}\left(\frac{\pi}{2},0\right)\right|^2=\frac{\tilde{l}}{2\pi^2(\tilde{l}^2-m^2)^{1/2}}, \tag{6}$$

we can sum over the magnetic quantum numbers m and m' in (5), having replaced the sum by integration with respect to m and m' as follows (see, for example, Ref. 36, Vol. 1):

$$\sum_{m=-l}^{l}\frac{\exp[-i(\varphi_{R'}-\varphi_R)m]}{(\tilde{l}^2-m^2)^{1/2}}=\int_{-\tilde{l}}^{\tilde{l}}\frac{dm}{(\tilde{l}^2-m^2)^{1/2}}\exp[-i(\varphi_{R'}-\varphi_R)m]=\pi J_0[\tilde{l}(\varphi_{R'}-\varphi_R)], \tag{7}$$

where $J_0(z)$ is the zero-order Bessel function. Next, starting with the exact expression for the phase of the quasiclassical wave function for an electron in the Coulomb field:

$$\Phi_r=p_rr-n\arcsin\left[\frac{1}{e_l}\left(1-\frac{r}{n^2}\right)\right]-\tilde{l}\arcsin\left[\frac{1}{e_l}\left(1-\frac{\tilde{l}^2}{r}\right)\right]+\left(n-\frac{\tilde{l}}{2}\right)\frac{\pi}{2}-\frac{\pi}{4}, \tag{8}$$

where $(e_l=(1-\tilde{l}^2/n^2)^{1/2}$ is the eccentricity of the orbit, we obtain the following expression for the phase difference $\Phi_{R'}-\Phi_R$ to within terms of the second order of small quantities in the difference $R'-R$:

$$\Phi_{R'}-\Phi_R=\left(\frac{d\Phi_R}{dR}\right)(R'-R)+O[(R'-R)^2], \quad \frac{d\Phi_R}{dR}=p_R=\left(\frac{2}{R}-\frac{1}{n^2}-\frac{\tilde{l}^2}{R^2}\right)^{1/2}. \tag{9}$$

As a result, neglecting the rapidly-oscillating terms $\cos(\Phi_{R'}+\Phi_R)$ in (5), we obtain the following formula for the probability of the collisional transition $nl\to n'l'$:

$$w_{nl,n'l'}(\rho)=\frac{L^2}{\pi^2n^6(2l+1)}\int_{-\infty}^{\infty}\frac{dt}{R^4}\int_{-\infty}^{\infty}dt'\exp[i\omega_{nl,n'l'}(t'-t)]\times\frac{\tilde{l}\cos[p_R(R'-R)]}{p_R}\times J_0[\tilde{l}(\varphi_{R'}-\varphi_R)]\frac{1}{p_R'}\tilde{l}'\cos[p_R'(R'-R)]J_0[\tilde{l}'(\varphi_{R'}-\varphi_R)]. \tag{10}$$

Henceforth, we shall use expansions for the quantities $R'-R$ and $(\varphi_{R'}-\varphi_R)$ in the integrand, neglecting terms of order higher than two in τ:

$$R'-R=\tau V_E\sin\varphi_R, \quad \sin\varphi_R=V_Et/R, \quad R(\varphi_{R'}-\varphi_R)=\tau V_E\cos\varphi_R, \quad \cos\varphi_R=\rho/R. \tag{11}$$

This is justified because most of the contribution to the integral (10) is due to time intervals $\tau=t'-t$ that are small in comparison with the characteristic time ($\tau_{\text{col}}\sim n^2/V_E$ for a collision between atoms A(nl) and B.

3. $n\to n'$ TRANSITIONS

We must now determine the probabilities and cross sections for inelastic collisional transitions ($\omega_{nn'}\neq 0$) between Rydberg levels ($n\to n'$) of an atom when different l sublevels corresponding to a given n are equally populated. This situation occurs even for relatively low buffer-gas densities because of the high cross sections for the quasielastic ($\omega_{nl,n'l'}=0$) l-mixing processes (see, for example, Ref. 2). The most interesting quantity is then the total probability $w_{nn'}$ (and cross section $\sigma_{nn'}$) of the transition from level n to n':

$$w_{nn'}=\frac{1}{n^2}\sum_{ll'}(2l+1)w_{nl,n'l'}, \tag{12}$$

summed over finite l' and averaged over the initial l degenerate states of the highly-excited atom.

If, in (12), we replace the sum of the probabilities $w_{nl,n'l'}$ (10) over the angular momenta l and l' by integration with respect to $\tilde{l}$ and $\tilde{l}'$, and use (11) to evaluate the corresponding integral (see, for example, Ref. 36, Vol. II), we obtain

$$\sum_l\frac{\tilde{l}\cos[p_R(R'-R)]}{R^2p_R}J_0[\tilde{l}(\varphi_{R'}-\varphi_R)] =\int_0^{k_RR}\frac{\tilde{l}\,d\tilde{l}}{R^2}\frac{\cos[(k_R^2-\tilde{l}^2/R^2)^{1/2}(R'-R)]}{(k_R^2-\tilde{l}^2/R^2)^{1/2}}J_0[\tilde{l}(\varphi_{R'}-\varphi_R)] =\frac{\sin\{k_R[(R'-R)^2+R^2(\varphi_{R'}-\varphi_R)^2]^{1/2}\}}{[(R'-R)^2+R^2(\varphi_{R'}-\varphi_R)^2]^{1/2}}\simeq\frac{\sin(k_RV_E\tau)}{V_E\tau}, \quad k_R=\left(\frac{2}{R}-\frac{1}{n^2}\right)^{1/2}. \tag{13}$$

The transition probability in which we are interested is then given by

$$w_{nn'}(\rho)=\frac{L^2}{\pi^2n^8}\int_{-\infty}^{\infty}dt\int_{-\infty}^{\infty}d\tau\exp(i\omega_{nn'}\tau)\frac{\sin(k_RV_E\tau)}{V_E\tau}\frac{\sin(k_R'V_E\tau)}{V_E\tau}. \tag{14}$$

Next, since we are assuming a rectilinear trajectory for the relative motion of particles A^+ ands B, we have

$$dt=RdR/V_E(R^2-\rho^2)^{1/2},$$

and, substituting $k_R=k_R'$ and using the dimensionless variables ($x=R/2n^2, y=\rho/2n^2$, and $z=k_RV_E\tau$, we obtain

$$w_{nn'}(y)=\frac{8L^2}{\pi^2 n^7 V_E^2}\int_y^1 dx\,\frac{(x-x^2)^{1/2}}{(x^2-y^2)^{1/2}}\int_0^\infty dz\,\frac{\sin^2 z}{z^2}\cos[\alpha(x)z], \tag{15}$$

where

$$\alpha(x)=\frac{\omega_{nn'}}{k_R V_E}=\frac{n\omega_{nn'}}{V_E}\frac{x^{1/2}}{(1-x)^{1/2}}. \tag{16}$$

The integral with respect to z in (15) assumes the following values:

$$\int_0^\infty dz\,\frac{\sin^2 z}{z^2}\cos[\alpha(x)z]=\begin{cases}{}^1/_2\pi[1-\alpha(x)/2], & \alpha(x)<2,\\ 0, & \alpha(x)>2,\end{cases} \tag{17}$$

and is therefore nonzero for $y\leqslant x\leqslant x_0$, where x_0 is determined from the condition $\alpha(x_0)=2$, i.e.,

$$x_0=\frac{1}{1+(\lambda_E/2)^2},\qquad \lambda_E=\frac{n\omega_{nn'}}{V_E}\approx\frac{\Delta n}{n^2 V_E}. \tag{18}$$

The total cross section for the $n\to n'$ transition is obtained by integrating $w_{nn'}(\rho)$ (15) over $2\pi\rho d\rho$ in the range $0\leqslant\rho\leqslant 2n^2x_0$, using (16) and (17):

$$\sigma_{nn'}(V_E)=(2n^2)^2\int_0^{x_0} w_{nn'}(y)\cdot 2\pi y\,dy$$

$$=\frac{32L^2}{n^3V_E^2}\int_0^{x_0} y\,dy\int_y^{x_0} dx\,\frac{(x-x^2)^{1/2}}{(x^2-y^2)^{1/2}}\left(1-\frac{\lambda_E x^{1/2}}{2(1-x)^{1/2}}\right). \tag{19}$$

Reversing the order of integration in (19), and evaluating the corresponding integrals, we finally obtain

$$\sigma_{nn'}(V_E)=\frac{2\pi L^2}{n^3V_E^2}F_{nn'}(\lambda_E),$$

$$F_{nn'}(\lambda_E)=\frac{2}{\pi}\left\{\operatorname{arctg}\left(\frac{2}{\lambda_E}\right)-\frac{2\lambda_E(3\lambda_E^2+20)}{3(4+\lambda_E^2)^2}\right\}. \tag{20}$$

It is readily seen that, in the limit of high quantum numbers $n\gg(\Delta n/V_E)^{1/2}$ (i.e., low frequencies $\omega_{nn'}$ for which $\lambda_E\ll 1$), we have $F_{nn'}(\lambda_E)\to 1$, and formula (20) becomes identical with Omont's result[6] for the quasielastic l-mixing process ($n'=n$ and $\omega_{nn'}=0$):

$$\sigma_{nn'}(V_E)=2\pi L^2/n^3V_E^2,\qquad \lambda_E\ll 1. \tag{21}$$

When $n_{\max}=0.95(\Delta n/V_E)^{1/2}$, so that $\lambda_E=1.1$, the cross section given by (20) has a maximum whose height is proportional to the total cross section $\sigma_{el}=4\pi L^2$ for the elastic scattering of a free slow electron by the incident atom:

$$\sigma_{nn'}^{max}(V_E)=0{,}16\sigma_{el}/|\Delta n|^{3/2}V_E^{1/2},\qquad \lambda_E=1{,}1. \tag{22}$$

For the quantum numbers $n\ll(\Delta n/V_E)^{1/2}$, i.e., for $\lambda_E\gg 1$, equation (20) yields

$$F_{nn'}(\lambda_E)=2^9/15\pi\lambda_E^5.$$

Correspondingly, the inelastic $n\to n'$ transition cross section undergoes a rapid reduction with decreasing n in this range:

$$\sigma_{nn'}(V_E)=\frac{256}{15\pi}\frac{\sigma_{el}V_E^3n^7}{|\Delta n|^5},\qquad \lambda_E\gg 1, \tag{23}$$

which is in contrast to the rapid increase $\sigma_{nn'}\propto n^{-3}$ in the cross section for the quasielastic transition.

Integrating (20) over the Maxwellian distribution of heavy particles, we obtain the following formulas for the rate constants for the excitation ($n'\to n$) and deexcitation ($n\to n'$) of Rydberg atoms by collision with the neutral particle ($n>n'$):

$$k_{nn'}(T)=\langle V_E\sigma_{nn'}(V_E)\rangle=\frac{\sigma_{el}}{\pi^{1/2}V_T n^3}\Phi_{nn'}(\lambda_T),$$

$$k_{n'n}(T)=\frac{n^2}{n'^2}k_{nn'}(T)\exp(-\omega_{nn'}/T), \tag{24a}$$

$$\Phi_{nn'}(\lambda_T)=\exp\left(\frac{\lambda_T^2}{8}\right)\left\{\exp\left(\frac{\lambda_T^2}{8}\right)\operatorname{erfc}\left(\frac{\lambda_T}{2}\right)\right.$$

$$\left.-\frac{\lambda_T^2}{(2\pi)^{1/2}}D_{-3}\left(\frac{\lambda_T}{\sqrt{2}}\right)-\frac{5\lambda_T}{\pi^{1/2}}D_{-4}\left(\frac{\lambda_T}{\sqrt{2}}\right)\right\}, \tag{24b}$$

where D_{-q} is the parabolic cylindrical function, erfc is the probability integral (see, for example, Ref. 37), and $\lambda_T=n\omega_{nn'}/V_T$, and $V_T=(2T/\mu)^{1/2}$ is the thermal velocity of the colliding atoms. Figure 1 shows a graph of the function $\Phi_{nn'}(\lambda_T)$. We can now use (24) to determine the asymptotic form of the function $\Phi_{nn'}(\lambda_T)$ for $\lambda_T\gg 1$ and its behavior for $\lambda_T\to 0$:

$$\Phi_{nn'}(\lambda_T)=2/\pi\lambda_T^5,\qquad \lambda_T\gg 1,$$

$$\Phi_{nn'}(\lambda_T)=1-8\lambda_T/3\pi^{1/2},\qquad \lambda_T\ll 1,$$

which leads us to the following limiting expressions for the rate constants for the $n\to n'$ ($n>n'$) deexcitation of the atom in the essentially inelastic ($\lambda_T\gg 1$) and quasielastic ($\lambda_T\ll 1$) regions:

$$k_{nn'}(T)=2^6\sigma_{el}V_T^4n^7/\pi|\Delta n|^5,\qquad \lambda_T\gg 1, \tag{25a}$$

$$k_{nn'}(T)=\sigma_{el}/\pi^{1/2}V_Tn^3,\qquad \lambda_T\ll 1. \tag{25b}$$

We have used (24) to calculate the rate constants for the excitation of hydrogen atoms in collisions with helium atoms: $H(n)+He\to H(n+1)+He$ (Fig. 2), which, on the whole, turns out to be in good agreement with Flannery's calculations.[31] The residual discrepancy between the results in the essentially nonresonant region $n\lesssim 15$ can be explained by errors due to the purely classical description of the motion of the outer electron. It is also clear that, even for transi-

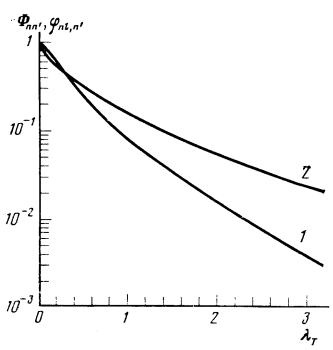

FIG. 1. Graphs of $\Phi_{nn'}(\lambda_T)$ (curve 1) and $\varphi_{nl,n'}(\lambda_T)$ (curve 2) calculated from (24b) and (38b), respectively.

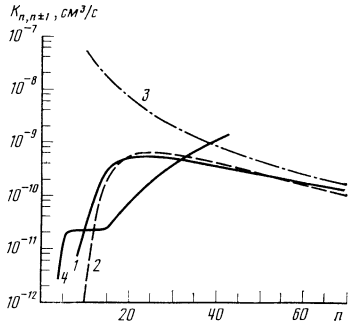

FIG. 2. Rate constants for $n \to n \pm 1$ transitions between neighboring Rydberg levels of hydrogen atoms in collisions with helium atoms: $H(n) + He \to H(n \pm 1) + He$ at 300 K. Curves 1, 2, and 3 correspond to the Fermi excitation mechanism $n \to n + 1 (\sigma_{el} = 4\pi L^2 = 5.6$ Å^2); 1—present results [calculated from (24)]; 2—semiclassical calculation[31]; 3—quasielastic result ($\omega_{nn'} = 0$ in the weak coupling approximation [see (25b)]; 4—competing mechanism of $n \to n - 1$ deexcitation (calculated in Ref. 38 in the dipole range of quantum numbers $n < (\mu V_E / M_{H^+})^{-1/2}$.

tions between neighboring levels ($\Delta n = 1$), the quasielastic (i.e., ignoring the energy defect $\Delta\varepsilon_{nn'} = \Delta n / n^3$) results reported by Omont[6] [formulas (21) and (25b)] become invalid beginning with some sufficiently high values $n \lesssim 50$ for which $\lambda_T \gtrsim 0.5$. In this region, the cross sections and rate constants for the n-mixing process must be calculated with the above general formulas (20) and (24). Figure 2 also shows a comparison between the rates of the two possible inelastic mechanisms for $n \to n \pm 1$ transitions that rely on the scattering of the incident $He(1s^2)$ atom by the weakly-bound electron and by the atomic residue H^+ of the highly-excited atom $H(n)$. It is clear that the second mechanism predominates for low ($n \lesssim 10$) and high ($n \sim 40$) values of n. When $n \lesssim 10$, this is due to the considerable speeding up of the He atom and the proton H^+ in the potential well describing their interaction, which leads to the absence of the reduction ($5 < n < 15$) in the cross sections for the $n \to n - 1$ deexcitation (curve 4) with a reduction in the principal quantum number (this effect is examined in Ref. 38). When $n \sim 40$, this is explained by the high transport cross section σ_{tr} (300 K) = 60 Å^2 for the scattering of the He atom by the proton, which determines (see Refs. 38 and 39) the n- and l-mixing cross sections for $n \sim (\mu V_E / M_{H^+})^{-1/2}$. The Fermi mechanism investigated here for the inelastic $n \to n'$ transitions predominates in the quantum number range $10 \lesssim n \lesssim 30$.

4. $nl \to n'$ TRANSITIONS

We shall now determine the cross section $\sigma_{nl,n'}$ for the collisional transition from a given atomic nl state to all the sublevels l' of another energy state $n' \neq n$. This cross section is of particular interest for current experiments on the collisional quenching of selectively excited atomic Rydberg states with given principal and orbital quantum numbers n, l in a buffer gas (see, for example, Ref. 2). If we sum the probabilities (10) over all the possible values of the orbital angular momentum l' in the final state with the aid of (13), and use (11) for the probability of a transition with an energy change $\omega_{nl,n'} = \varepsilon_{n'} - \varepsilon_{nl}$ of the highly-excited atom, we obtain

$$w_{nl,n'}(\rho) \equiv \sum_{l'} w_{nl,n'l'} = \frac{L^2}{2\pi^2 n^6} \int_{-\infty}^{\infty} \frac{dt}{R^2 p_R} \int_{-\infty}^{\infty} d\tau \times \exp(i\omega_{nl,n'}\tau) J_0\left(\tilde{l}\frac{\rho V_E \tau}{R^2}\right) \cos\left(p_R \frac{V_E^2 t\tau}{R}\right) \frac{\sin(k_R' V_E \tau)}{V_E \tau}. \quad (26)$$

Next, we assume again that the path is rectilinear, i.e., that $dt = RdR / V_E (R^2 - \rho^2)^{1/2}$, and transforming to the dimensionless variables $x = R/2n^2$, $y = \rho/2n^2$, and $z = k_R V_E \tau$, we obtain

$$w_{nl,n'}(y) = \frac{L^2}{\pi^2 n^7 V_E^2} \int_y^{x_2} \frac{dx}{[(x^2 - y^2)(x - x_1)(x_2 - x)]^{1/2}} \times \int_0^{\infty} dz \frac{\sin z}{z} \cos(\alpha z) \cos(\beta z) J_0(\gamma z), \quad (27)$$

where $x_{1,2} = (1 \pm e_l)/2$ are the turning points, the $\alpha(x)$ is given by (16) with $\omega = \omega_{nl,n'}$, and the functions $\beta(x,y)$ and $\gamma(x,y)$ have the form

$$\beta(x,y) = \frac{p_R (R^2 - \rho^2)^{1/2}}{k_R R} = \left[\frac{(x - x_1)(x_2 - x)}{x - x^2}\right]^{1/2} \frac{(x^2 - y^2)^{1/2}}{x}, \quad (28a)$$

$$\gamma(x,y) = \tilde{l}\frac{\rho}{R^2 k_R} = \frac{\tilde{l}}{2n} \frac{y}{(x^3 - x^4)^{1/2}}. \quad (28b)$$

The integral with respect to z in (27) can be written in the form[36]

$$\int_0^{\infty} \frac{dz}{z} \sin z \cos(\alpha z) \cos(\beta z) J_0(\gamma z) = \frac{1}{4} \sum_{k=1}^{4} \int_0^{\infty} \frac{dz}{z} \sin(b_k z) J_0(\gamma z)$$

$$= \frac{1}{4} \sum_{k=1}^{4} \begin{cases} \arcsin(b_k/\gamma), & 0 < |b_k| \leqslant \gamma, \quad (29a) \\ {}^1/_2\pi \operatorname{sign} b_k, & 0 < \gamma < |b_k|, \quad (29b) \end{cases}$$

where $b_{1,2} = 1 \pm \beta - \alpha$ and $b_{3,4} = 1 \pm \beta + \alpha$. The quantity $b_{3,4}(x,y)$ is positive for all the possible values of x, y, which follows directly from (28a).

From the standpoint of physical applications, there is considerable interest in the collisional decay of s, p, d, and f states with low values of the orbital angular momentum[1)] $l \ll n$. We can thus substitute $\gamma(x,y) = 0$ in (27)–(29) for all values of x, y. In that case, integrating the probability (27) over $2\pi\rho d\rho$, and using (29b), we obtain the following expression for the corresponding $nl \to n'$ cross section (for $l \ll n$):

$$\sigma_{nl,n'}(V_E) = (2n^2)^2 \int_0^1 w_{nl,n'}(y) 2\pi y\, dy$$

$$= \frac{2L^2}{n^3 V_E^2} \iint_{G(x,y)} dx\, dy \frac{y}{[(x^2 - y^2)(x - x^2)]^{1/2}}. \quad (30)$$

The integral in this formula is evaluated over the range of variation of the variables x, y ($0 \leqslant y \leqslant 1$, $y \leqslant x \leqslant 1$), that consists of the two regions $G_1(x,y)$ and $G_2(x,y)$ in which the two quantities $b_1(x,y) = 1 + \beta - \alpha$ and $b_2(x,y) = 1 - \beta - \alpha$ respectively are positive [see (16) and (28)]:

$$G_1(x,\ y)=\{\max\ [0,\ \xi_*(x)]\leqslant(x^2-y^2)^{1/2}\leqslant x,\quad 0\leqslant x\leqslant x_0\},$$
$$G_2(x,\ y)=\{0\leqslant(x^2-y^2)^{1/2}\leqslant\min\ [x,\ -\xi_*(x)],\quad 0\leqslant x\leqslant x_*\},\tag{31}$$

where x_0 is given by (18) and

$$\xi_*(x)=x[\lambda_E x^{1/2}/(1-x)^{1/2}-1],\quad x_*=1/(1+\lambda_E^2),$$
$$\lambda_E=n\omega_{nl,\,n'}/V_E,\tag{32}$$

in which $\omega_{nl,n'}=(\delta_l+\Delta n)/n^3$, and $\Delta n=n'-n$. Transforming in (30) from integration with respect to x, y to the new variables x, ξ, where $\xi=(x^2-y^2)^{1/2}$, and using (31), we obtain

$$\sigma_{nl,n'}(V_E)=\frac{2L^2}{n^3V_E^2}\left\{\int_0^{x_*}\frac{dx}{(x-x^2)^{1/2}}\int_0^{x}d\xi\right.$$
$$\left.+\int_{x_*}^{x_0}\frac{dx}{(x-x^2)^{1/2}}\int_{\xi_*(x)}^{x}d\xi+\int_0^{x_0}\frac{dx}{(x-x^2)^{1/2}}\int_0^{-\xi_*(x)}d\xi\right\}.\tag{33}$$

Evaluating the integrals in (33), and using (32), we obtain the final result for the cross section for the collisional transition $nl\to n'$ with an energy change $\Delta\varepsilon_{nl,n'}$ of the highly-excited atom:

$$\sigma_{nl,n'}(V_E)=\frac{2\pi L^2}{n^3V_E^2}f_{nl,n'}(\lambda_E),\qquad x_0=\frac{1}{1+(\lambda_E/2)^2},\tag{34a}$$

$$f_{nl,n'}(\lambda_E)=\frac{2}{\pi}\left\{B_{x_0}\left(\frac{3}{2},\frac{1}{2}\right)\right.$$
$$\left.+\frac{\lambda_E}{2}\left[\frac{1}{1+(\lambda_E/2)^2}-\ln\left(1+\frac{4}{\lambda_E^2}\right)\right]\right\},\tag{34b}$$

where B_x is the incomplete beta-function (see, e.g., Ref. 37).

For high quantum numbers $n\gg(|\delta_l+\Delta n|/V_E)^{1/2}$, i.e., for $\lambda_E\ll1$, we have $f_{nl,n'}\to1$, so that the general formula (34) leads directly to Omont's result[6] for the total cross section for the quasielastic ($\omega_{nl,n'}=0$) quenching of the nl level in the limit of weak coupling between states:

$$\sigma_{nl,\,n'}(V_E)=2\pi L^2/n^3V_E^2,\quad \lambda_E\ll1.\tag{35}$$

For given relative velocity V_E of the atoms, the cross section (34) is a maximum for $n_{\max}=0.9(|\delta_l+\Delta n|/V_E)^{1/2}$, and is then given by

$$\sigma_{nl,n'}^{max}(V_E)=0{,}1\sigma_{el}/|\delta_l+\Delta n|^{3/2}V_E^{1/2},\quad \lambda_E^{max}=1,2.\tag{36}$$

This is much lower than the corresponding cross section for the quasielastic $nl\to n$ transition for the same n. The reduction in the cross sections for inelastic $nl\to n'$ transitions with a reduction in the principal quantum number n (i.e., an increase in the separation $\Delta\varepsilon_{nl,n'}=(\delta_l+\Delta n)/n^3$ between the initial state nl with quantum defect δ_l and the final degenerate states $n'l'$ of another energy state n') in the region of low values of the principal quantum number $n\ll n_{\max}$ is described by the following formula:

$$\sigma_{nl,n'}(V_E)=\frac{4}{3\pi}\frac{\sigma_{el}V_En^3}{|\delta_l+\Delta n|^3},\qquad \lambda_E\gg1\tag{37}$$

and, consequently, occurs more slowly than in the case of the $n\to n'$ transitions. This expression takes into account the asymptotic behavior of (34b) for $\lambda_E\gg1$:

$$f_{nl,\,n'}(\lambda_E)=8/3\pi\lambda_E^3.$$

The average (for given gas temperature T) cross section for the $nl\to n'$ transition, which is of particular interest for experiments on nonresonant quenching of atomic Rydberg nl states, will now be obtained after averaging $\sigma_{nl,n'}(V_E)$ [see (34)] over the Maxwellian distribution of the velocities of the colliding particles A(nl) and B. In the case of the $nl\to n'$ deexcitation of the atom (when $\varepsilon_{nl}>\varepsilon_{n'}$, where $\varepsilon_{nl}=-1/2(n-\delta_l)^2$, $\varepsilon_{n'}=-1/2n'^2$) we have

$$\langle\sigma_{nl,n'}(V_T)\rangle=\frac{\langle V_E\sigma_{nl,n'}(V_E)\rangle}{\langle V_E\rangle}=\frac{2\pi L^2}{n^3V_T^2}\varphi_{nl,n'}(\lambda_T),\tag{38a}$$

$$\varphi_{nl,n'}(\lambda_T)=\frac{2^{3/2}}{\pi^{1/2}}\exp\left(\frac{\lambda_T^2}{8}\right)D_{-3}\left(\frac{\lambda_T}{\sqrt2}\right)+W(\lambda_T),$$

$$W(\lambda_T)=\frac{\lambda_T}{\pi}\int_0^\infty\frac{due^{-u}}{u^{1/2}}\left[\frac{u}{u+\lambda_T^2/4}-\ln\left(1+\frac{4}{\lambda_T^2}u\right)\right]$$
$$=\frac{\lambda_T^2}{4\pi^{1/2}}\exp\left(\frac{\lambda_T^2}{4}\right)\Gamma\left(-\frac12,\frac{\lambda_T^2}{4}\right)+\lambda_T^2\,{}_1F_1\left(\frac12,\frac32;\frac{\lambda_T^2}{4}\right)$$
$$+\frac{\lambda_T}{\pi^{1/2}}\left[\ln(\lambda_T^2)+C-\frac{\lambda_T^2}{2}\,{}_2F_2\left(1,1;2,\frac32;\frac{\lambda_T^2}{4}\right)\right],\tag{38b}$$

where $C=0.577\ldots$ is the Euler constant, $\langle V_E\rangle=2V_T/\pi^{1/2}=(8T/\pi\mu)^{1/2}$ is the mean thermal velocity, Γ is the incomplete gamma-function, and ${}_1F_1$ and ${}_2F_2$ are, respectively, the confluent and generalized hypergeometric functions (see, for example, Ref. 37). Figure 1 shows a plot of $\varphi_{nl,n'}(\lambda_T)$. Its asymptotic behavior for large and small values of the parameter $\lambda_T=n\omega_{nl,n'}/V_T=|\delta_l+\Delta n|/n^2V_T$ as follows:

$$\varphi_{nl,n'}(\lambda_T)=\begin{cases}1-\pi^{-1/2}\lambda_T\ln(1/\lambda_T^2), & \lambda_T\to0,\\ 2\pi^{-1/2}\lambda_T^{-3}, & \lambda_T\to\infty.\end{cases}$$

These expressions readily yield the behavior of the mean cross section for the $nl\to n'$ transitions both in the quasielastic ($\lambda_T\ll1$) and the inelastic ($\lambda_T\gg1$):

$$\langle\sigma_{nl,\,n'}(V_T)\rangle=\sigma_{el}/2n^3V_T^2,\quad \lambda_T\ll1,\tag{39a}$$

$$\langle\sigma_{nl,\,n'}(V_T)\rangle=\sigma_{el}V_Tn^3/\pi^{1/2}|\delta_l+\Delta n|^3,\quad \lambda_T\gg1.\tag{39b}$$

Figure 3 shows the theoretical [calculated from (38)] and experimental[26–28] data on the quenching of Rydberg ns levels of rubidium by helium atoms [the electron-scattering length on the He($1s^2$) atom is $L=1.19$ a.u.; Ref. 40]. The cross section for this process is largely determined by Rb(ns) + He$\to$Rb($n-3,l'>2$) + He transitions for which the resonance defect $\Delta\varepsilon_{ns,n'}=(\delta_s+\Delta n)/n^3=0.15/n^3$ is a minimum (for rubidium atoms, the quantum defect is $\delta_s=3.15$). It is important to draw attention to the fact that the cross sections (34)–(39) for transitions from ns levels to all the sublevels l' of another level n' (including states with $l'=0$, 1, 2,) are practically exact for $n\gg1$, including the cross section $\sigma(ns\to n',\,l'>2)$ in which we are interested here. This is due to the low statistical weight $g_{l'}=2l'+1\ll n'^2$ of the final $n's$, $n'p$, and $n'd$ states, and the reduction[12] in the partial

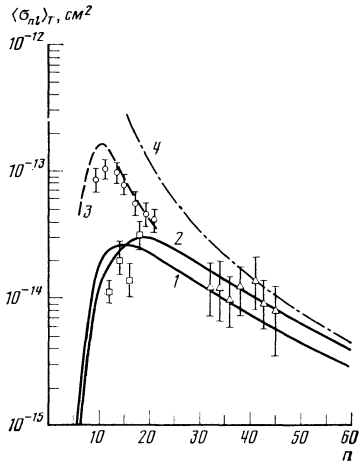

FIG. 3. Cross sections for the quenching of *ns* and *nf* levels of rubidium by helium atoms. Curves 1 and 2—present results [calculated from (38)] showing the average cross section $\langle\sigma_{ns,n-3}\rangle_T$ for the Rb(*ns*) + He→Rb($n-3, l'>2$) + He transition at 520 K and 296 K, △—experiment[27,28] at 296 K, □—experiment[26] at 520 K. Curve 3—calculated,[17] ○—experimental[21] cross section $\langle\sigma_{nf,n}\rangle_T$ for the quasielastic transition Rb(*nf*) + He→Rb($n, l'\neq 2$) + He. Curve 4—calculated from (39a) at 296 K for the quasielastic *nf*→*n* transition in the weak coupling approximation.

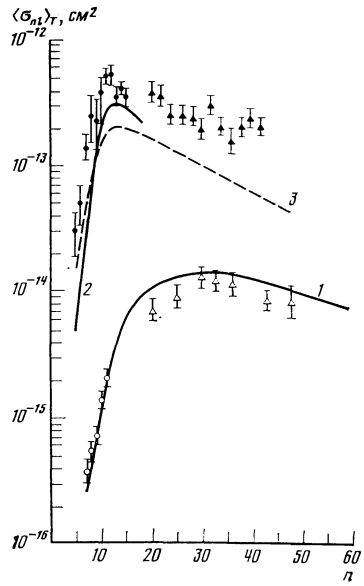

FIG. 4. Cross sections for the quenching of the *ns* and *nd* levels of sodium by argon atoms. Curve 1—present results on the mean cross section $\langle\sigma_{ns,n-1}\rangle_T$ of the transition Na(*ns*) + Ar→Na($n-1, l\geqslant 2$) + Ar [calculated from (38) at 450 K]; ○—experiment[22] at 425 K, △—experiment[23] at 450 K. Curves 2 and 3—theoretical data[11] and calculations[20] based on the approximate formula given by Hickman[17] for the quasielastic quenching cross section $\langle\sigma_{nd,n}\rangle_T$ for the quasielastic quenching of *nd* levels of Na in argon; ● and ▲—corresponding experimental data[18,20] for this process at 430 K and 450 K, respectively.

cross sections for the inelastic $nl\to n'l'$ transitions with decreasing l'. The good agreement between our results and experimental data shows that the appreciable reduction in the cross sections for the quenching of *ns* states of rubidium as compared with the quasiresonant ($\delta_f \ll 1$) quenching of *nf* states is due to the energy defect of the $ns\to n-3, l'>2$ transition, which is substantial (see Fig. 3) even for $n \lesssim 30$–40 for which $\lambda_T = 0.15/n^2 V_T \gtrsim 0.5$. We note also that our data are practically identical with the numerical calculations[12] performed for the weakly-inelastic region ($n \geqslant 34$).

Differences between nonresonant and quasiresonant *n*- and *l*-mixing of atomic Rydberg states can be seen particularly clearly in experiments on the quenching of *ns* (Refs. 22 and 23), *nd* (Refs. 18 and 20), and *nf* (Ref. 19) levels of sodium in inert gases (see Fig. 4). In this case, there is a smaller compensation of the quantum defect δ_s of the *ns* levels by the change $\Delta n = n' - n$ in the principal quantum number during the quenching process, so that the energy defect $\Delta\varepsilon = (\delta_s + \Delta n)/3$ is higher than for the quenching of Rb(*ns*) atoms. The quenching of the *ns* states of sodium is largely due to the $ns\to n-1$, $l'\geqslant 2$, transition for which $\Delta\varepsilon_{ns,n-1} = 0.35/n^3$ [for the Na(*ns*) atoms, the quantum defect is $\delta_s = 1.35$]. There is also a contribution (less than 30% even for $n \sim 30$–40) due to the $ns\to n-2, l'\geqslant 2$ transition for which $\Delta\varepsilon_{ns,n-2} = 0.65/n^3$.

To calculate the cross sections for the *n* and *l* mixing of atomic Rydberg states in the argon atmosphere, we must include both the short-range interaction of the Ar atoms with the outer electrons and the polarization interaction between these atoms. The result is a reduction of the total elastic scattering cross section $\sigma_{el}(\varepsilon)$ (as compared with the value[41] $\sigma_{el} = 4\pi L^2$ for $\varepsilon = 0, L_{exp} = -1.4$) for an ultraslow electron on the Ar atom, which occurs as the energy ε increases (Ramsauer effect) and the principal quantum number *n* decreases for a quasifree electron. We have taken this effect into account by introducing a simple dependence of the cross section σ_{el} on *n*, i.e., instead of $\sigma_{el}(\varepsilon = 0) = 4\pi L^2$, we substituted the experimental[41,42] cross section $\sigma_{el}(\varepsilon)$ into (38) at the kinetic energy $\varepsilon = 1/2n^2$ of the electron in orbit. This method was successfully used in Ref. 17 to describe quasielastic quenching.

It is clear from Fig. 4 that the experimental data[22,23] on the quenching of Na(*ns*) atoms in argon are satisfactorily reproduced by our formulas (34)–(39), based on the Fermi model and describing inelastic $nl\to n'$ transitions. We note that an increase in the energy defect in the $ns\to n-1, l'\geqslant 2$ transition in Na by a factor of only two as compared with the $ns\to n-3$, $l'>2$ transition in Rb leads to substantially greater differences between the nonresonant and quasiresonant quenching of Rydberg levels (see Figs. 3 and 4).

Estimates of the cross section for the competing noninertial quenching of Rb(*ns*) atoms in helium, performed by analogy[2)] with Ref. 38, show that this mechanism is unimportant throughout the range $n \leqslant 45$, which was examined experimentally in Refs. 26–28. A similar treatment of the system Na(*ns*) + Ar core provides a small contribution near the cross section maximum at $n_{max} = 32$, and even a smaller contribution for $n < n_{max}$. However, the role of this mechanism increases with increasing principal quantum number *n*, so that, in the quenching of the *ns* states of Na in argon, it may become important even for $n \sim 40$–50 and predominant for higher values of *n*.

5. CONCLUSIONS

The analysis performed in this paper has shown that the behavior and magnitude of the cross sections for nonreson-

ant collisional quenching of Rydberg levels nl with large quantum defect δ_l are qualitatively different as compared with the previously investigated nonresonant case $\delta_l \ll 1$. The position of the maximum $n_{\max} = (|\delta_l + \Delta n|/V_E)^{1/2}$ in the former case is shifted toward higher values of n, and the height of the maximum, $\sigma_{nl,n}^{\max}$ [see (36)], is substantially smaller than the corresponding l-mixing cross section[3)] and is very dependent on the energy change $\Delta\varepsilon \simeq V_E/n_{\max}$ of the highly-excited atom during the quenching process. Even for relatively low values of $\Delta\varepsilon$, for example, for the quenching of ns levels of Rb in helium, the maximum cross section $\sigma_{ns,n-3}^{\max}$ is lower by a factor of three as compared with the quenching of ns levels (see Fig. 3) As the energy defect $\Delta\varepsilon$ increases, the differences between nonresonant and quasiresonant processes become particuarly important. For example, in the quenching of ns levels of Na in argon, the maximum in the cross section occurs at $n_{\max} = 32$ instead of $n_{\max} = 8$ (as for the nd levels), whereas the cross sections $\sigma_{ns}^{\max}$ and $\sigma_{nd}^{\max}$ already differ by two orders of magnitude (see Fig. 4).

For large values of the principal quantum number, $n \gg n_{\max}$, the cross sections for inelastic transitions tend to the quasielastic limit of weakly coupled states ($\sigma \sim n^{-3}$), due to the reduction in the energy defect $\Delta\varepsilon = |\delta_l + \Delta n|/n^3$ with increasing n. For $n \ll n_{\max}$ they fall rapidly and it is found that $\sigma_{nn'} \propto n^7$ and $\sigma_{nl,n'} \propto n^3$ for $n \to n'$ and $nl \to n'$ transitions, respectively. The essential point is that this reduction in cross sections for $n < n_{\max}$ (like the very appearance of the maximum) is explained by a different physical factor from the quasielastic case, for which $\Delta\varepsilon = 0$. It is due to the sharp reduction, compared with the size of the electron orbit, in the range of impact parameters ($\rho_{\max} \sim 2n^2/(1+\lambda_E^2) \ll 2n^2$ for $\lambda_E \gg 1$) in which collisions between Rydberg atoms and incident particles are nonadiabatic and, in contrast to l mixing, the process of nonresonant quenching of Rydberg levels can be described by perturbation theory in the entire range of quantum numbers.

The cross sections for the quenching of the ns levels of alkali metals in inert gases, calculated from the theory of inelastic transitions developed in this paper, are in good agreement with existing experimental data[22,23,26–28] (see Figs. 3 and 4). We may therefore conclude that the results of these experiments on the nonresonant quenching of highly excited states can be described, as in the quasielastic case, by the Fermi model, and their explanation does not require the use of other mechanisms, as suggested in Refs. 22 and 23.

On the other hand, there are many cases in which the n- and l-mixing process is dominated by a competing mechanism involving the scattering of the incident atom by the ion core of the highly-excited atom. In experiments on the collisional quenching of the Rydberg levels of an atom A(nl) by atoms B of a second gas, this mechanism may be significant in the following situations.

(1) High values of the principal quantum number n (Ref. 39). The reason for this lies in the reduction in the total Fermi cross sections[6]

$$\sigma_n \sim \sigma_{nl} = \sum_{n'} \sigma_{nl,n'} \sim \sigma_{el}^{e^-,B}/nV_E, \qquad n \gg V_E^{-1/2} \tag{40}$$

with increasing n and the resultant rapid reduction in the total cross sections for the quenching of highly-excited states by the nonintentional mechanism (see Refs. 38 and 39 for further details):

$$\sigma_n \sim \sigma_{nl} \sim \begin{cases} (\mu V_E/M_{A^+})^2 n^4 \sigma_{tr}^{A^+,B}(V_E), & n \leqslant (M_{A^+}/\mu V_E)^{1/3}, \quad (41a) \\ \sigma_{el}^{A^+,B}(V_E), & n \gg M_{A^+}/\mu V_E, \quad (41b) \end{cases}$$

where $\sigma_{tr}^{A^+,B}$ and $\sigma_{el}^{A^+,B}$ are, respectively, the transport and total elastic cross sections for the scattering of atom B by the core A^+, and $\sigma_{el}^{A^+,B}(V_E) \gg \sigma_{tr}^{A^+,B}(V_E)$. for thermal velocities V_E. We note that (41a) and (41b) can be obtained in the well-known "shakeout" model of a quantum system (see, for example, Refs. 35 and 44). For the collision between Rydberg atoms and neutral particles, this model can be used[38] for $\Delta\varepsilon \ll V_E/R_{BA^+} n^2 \gg R_{BA}$ (where $R_{BA^+} \sim (\sigma_{tr}^{A^+,B}/\pi)^{1/2}$ is the characteristic size of the region of interaction between particles A^+ and B). Comparison of (40) with (41)[4)] will show that, beginning with a certain value n_0, the noninertial mechanism become more effective (for $n > n_0$) than the usual Fermi mechanism. The specific value of n_0 depends on the relative velocity V_E and masses M_A, M_B of the colliding atoms, as well as on the ratio of cross sections $\sigma_{el}^{e^-,B}$ and $\sigma_{tr}^{A^+,B}$. At thermal collision velocities, this occurs for $n > 40$–50 (see, for example, curves 3 and 4 in Fig. 2) and, in many cases, for higher values ($n \gtrsim 100$).

(2) Nonresonant quenching of Rydberg levels for which this process is accomplished by a substantial change in the energy $\Delta\varepsilon \gtrsim V_E/n$. It follows from our results that, in this range of energy defects $\Delta\varepsilon$, there is an appreciable reduction in the Fermi cross sections for the $n \to n'$ and $nl \to n'$ transitions compared with the case of precise resonance for which $\Delta\varepsilon = 0$ [see (22), (23), (36), and (37), and Figs. 2–4]. Hence, for inelastic transitions with an energy change $\Delta\varepsilon$, the noninertial mechanism [see (41)] may become important for values of the principal quantum number n smaller than in the quasielastic case. For example, in the nonresonant (inelastic) quenching of H(n) atoms in helium, this occurs for $n \gtrsim 30$ (see curves 1 and 4 in Fig. 2). We note that, for the reasons stated above, the noninertial mechanism should begin to be appreciable in experiments on the quenching of nl levels of atoms for high values of n, at first for levels with high quantum defect δ_l (not equal to the integer $|\Delta n|$) and then for $\delta_l \ll 1$.

(3) Relatively low values of n in the case where the interaction between atom B and core A^+ forms a deep potential well and high bottom vibrational energy ($n \sim 5$–10 for H(n) + He).[38] The behavior of the cross sections for inelastic $n \to n'$ and $nl \to n'$ transitions due to the scattering of atom B by the core A^+ in the essentially nonresonant region $\Delta\varepsilon \gtrsim V_E/R_{BA^+}$ is then radically different from the opposite limit of electron "shakeout." This is due to the sharp rise in the relative velocity of particles A^+ and B as they speed up in the potential well, which produces a substantial increase in the role of the noninertial mechanism. In addition, there is a further important mechanism that relies on the interaction between the outer electron and the dipole moment of inner

electrons in the quasimolecule ($BA^+ + e^-$), induced during the collision. Both mechanisms may be considerably more effective than the traditional Fermi mechanism (see Fig. 2).

In conclusion, let us examine the validity of the Fermi pseudopotential model in the analysis of inelastic collisional transitions between atomic Rydberg levels. The model assumes that the scattering of atom B by the weakly-bound (quasifree) electron e^- and by the atomic residue (core) A^+ occurs independently. This is true if the principal contribution to the cross section for a transition with an energy change $\Delta\varepsilon$ is due to nuclear separations $R(\Delta\varepsilon)$ and, consequently, distances $r_n(\Delta\varepsilon) \sim R(\Delta\varepsilon)$ between the core A^+ and electron e^- that substantially exceed the characteristic dimensions R_{BA^+} and R_{Be^-} of the regions of interaction between atom B and atomic core A^+ and electron e^-. The length r_{Be^-} is of the order of the de Broglie wavelength $\lambda\!\!\!^{-}_n(\Delta\varepsilon) \sim 1/q_n(\Delta\varepsilon)$ of the electron during its motion at distances $r_n(\Delta\varepsilon)$ from the core for which the above transition takes place [$q_n(\Delta\varepsilon)$ is the corresponding electron momentum]. According to the analysis of $n \to n'$ and $nl \to n'$ transitions performed in this paper, the quantity $R(\Delta\varepsilon) \sim 2n^2 x_0$ (or $2n^2 x_*$) is given by (18) and (32) [see also (19) and (33)], so that the above conditions assume the form

$$R(\Delta\varepsilon) \sim r_n(\Delta\varepsilon) \sim 2n^2/(1+\lambda_E^2) \gg \begin{cases} R_{BA^+} \sim (\sigma_{tr}^{A^+,B}/\pi)^{1/2}, & \text{(42a)} \\ \lambda\!\!\!^{-}_n(\Delta\varepsilon) \sim 1/q_n(\Delta\varepsilon). & \text{(42b)} \end{cases}$$

For quasielastic transitions $\Delta\varepsilon \ll V_E/n$ (and $\lambda_E \ll 1$), the quantity $r_n(\Delta\varepsilon)$ is of the order of the atomic orbital radius $r_n \sim 2n^2$ and the momentum of the electron is $q_n \sim 1/n$. For an essentially inelastic transition with $\Delta\varepsilon \gg V_E/n$ (and $\lambda_E \ll 1$), small distances $r_n(\Delta\varepsilon) \sim 2n^2/\lambda_E^2$ [and, correspondingly, small impact parameters $\rho(\Delta\varepsilon) \sim r_n(\Delta\varepsilon)$] contribute to the cross section, so that the momentum $q_n(\Delta\varepsilon) \sim [2/r_n(\Delta\varepsilon)]^{1/2}$ of the electron becomes large as it speeds up in the Coulomb field of the ion core A^+, but the wavelength is reduced: $\lambda\!\!\!^{-}_n(\Delta\varepsilon) \sim n/\lambda_E \ll n$. Conditions (42a) and (42b) then lead to the following restrictions on the permissible values of the energy $\Delta\varepsilon$ in inelastic transitions:

$$\Delta\varepsilon \ll \Delta\tilde{\varepsilon} = 2^{1/2} V_E / R_{BA^+}^{1/2}, \quad \text{(43a)}$$

$$\Delta\varepsilon \ll V_E, \quad \text{(43b)}$$

where, since $R_{BA^+} \sim (\sigma_{tr}^{A^+,B}/\pi)^{1/2} \gg 1$ au, condition (43a) must, in fact, be satisfied. For the specific systems that we have examined, we have $\Delta\tilde{\varepsilon} = 6 \cdot 10^{-4}$ au [H(n) + He], $\Delta\tilde{\varepsilon} = 4 \cdot 10^{-4}$ au [Rb (ns) + He], and $\Delta\tilde{\varepsilon} = 10^{-4}$ au [Na(ns) + Ar], which coincides with the estimated limiting energy $\Delta\tilde{\varepsilon}$ reported previously in Ref. 7. Condition (43a) leads to the following conditions for the principal quantum number: $n \gg 12$, 7, and 13, respectively.

One further condition for the energy defect $\Delta\varepsilon$ follows directly from the well-known expansion (see Ref. 40) for the elastic-scattering amplitude of a slow free electron e^- on the atom B in powers of transferred momenta Q (see also Refs. 9, 12, and 29):

$$Q \sim q_n(\Delta\varepsilon) \sim \Delta\varepsilon/V_E \ll 4L/\pi\alpha, \quad \text{(44)}$$

where α is the polarizability of atom B. This corresponds to the scattering length approximation in the free-electron model, and shows that we can neglect the long-range (polarization) part of the interaction potential between the electron e^- and atom B compared with the short-range part defined by the zero-range Fermi pseudopotential.

[1)]The initial expressions (26) and (27) for the $nl \to n'$ transition probabilities were obtained above by using the quasiclassical representation (6) for the spherical harmonics Y_{lm} and by replacing summation over quantum numbers m and l with the corresponding integration [see (7) and (13)]. This is formally valid for $l \gg 1$ (see, for example, Refs. 34 and 35) and, consequently, is certainly justified in the summation of partial probabilities over the final degenerate states m' and l' (when the main contribution to the total $nl \to n'$ transition probability is provided by large values $l' \sim n'$). However, such approximations work well in practice even for low values of l. In particular, in the case of an ns level, they lead to precisely the same result [see (26) and (27) where $\gamma = 0$ and, correspondingly, $J_0(\gamma z) = 1$] as when the quantum-mechanical expression $|Y_{00}(\theta,\varphi)|^2 = \frac{1}{4}\pi$ is used for the angular part of the initial-state wave function.

[2)]The only difference as compared with Ref. 38 (which investigated noninertial $n \to n'$ transitions for equally populated l sublevels) is that, in the present case, we are interested in cross sections for $nl \to n'$ transitions for fixed initial-state orbital angular momentum l. When the cross sections for such transitions were estimated in the dipole region $n \ll (\mu V_E/M_{A^+})^{-1/2}$, the Kramers formula for the radial matrix elements of the position vector of the highly-excited electron in the Coulomb field was replaced with the quasiclassical expressions[43] for the quantities $\langle nl|r|n', l \pm 1\rangle$.

[3)]We recall that the quasielastic cross section for the quenching of atomic Rydberg states is a maximum for $n_{max} \sim (L/V_E)^{2/7}$ (Ref. 6), i.e., $n_{max} = 8$–15 for thermal collisions with inert-gas atoms (see Ref. 2). The quantity n_{max} then separates the region of strong coupling in which $n \lesssim n_{max}$ and the cross sections are determined by the size of the electron orbit $\sigma \propto n^4$, from the region of weak coupling in which $n \gg n_{max}$, perturbation theory is valid, and $\sigma \propto n^{-3}$ (see Figs. 3 and 4).

[4)]Formula (41a) is valid in the dipole region $pn^2 \ll 1$ (where $p = \Delta V_{A^+}$ is the electron momentum corresponding to the change $\Delta V_{A^+} \lesssim \mu V_E/M_{A^+}$ in the velocity of the core A^+ during collision with atom B) and formula (41b) determines the limiting value of the total cross section for the quenching of a Rydberg level for $n \gg 1/p \gtrsim 10^3$. The "shakeout" parameter[44] N (defined as the ratio of the de Broglie wavelength of the electron in orbit, $\lambda\!\!\!^{-}_n \sim n$, to the de Broglie wavelength of the same electron calculated from the transferred momentum $\lambda\!\!\!^{-}_p \sim 1/p$,) becomes large: $N \sim \lambda\!\!\!^{-}_n/\lambda\!\!\!^{-}_p \approx 1$, so that the total shakeout probability in the shell n approaches unity ($W_n \to 1$) and, correspondingly, the total quenching cross section σ_n becomes equal to $\sigma_{el}^{A^+,B}$.

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