Collisional quenching of Rydberg atoms in the presence of a resonance on a quasidiscrete level of the perturbing particle

V. S. Lebedev

P. N. Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow

V. S. Marchenko

I. V. Kurchatov Institute of Atomic Energy, Moscow

(Submitted 9 December 1985)
Zh. Eksp. Teor. Fiz. **91**, 428–444 (August 1986)

Formulas relating the cross sections for collision-induced $nl \to n'$ and $n \to n'$ transitions between highly excited atomic levels to the differential cross section for elastic scattering of an ultralow-energy electron by the perturbing atom and the kinetic energy distribution function for a weakly bound electron in the initial state are derived within the framework of the quasi-free electron model with the aid of the impulse approximation. A theory, based on these formulas, of the collisional quenching of the Rydberg states of an atom $A(nl)$ is developed which, together with the potential scattering of an electron e^- by the perturbing atom B, takes account of the presence of a low-energy resonance on a quasi-discrete level of the negative ion B^-, and is therefore applicable to collisions with the alkali-metal atoms. It is shown that the behavior and magnitudes of the cross sections for this process differ essentially from what was found in earlier investigations of the case of quenching of Rydberg states by inert-gas atoms, for which it is sufficient to use the scattering-length approximation. Specific calculations of the cross sections for inelastic and quasielastic quenching of the nS and nD states of Li and Na atoms in their own gases (for which atoms reliable values for the ^3P-resonance energy E_r and width Γ_r are available) are carried out. It is established, in particular, that the relative roles of the potential and resonance scattering depend essentially on the principal quantum number n and the magnitude of the energy defect $\Delta\varepsilon_{nl,n'}$ for the $nl \to n'$ transition. The results obtained in the paper are used to explain the available experimental data on the $Rb(nS) + Rb$ Rydberg-level quenching and $K(nS) + Rb$ Rydberg-level broadening processes, and the energy E_r and width Γ_r of the ^3P resonance on the quasidiscrete level of the negative ion Rb^- are determined from the experimental data.

1. INTRODUCTION

At present the processes of collisional quenching of the Rydberg states of atoms by neutral particles are being actively investigated both experimentally and theoretically.[1,2] The theory of these processes is based on Fermi's quasi-free electron model, which was developed in a number of papers[3–7] (for a more comprehensive bibliography, see Ref. 1, Chaps. 6–8). In this model the collision of a highly excited atom $A(nl)$ with a perturbing atom B is treated as an elastic scattering of the outer quasi-free electron by this atom, the ion core A^+ being only responsible for the shaping of the electron momentum distribution in the given Rydberg state $|nl\rangle$. The major portion of the theoretical investigations has, until recently, been devoted to the investigation of the process of quasielastic quenching of Rydberg levels as a result of $nl \to nl'$ transitions involving a change in the orbital angular momentum, but not in the principal quantum number n [i.e., as a result of l-mixing transitions (see Ref. 1, Chaps. 6 and 8)].

But recently there were independently obtained analytic formulas for the cross sections for inelastic $n \to n'$ (Refs. 8–10) and $nl \to n'$ (Refs. 9 and 10) transitions between highly excited atomic states and also for the corresponding rate constants.[9] In Ref. 9 the semiclassical approach developed in Ref. 7 for the l-mixing process ($\Delta\varepsilon_{nl,nl'} = 0$) is generalized to the case of transitions involving a change in the energy of the Rydberg atom ($\Delta\varepsilon_{nl,n'} \neq 0$), while the results obtained in Ref. 8 and 10 are based on the impulse approximtion[5,6] and the binary theory of form factors (see Ref. 1, Chap. 11 and Ref. 11). These formulas are used in Refs. 9 and 10 to quantiatively explain the experimental data on the inelastic-collision-induced quenching of the Rydberg nl levels of alkali-metal atoms in inert gases in the case of low l values, when, because of the large magnitude of the quantum defect δ_l, the major role is played by the transitions involving a change in the principal quantum number n. Numerical calculations of the cross sections for quenching of atomic nl levels in inert gases are carried out in Refs. 12 and 13 within the framework of the impulse approximation for the region of small values of the $nl \to n'$ transition energy defects $\Delta\varepsilon_{nl,n'}$ (i.e., for sufficiently high values of n). It should be noted that the dominant contribution to the cross sections for both quasielastic and inelastic quenching of the highly excited levels in the experimentally investigated region of quantum numbers n is, as a rule, made by the scattering of the perturbing atom B on the weakly bound (quasifree) electron e^- of the atom $A(nl)$. But in a number of situations the scattering on the ion core A′ is important, even decisive (see, for example, Refs. 14–16 and 9).

 0038-5646/86/080251-10$04.00

The presently existing theory, based on the quasifree electron model, of collisional quenching of the Rydberg states of atoms (Ref. 1, Chaps. 6 and 8, and Refs. 6–12) pertains to the case of slightly polarizable perturbing atoms B (in particular, the atoms of the inert gases), for which the standard variant[17] of the effective-radius theory is valid. For such atoms the first term of the expansion[17] of the amplitude f_{eB} of the elastic scattering of an ultralow-energy electron e^- reduces to the scattering length L and a second (correction) term, due to the polarization interaction, depends only on the magnitude Q of the momentum transferred in the collision of the particles e^- and B. A qualitatively different situation obtains in the presence of a low-energy resonance at a quasidiscrete level of the perturbing particle B, a resonance whose role in the broadening and shifting of the Rydberg levels is investigated within the framework of Alekseev and Sobel'man' theory[5] in Refs. 18 and 19. Thus for example, for the alkali-metal atoms the presence of the low-energy ^3P resonance[20,21] and the fact that they are highly polarizable lead to a situation in which the amplitude f_{eB} of the elastic scattering of the ultralow-energy electrons essentially depends on both the electron energy $\varepsilon = k^2/2$ and the scattering angle $\theta_{kk'}$. In this case the cross sections for collision-induced $nl \to n'$ and $n \to n'$ transitions between the Rydberg levels cannot be expressed in terms of the form factors [as is usually done (see Refs. 1, 6, and 11)], and there are no formulas that are valid for an arbitrary form of the elastic electron-atom scattering amplitude $f_{eB}(\varepsilon, \theta_{kk'})$.

In the present paper we derive such formulas with the aid of the impulse approximation and also with the use of the quasicontinuum approximation for highly excited atomic states (see Sec. 2). We show that, to compute the cross sections for collision-induced $nl \to n'$ and $n \to n'$ transitions, we need information about the energy and angle dependences of the scattering amplitude $f_{eB}(\varepsilon, \theta_{kk'})$, whereas the cross sections for broadening and shifting of the Rydberg levels are determined within the framework of the Alekseev-Sobel'man theory[5] by the electron-atom forward scattering amplitude $f_{eB}(\varepsilon, \theta_{kk'} = 0)$. We carry out on the basis of the formulas obtained a theoretical analysis of the processes of collisional quenching of the highly excited states of an atom $A(nl)$ for the case in which a low-energy resonance occurs at a quasidiscrete level of the negative ion B^- in the elastic scattering of the ultralow-energy electrons e^- by the perturbing particle B (see Sec. 3). We carry out specific calculations of the cross sections for inealstic and quasielastic quenching of the nS and nD levels of alkali-metal atoms by atoms of their own gases [Li(2S), Na(3S), and Rb(5S)] with allowance for both the resonance and potential scattering (see Sec. 4). For the case of the quenching of lithium and sodium atoms we identify ranges of the values of the quantum number n (see Figs. 1 and 2 below) in which the role of the low-energy ^3P resonances at the quasidiscrete levels is expecially important.

We find that the experimentally observed large cross sections for quenching[22] and broadening[23] of the nS Rydberg levels of rubidium and potassium atoms in collisions with Rb (5S) atoms (see Fig. 3 below) are accounted for by the contribution of the ^3P resonance, and cannot be described within the framework of the Fermi model with the use of only potential scattering. We propose a method for determining the parameters of the low-energy resonances in electron-atom ($e^- \to B$) scattering from the points on, and the slope of, the plot of the experimentally obtained quenching or broadening cross sections for the highly excited levels of the atom $A(nl)$ against the principal quantum number n. We find with the aid of this method that, for the ^3P resonance in the elastic scattering of electrons on Rb (5S) atoms, $E_r = 1.8\times10^{-2}$ eV and $\Gamma_r = 2.3\times10^{-2}$ eV. They are in good agreement with the theoretical data obtained in Ref. 21 on the basis of a modified effective-radius theory.

2. CROSS SECTIONS FOR COLLISION-INDUCED $nl \to n'$ and $n \to n'$ TRANSITIONS BETWEEN HIGHLY EXCITED ATOMIC LEVELS IN THE IMPULSE APPROXIMATION

Let us derive the formulas relating the cross sections for collision-induced transitions between the Rydberg states of the atom $A(nl)$ to the differential cross section for elastic scattering of an ultralow-energy electron e^- on the perturbing atom B. In the case when the colliding atoms $A(nl)$ and B have thermal energies E, their relative velocity $V_E = (2E/\mu)^{1/2}$ (μ is the reduced mass of the particles A^+ and B) is substantially smaller than the velocity $v_e \sim 1/n$ of the weakly bound electron in an orbit in the entire region of not too high values of n ($\lesssim 100$) that is normally investigated in experiments. In this case the cross section for collision-induced $nl \to n'$ transition is given in the impulse approximation by the following formula[1)] (see Ref. 1, Chap. 8):

$$\sigma_{nl,n'} = \frac{1}{2l+1}\frac{q'}{q}\sum_{m,m'l}\int dO_{qq'}\,|f_{nlm}^{n'l'm'}(\mathbf{q},\mathbf{q}')|^2, \qquad \mathbf{k}'-\mathbf{k}=\mathbf{q}-\mathbf{q}'=\mathbf{Q},$$
$$f_{nlm}^{n'l'm'}(\mathbf{q},\mathbf{q}') = \mu\langle G_{n'l'm'}(\mathbf{k}+\mathbf{Q})\,|\,f_{eB}(\mathbf{k},\mathbf{k}+\mathbf{Q})\,|\,G_{nlm}(\mathbf{k})\rangle. \tag{1}$$

Here $f_{nlm}^{n'l'm'}(\mathbf{q},\mathbf{q}')$ is the $nlm \to n'l'm'$ transition amplitude; $\mathbf{k}$, $\mathbf{k}' = \mathbf{k}+\mathbf{Q}$ and $\mathbf{q} = \mu V_E$, $\mathbf{q}' = \mathbf{q}-\mathbf{Q}$ are electron (e^-) momenta and the momenta associated with the relative motion of the particles A^+ and B before and after the collision; $\mathbf{Q}$ is the momentum transfer; $f_{eB}(\mathbf{k},\mathbf{k}')$ is the elastic electron-atom scattering amplitude; and $G_{nlm}(\mathbf{k})$ is the electron wave function in the momentum representation. Further, let us see (as is done in form-factor calculations for bound-bound transitions between highly excited atomic states [see, for example, Ref. 11)] the quasicontinuum approximation. Accordingly, let us represent the cross section (1) in the form

$$\sigma_{nl,n'} = \frac{1}{2l+1}\frac{q'}{q}\sum_{m,m'l'}\int dO_{qq'} \times \int d\varepsilon_f\,|f_{nlm}^{n'l'm'}(\mathbf{q},\mathbf{q}')|^2\delta(\varepsilon_f-\varepsilon_i-\Delta\varepsilon_{nl,n'})$$
$$\approx \frac{\mu^2}{2l+1}\frac{q'}{q}\sum_{m}\int dO_{qq'}\frac{1}{n'^3}\cdot \times \sum_f \langle G_i(\mathbf{k})\,|\,f_{eB}^*(\mathbf{k},\mathbf{k}+\mathbf{Q})\,|\,G_f(\mathbf{k}+\mathbf{Q})\rangle$$
$$\times\langle G_f(\mathbf{k}+\mathbf{Q})\,|\,f_{eB}(\mathbf{k},\mathbf{k}+\mathbf{Q})\,|\,G_i(\mathbf{k})\rangle\delta(\varepsilon_f-\varepsilon_i-\Delta\varepsilon_{nl,n'}), \tag{2}$$

where $\Delta\varepsilon_{nl,n'} = \varepsilon_{n'} - \varepsilon_{nl}$ is the change that occurs in the energy of the highly excited atom on undergoing the $nl \to n'$ transition in question [$\varepsilon_{n'} = -1/2n'^2$, $\varepsilon_{nl} = -1/2(n-\delta_l)^2$, and δ_l is the quantum defect], $|i\rangle = |nlm\rangle$, and $|f\rangle = |n_f l_f m_f\rangle$. The $d\varepsilon_f = dn_f/n_f^3$ integration in (2) has been replaced by summation over n_f. It should be noted that the formula (2) gives the cross section for transition from the initial nl level of the atom A(nl) to all the $n'l'$ sublevels of the final n' level that are hydrogenlike, and thus have the same energy $\varepsilon_{n'} = -1/2n'^2$. Owing to the rapid decrease of the quantum defects $\delta_{l'}$ as the quantity l' increases, the final Rydberg $n'l'$ states (even for the heavy alkali-metal atoms being investigated here) can practically be considered to be hydrogenlike, starting from $l' > 2$ or 3. As to the contribution of the first few nonhydrogenic $n'l'$ states (i.e., of the states with $l' \leqslant 2$ or 3) to the total $nl \to n'$ transition cross section

$$\sigma_{nl,n'} = \sum_{l'=0}^{n'-1} \sigma_{nl,n'l'},$$

it can be neglected in the case when $n, n' \gg 1$ because of the small statistical weights of these states (for greater details, see Refs. 8 and 9).

Let us perform the subsequent transformations in the Heisenberg representation. To do this, we use the spectral decomposition of the δ function, as well as the well-known properties of the time-translation operators $\exp(-i\hat{H}t)$:

$$\delta(\varepsilon_f - \varepsilon_i - \Delta\varepsilon_{nl,n'}) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \exp[i(\varepsilon_f - \varepsilon_i - \Delta\varepsilon_{nl,n'})t]\,dt,$$

$$\exp(-i\hat{H}t)\,|G_i(\mathbf{k})\rangle = \exp(-i\varepsilon_i t)\,|G_i(\mathbf{k})\rangle,$$

$$\langle G_f(\mathbf{k}')|\exp(i\hat{H}'t) = \langle G_f(\mathbf{k}')|\exp(i\varepsilon_f t), \qquad (3)$$

$$\hat{H} \equiv \hat{H}(\mathbf{k}, \hat{\mathbf{r}}) = \mathbf{k}^2/2 + \hat{U}, \quad \hat{H}' \equiv \hat{H}(\mathbf{k}', \hat{\mathbf{r}}) = (\mathbf{k}+\mathbf{Q})^2/2 + \hat{U}.$$

Here $\hat{H}$ and $\hat{H}'$ are the Hamiltonians corresponding to the initial $\mathbf{k}$ and final $\mathbf{k}' = \mathbf{k} + \mathbf{Q}$ momenta of the highly excited electron in the momentum representation; $\hat{U}(\hat{\mathbf{r}})$ is the potential-energy operator for the interaction of this electron e^- with the ion core A^+; and $\hat{r} = i\partial/\partial\mathbf{k}$ is the radius-vector operator. We can, using the relations (3), transform the expression (2) for the collision-induced $nl \to n'$ transition cross section into the following form:

$$\sigma_{nl,n'} = \frac{\mu^2}{2\pi(2l+1)n'^3}\frac{q'}{q}\sum_m \int dO_{\mathbf{qq}'} \int_{-\infty}^{\infty} dt \exp(-i\Delta\varepsilon_{nl,n'}t) \times \sum_f \langle G_i(\mathbf{k})\,|f_{eB}^*(\mathbf{k}, \mathbf{k}+\mathbf{Q})\,|G_f(\mathbf{k}+\mathbf{Q})\rangle \times \langle G_f(\mathbf{k}+\mathbf{Q})\,|\exp(i\hat{H}'t) f_{eB}(\mathbf{k}, \mathbf{k}+\mathbf{Q}) \exp(-i\hat{H}t)\,|G_i(\mathbf{k})\rangle. \qquad (4)$$

Further, let us use the following operator relation:

$$\exp(i\hat{H}t) f_{eB} \exp(-i\hat{H}t) = f_{eB} + i[\hat{H}, f_{eB}]t + {}^1/_2[\hat{H}, [\hat{H}, f_{eB}]](it)^2 + \ldots = f_{eB} + i[\hat{U}, f_{eB}]t + {}^1/_2[\hat{U}, [\hat{U}, f_{eB}]](it)^2 + \ldots, \qquad (5)$$

keeping in mind the fact that the degree of accuracy aimed at in the impulse approximation being used here would be exceeded if all the terms of the expansion after the first one were retained (since all the terms containing the potential-energy operator $\hat{U}$ for the interaction of the electron e^- with the ion core A^+ were neglected in the derivation of the initial formula (1) [see Ref. 24, Chap. 11)]. Accordingly, in (4) we can assume that the operator $\exp(-i\hat{H}t)$ commutes with the scattering amplitude $f_{eB}(\mathbf{k},\mathbf{k}')$, so that, using the completeness property $\Sigma_f |G_f\rangle\langle G_f| = 1$ of the eigenfunctions of the Hamiltonian $\hat{H}$ for the outer electron of the Rydberg atom A(nl), we arrive at the following result:

$$\sigma_{nl,n'} = \frac{\mu^2}{(2l+1)n'^3}\frac{q'}{q}\sum_m \int dO_{\mathbf{qq}'} \langle G_i(\mathbf{k})\,|\frac{1}{2\pi}\int_{-\infty}^{\infty} dt \times \exp(-i\Delta\varepsilon_{nl,n'}t) f_{eB}^*(\mathbf{k}, \mathbf{k}+\mathbf{Q}) \exp(i\hat{H}'t) \times \exp(-i\hat{H}t) f_{eB}(\mathbf{k}, \mathbf{k}+\mathbf{Q})\,|G_i(\mathbf{k})\rangle. \qquad (6)$$

Thus, we can, within the framework of the quasifree electron model, eliminate the dependence of the cross section for collision-induced $nl \to n'$ transition between the Rydberg levels on the final state, and express this cross section in terms of some operator averaged over the initial state $|i\rangle$ of the atom. This fact is a consequence of the impulse approximation, and also of the quasicontinuum approximation for the highly excited atomic levels, and is in accord with the general results of the theory of quasifree scattering on a system of weakly bound particles (see, for example, Ref. 24, Chap. 11).

Next, let us use the well-known Baker-Campbell-Hausdorff formula

$$\exp(\hat{A})\exp(\hat{B}) = \exp(\hat{A}+\hat{B}+{}^1/_2[\hat{A}, \hat{B}]+{}^1/_{12}[\hat{A}, [\hat{A}, \hat{B}]] + {}^1/_{12}[[\hat{A}, \hat{B}], \hat{B}]+\ldots), \qquad (7)$$

to expand in a series the operator $\exp(i\hat{H}'t)\exp(-i\hat{H}t)$, which determines the magnitude of the $nl \to n'$ transition cross section [see the formula (6)]:

$$\exp(i\hat{H}'t)\exp(-i\hat{H}t) = \exp[i(\hat{H}'-\hat{H})t + {}^1/_2[\hat{H}', \hat{H}]t^2 + \ldots] = \exp[i(\mathbf{kQ}+Q^2/2)t + i\mathbf{Q}\hat{\mathbf{F}}t^2/2 + \ldots]. \qquad (8)$$

The following relations were also used in the derivation of the expression (8):

$$\hat{H}' - \hat{H} = [(\mathbf{k}+\mathbf{Q})^2 - \mathbf{k}^2]/2 = \mathbf{kQ} + Q^2/2, \qquad (9a)$$

$$[\hat{H}', \hat{H}] = \mathbf{Q}[\mathbf{k}, \hat{U}] = i\mathbf{Q}\hat{\mathbf{F}}. \qquad (9b)$$

Here $\hat{\mathbf{F}} = \hat{\mathbf{F}}(\hat{\mathbf{r}})$ is the operator for the force [exerted by the ion core A^+ on the outer electron e^- of the atom A(nl)] in the momentum representation. Notice that it is more convenient to derive the second relation (9b) in the coordinate representation (in which the force $\mathbf{F} = -\partial U/\partial\mathbf{r}$ and the momentum operator $\hat{\mathbf{k}} = -i\partial/\partial\mathbf{r}$), and then take into account the property of invariance of commutation relations on going from one representation to another.

As is well known, for the quasifree electron model to be applicable, it is necessary that there be transferred to the outer electron of the highly excited atom A(nl) during its scattering by the perturbing atom B a characteristic momentum Q_{eB} substantially greater than the impulse $\Delta p \sim F_{eA} + \tau_{eB}$ of the force exerted on this electron by the

ion core A^+ during the characteristic e^--B interaction time τ_{eB}, i.e., it is necessary that the following conditions be satisfied (see, for example, Ref. 1):

$$Q_{eB} \gg F_{eA^+}\tau_{eB} \sim \tau_{eB}/r_{eA^+}^2. \tag{10}$$

Here r_{eA^+} is the characteristic dimension of the region of interaction between the electron e^- and the core A^+ ($F_{eA^+} \sim r_{eA^+}^{-2}$ is the corresponding force), i.e., of the e^--A^+ interaction region that makes the dominant contribution to the cross section for the $nl \to n'$ transition in question. Thus, within the framework of the impulse approximation used in the present paper, we should neglect in the formula (8) the change that occurs in the e^--A^+ interaction potential energy during the short period τ_{eB} of quite intense interaction between the electron e^- and the perturbing atom B, and retain only the first term (i.e., the term linear in t), which determines the change that occurs in the kinetic energy of the quasifree electron in the course of the scattering of this electron by the particle B. Substituting, with allowance made for the foregoing, the result (8) into the expression (5), we obtain for the collision-induced $nl \to n'$ transition cross section the expression

$$\sigma_{nl,n'} = \frac{\mu^2 q'}{(2l+1)2\pi n'^3 q} \sum_m \int dO_{qq'} \langle G_i(\mathbf{k}) | f_{eB}^*(\mathbf{k}, \mathbf{k}+\mathbf{Q}) \int_{-\infty}^{\infty} dt \times \exp[i(\mathbf{kQ} + Q^2/2 - \Delta\varepsilon_{nl,n'})t] f_{eB}(\mathbf{k}, \mathbf{k}+\mathbf{Q}) | G_i(\mathbf{k}) \rangle. \tag{11}$$

Evaluating the time integral in (11), and replacing the $dO_{qq'} = d\varphi_{qq'} QdQ\,|qq'$ integral ($O_{qq'}$ is the solid angle in the relative motion of the heavy particles A^+ and B) by an integral taken over the polar angle $\varphi_{qq'}$ and all possible values of the momentum transfer Q, we have

$$\sigma_{nl,n'} = \frac{1}{V_E^2 n'^3 (2l+1)} \int_{Q_{min}}^{Q_{max}} Q\,dQ \int_0^{2\pi} d\varphi_{qq'} \int d\mathbf{k} \sum_m |G_{nlm}(\mathbf{k})|^2 \times |f_{eB}(\mathbf{k}, \mathbf{k}+\mathbf{Q})|^2 \delta(kQ\cos\theta_{kQ} + Q^2/2 - \Delta\varepsilon_{nl,n'}), \tag{12}$$

where

$$Q_{min} = |q'-q| \approx |\Delta\varepsilon_{nl,n'}|/V_E, \quad Q_{max} = q'+q \approx 2\mu V_E.$$

Notice that the δ function in this formula separates out from the entire momentum space those momentum values which correspond to the given classical energy transfer $\Delta\varepsilon_{nl,n'}$ for the $nl \to n'$ transition, and plays the role of a microcanonical distribution.

Let us represent the momentum wave function of the Rydberg electron in the form of a product of a radial and an angular part: $G_{nlm}(\mathbf{k}) = g_{nl}(k)(k) Y_{lm}(\theta_k, \varphi_k)$, and sum over the magnetic quantum numbers m in (12) with the aid of the following well-known relation for the spherical harmonics:

$$\sum_m Y_{lm}^*(\theta_k, \varphi_k) Y_{lm}(\theta_k, \varphi_k) = (2l+1)/4\pi.$$

Let us orient the z axis of the coordinate system along the vector $\mathbf{Q}$ (so that $\cos\theta_{kQ} = \cos\theta_k = \xi$), and let us represent the element of solid angle associated with the electron in the form $d\Omega_k = -d\xi d\varphi_k$. Then, taking account of the fact that $d\mathbf{k} = k^2 dk d\Omega_k$, and performing in the formula (12) the integration over the electron and heavy-particle polar angles $d\varphi_k$ and $d\varphi_{qq'}$, we obtain the following expression for the cross section for collision induced $nl \to n'$ transition between Rydberg atomic levels:

$$\sigma_{nl,n'} = \frac{\pi}{V_E^2 n'^3} \int_{Q_{min}}^{Q_{max}} Q\,dQ \int_0^{\infty} k^2\,dk |g_{nl}(k)|^2 |f_{eB}(k, Q)|^2 \times \int_{-1}^{1} d\xi\, \delta[kQ(\xi - \xi_0)], \tag{13}$$

where

$$\xi_0 = k_0(Q)/k, \quad k_0(Q) = (\Delta\varepsilon_{nl,n'} - Q^2/2)/Q.$$

The amplitude of the elastic scattering of the electron e^- by the perturbing atom B in this formula is considered to be a function of the wave number and the momentum transfer Q, which is uniquely connected with the electron-scattering angle: $Q = 2k\sin(\theta_{kk'}/2)$. It can be seen directly from (13) that, for a given value of the momentum transfer Q, only those values of the wave number which lie in the range $|k_0(Q)| < k < \infty$ (i.e., for which the condition $0 \leqslant |\xi_0| \leqslant 1$ is fulfilled) contribute to the $nl \to n'$ transition cross section. Evaluating the $d\xi$ integral in the formula (13) with allowance for this circumstance, we arrive at the following result:

$$\sigma_{nl,n'} = \frac{\pi}{V_E^2 n'^3} \int_{Q_{min}}^{Q_{max}} dQ \int_{|k_0(Q)|}^{\infty} dk |f_{eB}(k, Q)|^2 |g_{nl}(k)|^2 k. \tag{14}$$

In the particular case when the quantity $f_{eB} = f_{eB}(Q)$, i.e., when f_{eB} depends only on the momentum transfer Q (and, consequently, the $nl \to n'$ transition cross section can be expressed in terms of the corresponding form factors), the well-known binary-theory result[11] for the bound-bound transition cross section follows directly from the formula (14) obtained above.

Let us now derive a more convenient— for specific calculations— expression for the cross section in terms of the scattering amplitude $f_{eB}(\varepsilon, \nu)$, treated as a function of the electron kinetic energy $\varepsilon = k^2/2$ and the cosine of the scattering angle $\nu = \cos\theta_{kk'}$. Let us at the same time take account of the fact that, in the region of quantum numbers $n \lesssim 100$ of interest to us, we have, for all values of $Q \geqslant Q_{min} \approx |\Delta\varepsilon_{nl,n'}|/V_E$, $|\Delta\varepsilon_{nl,n'}| \approx |\delta_l + \Delta n|/n^3 \ll Q^2/2$, so that we can set $|k_0(Q)| \approx Q/2$ and $Q_{max} \approx \infty$ in (14). Then, setting in (14) $\varepsilon = k^2/2$ and $\nu = 1 - Q^2/4\varepsilon$, and changing the order of integration, we finally have

$$\sigma_{nl,n'} = \frac{\pi}{V_E^2 n'^3} \int_{\varepsilon_{min}}^{\infty} d\varepsilon |g_{nl}(\varepsilon)|^2 \varepsilon^{1/2} \int_{-1}^{\nu_{max}(\varepsilon)} \frac{d\nu}{(1-\nu)^{1/2}} |f_{eB}(\varepsilon, \nu)|^2, \quad \nu_{max}(\varepsilon) = 1 - \frac{2\varepsilon_{min}}{\varepsilon}, \tag{15}$$

where $\varepsilon_{min} = Q_{min}^2/8 \approx |\Delta\varepsilon_{nl,n'}|^2/8V_E^2$. This formula gives the sought relation connecting the cross section for collision-

induced $nl \to n'$ transition between Rydberg levels of the atom A(nl) with the differential cross section $d\sigma_{el}^{eB}/d\Omega_{kk'} = |f_{eB}(\varepsilon,\theta_{kk'})|^2$ for elastic electron-atom scattering and the kinetic energy distribution function $|g_{nl}(\varepsilon)|^2$ for the highly excited electron e^- in the initial state.

It should be noted that, in experiments on the collisional quenching of the Rydberg levels of an atom in a buffer, or its own, gas, it is the total $nl \to n'$ transition cross section $\sigma_{nl}^{Q} = \Sigma_{n'}\sigma_{nl,n'}$ summed over all the final levels n' [or, more exactly, the mean value $\langle\sigma_{nl}^{Q}\rangle_T = \langle V_E\sigma_{nl}^{Q}(V_E)\rangle_T/\langle V_E\rangle_T$ of this quantity at the given gas temperature T] that is measured. Then, in the case of relatively low gas pressures, we, as a rule, deal with the cross sections $\langle\sigma_{nl}^{Q}\rangle_T$ for quenching of specified, selectively excited (with the aid of tunable lasers) Rydberg nl levels with definite values of the principal (n) and orbital (l) quantum numbers (see Ref. 1). For hydrogenlike nl levels the highly-excited electron kinetic energy distribution function $|g_{nl}(\varepsilon)|^2$ needed for the computation of the $nl \to n'$ transition cross sections from the formula (15) can, in the general case, be expressed in terms of the Gegenbauer polynomials (see, for example, Ref. 25). In the case, being considered in the present paper, of Rydberg nl levels of alkali-metal atoms with small orbital angular momentum values, i.e., with $l \ll n$ (when the quantum defect δ_l of the initial nonhydrogenic nl level can be substantial) we shall use for the function $|g_{nl}(\varepsilon)|^2$ in the formula (15) the well-known result[7,18]

$$|g_{nl}(\varepsilon)|^2 = 2n_{eff}/\pi\varepsilon(1+2n_{eff}^2\varepsilon)^2, \qquad n_{eff} = n-\delta_l, \tag{16}$$

in which averaging over the period of the rapidly oscillating component of the semiclassical kinetic-energy ($\varepsilon = k^2/2$) distribution function for the electron e^- has been carried out.

At high gas pressures, because of the large values of the cross sections for the l-mixing process, there rapidly get established conditions for the uniform population of all the degenerate hydrogenlike l sublevels (in accordance with their statistical weights $2l+1$) within the limits of one energy level with principal quantum number n. In this case the formula for the cross section $\sigma_{nn'}$ for collision-induced $n \to n'$ transition between Rydberg atomic levels with different principal quantum numbers can be obtained directly from (14) and (15) by replacing the function $|g_{nl}(\varepsilon)|^2$ by its l-averaged value $|g_n(\varepsilon)|^2$. The function $|g_n(\varepsilon)|^2$ is then given by the following well-known formula (see Refs. 4 and 7):

$$|g_n(\varepsilon)|^2 = \frac{1}{n^2}\sum_{l=0}^{n-1}(2l+1)|g_{nl}(\varepsilon)|^2 = \frac{2^5n^3}{\pi(1+2n^2\varepsilon)^4}. \tag{17}$$

3. THE $nl \to n'$ AND $n \to n'$ TRANSITIONS IN THE PRESENCE OF A RESONANCE AT A QUASIDISCRETE LEVEL OF THE PERTURBING PARTICLE

Let us, using the formula (15) obtained in Sec. 2, investigate the collision-induced $nl \to n'$ and $n \to n'$ transitions between Rydberg atomic states in the presence of a low energy resonance at a quasidiscrete level of the perturbing atom B. In this case the total elastic electron-atom scattering amplitudes $f_{eB}^{(S)}$ corresponding to the two possible values $S = |s \pm 1/2|$ of the total spin of the $e^- + B$ system (with the particle B having the spin s) can be represented in the following form (see, for example, Ref. 26, §§ 133 and 134):

$$f_{eB}^{(S=S_r)}(\varepsilon,\nu) = f_{S_r}^{p}(\varepsilon,\nu) + (2L_r+1)f_{L_r}^{r}(\varepsilon)P_{L_r}(\nu),$$
$$f_{eB}^{(S\neq S_r)}(\varepsilon,\nu) = f_{(S\neq S_r)}^{p}(\varepsilon,\nu), \tag{18}$$
$$f_{L_r}^{r}(\varepsilon) = -\gamma\varepsilon^{L_r}/2^{1/2}(\varepsilon-\varepsilon_0+i\gamma\varepsilon^{L_r+1/2}).$$

Here f^p and f^r are respectively the potential and resonance scattering amplitudes, $P_{L_r}(\nu)$ is a Legendre polynomial, S_r and L_r are the spin and orbital angular momentum of the quasidiscrete level of the negative ion B^-, and ε_0 and γ are constants determining the energy E_r and width Γ_r of the resonance. From (18) it follows that the differential elastic e^--B scattering cross section $d\sigma_{el}^{(eB)}/d\Omega_{kk'}$ averaged over the two possible values of the total spin S is, in the presence of a resonance, given by the following formula:

$$\frac{d\sigma_{el}^{(eB)}}{d\Omega_{kk'}} = |f_{eB}(\varepsilon,\nu)|^2 = (2L_r+1)^2C(S_r)|f_{L_r}^{r}(\varepsilon)|^2P_{L_r}^2(\nu)$$
$$+|f^p(\varepsilon,\nu)|^2+2(2L_r+1)C(S_r)P_{L_r}(\nu)[\mathrm{Re}\,f_{L_r}^{r}(\varepsilon)\,\mathrm{Re}\,f_{S_r}^{p}(\varepsilon,\nu)$$
$$+\mathrm{Im}\,f_{L_r}^{r}(\varepsilon)\,\mathrm{Im}\,f_{S_r}^{p}(\varepsilon,\nu)], \tag{19}$$

where $C(S_r) = (2S_r+1)/2(2s+1)$ is the spin factor. Notice that the first (resonance) and second [describing the spin-averaged differential cross section $d\sigma_{el}^{p}/d\Omega_{kk'} = |f_{eB}^{p}(\varepsilon,\nu)|^2$ for potential scattering] terms in the formula (19) are, respectively, the decisive terms at electron energies ε close to ($\varepsilon \sim E_r$), and far from ($|\varepsilon - E_r| \gg E_r$), the resonance. The third interference term in (19) is (as follows from the specific calculations carried out in Sec. 4) insignificant, and has a slight effect on the value of the cross section $d\sigma_{el}^{(eB)}/d\Omega_{kk'}$ only in the narrow transition region between the resonance- and potential-scattering domains.

Substituting the first term in (19) into the formula (15), we obtain a general expression for the contribution $\sigma_{nl,n'}^{r}$ of the resonance scattering to the cross section for collision-induced transition between Rydberg atomic levels:

$$\sigma_{nl,n'}^{r} = C(S_r)(2L_r+1)^2\frac{\pi}{V_E^2n'^3}\int_{\varepsilon_{min}}^{\infty}d\varepsilon\,\varepsilon^{1/2}|g_{nl}(\varepsilon)|^2$$
$$\times|f_{L_r}^{r}(\varepsilon)|^2\int_{-1}^{\nu_{max}(\varepsilon)}\frac{d\nu}{(1-\nu)^{1/2}}P_{L_r}^2(\nu), \tag{20a}$$
$$|f_{L_r}^{r}(\varepsilon)|^2 = \gamma^2\varepsilon^{2L_r}/2[(\varepsilon-\varepsilon_0)^2+\gamma^2\varepsilon^{2L_r+1}]. \tag{20b}$$

In the case, of interest to use here, of the ^3P resonance on an alkali-metal atom, when

$$s = 1/2, \quad S_r = 1, \quad C(S_r) = 3/4, \quad L_r = 1, \quad P_{L_r}(\nu) = \nu = \cos\theta_{kk'},$$

the angle integral in the formula (20a) can easily be evaluated. This enables us to relate the resonance contribution $\sigma_{nl,n'}^{r}$ to the $nl \to n'$ transition cross section directly with the total cross section $\sigma_{el}^{r}(\varepsilon)$ for elastic resonance scattering of an ultralow-energy electron e^- by the perturbing atom B and the kinetic-energy distribution function $|g_{nl}(\varepsilon)|^2$ for the

Rydberg electron of the atom A(nl):

$$\sigma^r_{nl,n'} = \frac{7}{2^{1/2}\cdot 5}\frac{1}{V_E^2 n'^3}\int_{\varepsilon_{min}}^{\infty}\left[1+\sum_{q=1}^{3}(-1)^q c_q\left(\frac{\varepsilon_{min}}{\varepsilon}\right)^{q-1/2}\right] \times \sigma_{el}^r(\varepsilon)\,|g_{nl}(\varepsilon)|^2\varepsilon^{1/2}\,d\varepsilon. \quad (21)$$

Here the c_q coefficients are equal to $c_1 = 15/7$, $c_2 = 20/7$, and $c_3 = 12/7$ and the cross section σ^r_{el} is, as follows from (19) and (20b), given in the case of the ^3P resonance by the following formula:

$$\sigma_{el}^r(\varepsilon) = \int |f_{eB}^r(\varepsilon,\theta_{\mathbf{kk}'})|^2 d\Omega_{\mathbf{kk}'} = 9\pi|f^r_{L_r=1}(\varepsilon)|^2 = \frac{9\pi\gamma^2\varepsilon^2}{2[(\varepsilon-\varepsilon_0)^2+\gamma^2\varepsilon^3]}. \quad (22)$$

For this shape of the resonance contour the energy E_r of the quasidiscrete level (i.e., the position of the peak in the elastic electron-atom scattering cross section $\sigma^r_{el}(E_r) = \sigma^r_{max}$) is given in terms of the prescribed ε_0- and γ-parameter values by the expression

$$E_r = (\varepsilon_0/\gamma)^{2/3}\{[1+(1+8/27\varepsilon_0\gamma^2)^{1/2}]^{1/3}+[1-(1+8/27\varepsilon_0\gamma^2)^{1/2}]^{1/3}\}.$$

It can be seen from (21) and (22) that the absolute value of the cross section $\sigma^r_{nl,n'}$ is greatest in the case of the $nl\to n'$ transitions for which $\Delta\varepsilon_{nl,n'} = 0$ and, in particular, in the case of the quasielastic process of mixing of Rydberg atomic states with different oribital angular momenta l, but the same principal quantum number n. In this case the quantity $\varepsilon_{\min} = |\Delta\varepsilon_{nl,n'}|^2/8V_E^2 = 0$ and all the electron energies $0\leqslant\varepsilon<\infty$ [whose distribution is given by the function $|g_{nl}(\varepsilon)|^2$] contribute to the cross section $\sigma^r_{nl,n'}$. In other words, the entire resonance contour $|f_{L_r}(\varepsilon)|^2$ of the electron-atom scattering amplitude lies [see (21)] within the integration domain. In the case of inelastic $nl\to n'$ transitions with energy defects $\Delta\varepsilon_{nl,n'}\approx(\delta_l+\Delta n)/n^3$ (where $\Delta n = n'-n$) the presence of a resonance begins to have a significant effect on the value of the cross section $\sigma_{nl,n'} = \sigma^r_{nl,n'} + \sigma^p_{nl,n'}$ in the region of principal quantum number values

$$n\gtrsim n_r = (|\delta_l+\Delta n|/2k_rV_E)^{1/3}, \quad (23)$$

for which the quantity $\varepsilon_{min}\lesssim E_r$. For $n\ll n_r$, the resonance region $\varepsilon\sim E_r = k_r^2/2$ falls outside the integration domain $\varepsilon_{min}\leqslant\varepsilon<\infty$, so that the quantity $\sigma^r_{nl,n'}$ is small, and the $nl\to n'$ transition cross section is determined largely by the potential scattering [the second term in (19)]. It should also be noted that the contribution $\sigma^r_{nl,n'}$ of the resonance scattering decreases rapidly as the principal quantum number n increases in the region $n\gg(2E_r)^{-1/2}$. It is explained by the fact that, in this region, the increase of n leads to the rapid decrease of the electron density $|g_{nl}(\varepsilon)|^2$ [see the formula (16)] corresponding to the resonance energies $\varepsilon\sim E_r$. Therefore, the resonance in the electron-atom (i.e., $e^-\to B$) scattering should most clearly manifest itself in the inelastic $nl\to n'$ quenching of the Rydberg levels of the atom A(nl) if its energy E_r satisfies the condition $E_r\ll V_E/|\delta_l+\Delta n|$ and, consequently, the quantity $n_r\ll(2E_r)^{-1/2}$.

In the case of a narrow resonance, i.e., for $\Gamma_r\ll E_r$, it is possible to obtain a simple analytic formula for the magnitude $\sigma^r_{nl,n'}$ of the resonance contribution to the quasielastic ($\Delta\varepsilon_{nl,n'} = 0$) $nl\to n'$ transition cross section. Indeed, in this case we can set the energy and width of the resonance equal to $E_r\approx\varepsilon_0$ and and $\Gamma_r\approx 2\gamma\varepsilon_0^{1/2}$ (see Ref. 26, $\S$ 133) and replace the contour $|f^r_{L_r=1}(\varepsilon)|^2$ of the resonance part of the scattering amplitude [and, consequently, $\sigma^r_{el}(\varepsilon)$] in the formula (21) by the Lorentz contour

$$|f^r_{L_r=1}(\varepsilon)|^2\approx\frac{1}{2E_r}\frac{(\Gamma_r/2)^2}{(\varepsilon-E_r)^2+(\Gamma_r/2)^2}. \quad (24)$$

Next, using for the distribution function $g_{nl}(\varepsilon)|^2$ in the region of small values of the orbital angular momentum of the initial level of the atom A(nl), i.e., in the region $l\ll n$, the expression (16), and also setting in the formula (21) the transition energy defect $\Delta\varepsilon_{nl,n'} = 0$ (and, accordingly, $\varepsilon_{min} = 0$), we arrive, after evaluating the corresponding integral, at the following result:

$$\sigma^r_{nl,n'}\approx\frac{63\pi}{2^{1/2}\cdot 10}\frac{n_{eff}\Gamma_r}{V_E^2 n'^3(1+2n_{eff}^2E_r)^2E_r^{3/2}}. \quad (25)$$

Notice that this formula can be used in the region of sufficiently high values of n, specifically, in the region $n\gg n_r$ (where $\varepsilon_{min}\ll E_r$), to estimate the magnitudes $\sigma^r_{nl,n'}$ of the cross sections for the $nl\to n'$ transitions with small energy defects $\Delta\varepsilon_{nl,n'}$, and also in the case when the resonance width and energy are of the same order of magnitude: $\Gamma_r\sim E_r$.

The collision-induced $nl\to n'$ transition cross sections $\sigma^p_{nl,n'}$ corresponding to the potential scattering of the electron e^- by the perturbing atom B should, in the case when the differential cross sections $d\sigma^p_{el}/d\Omega_{\mathbf{kk}'} = |f^p_{eB}(\varepsilon,\theta_{\mathbf{kk}'})|^2$ are determined at low energies ε by the contribution of a number of partial waves $l_e = 0, 1, 2, \ldots$, be computed from the formula (15). In the present paper we shall, for the purpose of elucidating the roles played by the resonance and potantial scatterings in the quenching of highly excited atomic levels by the alkali-metal atoms, use the following approximation in the computations of the quantity $\sigma^p_{nl,n'}$:

$$|f_{eB}^p(\varepsilon,\theta_{\mathbf{kk}'})|^2 = \frac{3}{4}|f_+^p(\varepsilon,\theta_{\mathbf{kk}'})|^2+\frac{1}{4}|f_-^p(\varepsilon,\theta_{\mathbf{kk}'})|^2 \approx\langle\sigma_{el}^p(\varepsilon)\rangle_\varepsilon/4\pi = L_{eff}^2,$$

i.e., we shall use the formula

$$\sigma^p_{nl,n'} = \frac{2\pi L_{eff}^2}{V_E^2 n'^3}F^p_{nl,n'}(\lambda_E),\quad \lambda_E = \frac{n|\Delta\varepsilon_{nl,n'}|}{V_E},\quad x_0 = \frac{1}{1+(\lambda_E/2)^2}, \quad (26a)$$

$$F^p_{nl,n'}(\lambda_E) = \frac{2}{\pi}\left\{B_{x_0}\left(\frac{3}{2},\frac{1}{2}\right)+\frac{\lambda_E}{2}\left[\frac{1}{1+(\lambda_E/2)^2}-\ln\left(1+\frac{4}{\lambda_E^2}\right)\right]\right\}, \quad (26b)$$

obtained in Ref. 9 within the framework of Fermi's zero-range pseudopotential model (here B_x is the incomplete beta function). In this case the quantity L_{eff} and also the param-

eters ε_0 and γ (which determine the energy E_r, width Γ_r, and contour of the ^3P resonance) are chosen such that the quantity $\sigma_{el}^{eB}(\varepsilon) = \sigma_{el}^r(\varepsilon) + 4\pi L_{eff}^2$ furnishes the best description of the behavior of the total cross section for elastic scattering of the ultralow-energy electrons both in the near resonance region $\varepsilon \sim E_r$ (where $\sigma_{el}^p \ll \sigma_{el}^r$) and in the far-off region $|\varepsilon - E_r| \gg E_r$ (where $\sigma_{el}^p \gg \sigma_{el}^r$). This is justified, since the energy dependence of the resonance part $\sigma_{el}^r(\varepsilon)$ of the elastic scattering cross section is much more critical than that of the potential part $\sigma_{el}^p(\varepsilon)$ of the cross section in the not too broad range of electron energies ε corresponding to the range of principal quantum numbers n in question. It should be noted that, in the case of $n \to n'$ transitions between degenerate hydrogenlike atomic levels under conditions of uniformly populated l subshells, instead of the expression (26) we should use the l-averaged expression

$$\sigma_{nn'}^p = \frac{1}{n^2}\sum_l (2l+1)\sigma_{nl,n'}^p$$

[see the formulas (20) and (24) in Ref. 9]. Similarly, the formula for the resonance contribution $\sigma_{nn'}^r$ to the $n \to n'$ transition cross section is obtained directly from (21) by replacing the distribution function $|g_{nl}(\varepsilon)|^2$ [see (16)] by the function $|g_n(\varepsilon)|^2$ [see (17)].

Let us now discuss the limits of applicability of the impulse approximation for the process of collisional quenching of the Rydberg states of an atom. In the case of the potential scattering of the outer electron e^- of a highly excited atom A(nl) by a perturbing atom B the characteristic e^--B collision time $\tau_{eB} \sim \lambda_{eB}/v_{eB}$ is determined by the wavelength $\lambda_{eB} \sim 1/k(r_{eA^+})$ and velocity $v_{eB} \sim k(r_{eA^+})$ in the relative motion of the particles e^- and B in the region of distances $\sim r_{eA^+}$ that is important for the $nl \to n'$ (or $n \to n'$) transition in question, and the momentum transfer is of the order of the corresponding electron momentum, i.e., $Q_{eB} \sim k(r_{eA^+}) \sim (2/r_{eA^+})^{1/2}$. Therefore, the condition (10) for quasifree scattering (a condition which implies at the same time the suddenness of the perturbation) can be transformed into the following form: $r_{eA^+}^{1/2} \gg 1$. Furthermore, for the impulse approximation to be applicable, the conditions $r_{eA^+} \gg |f_{eB}|$, $|f_{A^+B}|$ and $r_{eA^+} \lambda_{eB}$, which determine whether or not we can separately consider the two collisional-quenching mechanisms stemming from the scattering of the perturbing particles B by the weakly bound electron e^- and the core A^+ of the highly excited atom A(nl), and also allow us to neglect the corresponding interference effects,[24] should be fulfilled. The characteristic dimension of the e^--A^+ interaction region that makes the dominant contribution to the cross sections for $nl \to n'$ and $n \to n'$ transitions between Rydberg levels with energies differing by $\Delta\varepsilon$ is given by the relation[9] $r_{eA^+} \sim 2n^2/[1 + (n\Delta\varepsilon/V_E)^2]$. Therefore, taking account of the fact that the B-on-A^+ scattering amplitude [which is determined by the characteristic dimension of the region of interaction of these particles: $|f_{A^+B}| \sim R_{A^+B} \sim (\sigma_{el}^{A^+B}/\pi)^{1/2}$, where $\sigma_{el}^{A^+B}(V_E)$ is the total elastic-scattering cross section] satisfies the inequality $|f_{A^+B} \gg 1$ a.u. in the region of thermal collision velocities V_E, and that the amplitude $|f_{eB}| \sim L_{eff} \gtrsim 1$ a.u., we arrive at the following restriction on the admissible values of the principal quantum number n:

$$r_{eA^+} \sim 2n^2/[1+(|\delta_l+\Delta n|/n^2V_E)^2] \gg |f_{eB}|,\ R_{A^+B}. \qquad (27)$$

Specific estimates show that the impulse approximation can be used to describe the quenching of highly excited levels in the region of sufficiently high values of n, specifically, in the region $n \gtrsim n_0$, where the quantity n_0 depends on the types colliding atoms A(nl) and B. For inelastic collisions of Rydberg atoms with inert-gas atoms, the characteristic values of n_0 in the thermal-velocity region range roughly from 10 to 15 (for greater details, see Ref. 9).

Let us now consider the situation in which the resonance scattering plays an important role. In this case in the region of small values of the energy defect $\Delta\varepsilon_{nl,n'}$, where $\varepsilon_{min} \ll E_r$, the dominant contribution to the quenching cross sections is made by electron energies $\varepsilon \sim E_r = k_r^2/2$ and, correspondingly, distances $r_{eA^+} \sim E_r^{-1}$, while the scattering amplitude $|f_{eB}(\varepsilon \sim E_r)| \sim \lambda_r = 1/k_r$. Therefore, the conditions $r_{eA^+} \gg |f_{eB}|$, $|f_{A^+B}|$ and $r_{eA^+} \gg \lambda_{eB}$ assume the following form in the present case:

$$k_r \ll 1, \quad k_r^2 R_{A^+B} \ll 1, \qquad (28)$$

and are consequently fulfilled in the case of low-energy resonances. For the impulse approximation and the standard decay model for a quasidiscrete level in a background of a quasicontinuum of highly excited atomic states to be applicable, it is also necessary that the resonance width Γ_r be significantly greater than the energy level spacing $\Delta\varepsilon_{n,n\pm1} \sim n^{-3}$, i.e., that

$$\Gamma_r \gg 1/n^3. \qquad (29)$$

In the case, under consideration here, of the ^3P resonances on the atoms of the alkali metals Li, Na, and Rb, this condition is fulfilled when $n \gg 8$, 7, and 10 respectively. In the case of inelastic quenching in the region $n \lesssim n_r$ ($\varepsilon_{min} \gtrsim E_r$) the dominant contribution to the $nl \to n'$ transition cross section is made by the electron energies $\varepsilon \gtrsim \varepsilon_{min}$ even in thge presence of resonance scattering. Accordingly, the region of distances r_{eA^+} is determined as before by the condition (27). But in the case of thermal collisions of Rydberg atoms with alkali-metal atoms, the characteristic dimension of the B-A^+ interaction region, as determined by the polarization interaction, i.e., the quantity $R_{A^+B} \sim (\alpha_B/V_E)^{1/3}$, turns out to be substantially greater than the corresponding quantity for collisions with inert-gas atoms. For example, for the Rb(nS) + Rb($5S$) quenching process we have $R_{A^+B} \sim 100$ a.u. ($\alpha_{Rb} = 310$ a.u.), so that, on account of (27), the impulse approximation is valid when $n \gtrsim n_0$, where n_0 lies in the range from 25 to 30. It should also be noted that, for the results obtained in the present paper to be applicable in both the case of potential, and the case of resonance, scattering of the electron e^- by the perturbing atom B, it is necessary that the quenching cross sections given by the formulas (21) and (26) do not exceed the cross section of the Rydberg atom, i.e., that $\sigma_{nl,n'} \ll (5\pi/2)n^4$.

4. DATA ON THE QUENCHING AND BROADENING OF RYDBERG ATOMIC LEVELS OF THE ALKALI METAL ATOMS

Of primary interest to us, in investigating the process of collisional quenching of Rydberg atoms by alkali-metal atoms, is the analysis of the role of the low-energy ^3P resonances in the elastic electron-atom scattering. It can be assumed that the parameters of these resonances for the Li and Na atoms have been determined sufficiently accurately, since the results obtained in different investigations (see, for example, Refs. 20, 21, and 27) are in good agreement with each other. For the K and Rb atoms the accuracy of the numerical computations of the elastic electron scattering cross sections is, as noted in Ref. 20, much lower. At the same time even the present-day experimental procedures for the direct measurement of such cross sections do not allow us to get into the region of ultralow energies $\varepsilon \sim 10^{-2}$ eV characteristic of the ^3P resonances on the K and Rb atoms,[27] and only indicate the existence of these resonances. Apparently, the most accurate values for the energy E_r and width Γ_r of these resonances are the values obtained in Ref. 21 within the framework of a modified effective-radius theory. As will be seen below, the experimental data on the broadening and quenching of Rydberg atomic levels by alkali-metal atoms in the region of sufficiently high values of the principal quantum number n [where the formulas (15) and (21) are applicable] can also be used to determine the parameters of the low-energy ^3P resonances.

Let us first give the results obtained in the present investigation for the cross sections for quenching of the Rydberg nS and nD levels of lithium and sodium atoms in their own gases, since there are available in this case detailed numerical-computation data[20] on the cross sections for elastic scattering of ultralow-energy electrons by Li(2S) and Na(3S) atoms. Using these data, we determined the parameters ε_0, γ, and L_{eff}, which we need for computations with the formulas (21) and (26) (see the captions to Figs. 1 and 2), and which determined within the framework of the theory presented here the behavior and magnitudes of the cross sections for resonance $[\sigma^r_{el},(22)]$ and potential ($\sigma^p_{el} \approx 4\pi L$) scattering. As can be seen from Figs. 1 and 2, the relative role of the potential and resonance electron-atom scattering in the process of collisional quenching of highly excited levels depends essentially on the magnitude of the $nl \to n'$ transition energy defect $\Delta\varepsilon_{nl,n'}$ and the principal quantum number n. The quenching of the nD levels of lithium and sodium atoms in the region of not too high values of n occurs largely without a change in the principal quantum number, i.e., is largely due to the quasielastic transitions $nD \to nl'$ ($l' > 2$), because of the small values of the quantum defects ($\delta_D^{\mathrm{Li}} = 0.002$ and $\delta_D^{\mathrm{Na}} = 0.015$). In this case the contributions of the resonance and potential scatterings are of the same order of magnitude in a broad range of n values (see the curves 3 and 1 in Figs. 1 and 2).

In the case of the quenching of the nS levels of lithium and sodium atoms, which on account of the large values of the quantum defects ($\delta_S^{\mathrm{Li}} = 0.4$ and $\delta_S^{\mathrm{Na}} = 1.35$), is due to inelastic $nS \to n'$ transitions between levels with different or identical principal quantum numbers ($n' = n$ and $n-1$ for Li; $n' = n-1$ and $n-2$ for Na), the resonance scattering plays a much greater relative role. This pertains also to the inelastic $nl \to n'$ transitions between highly excited levels with $\Delta n = \pm 1, \pm 2, \pm 3, \ldots$ in the case when the initial nl states have small quantum defects ($\delta_l \ll 1$). In the region of n values ranging roughly from 20 to 40 the contribution of the resonance scattering to the quenching cross section is several times greater than that of the potential scattering (see the curves 2 and 4–6 in Fig. 1 and curve 2 in Fig. 2). As n increases further, the role of the ^3P resonance begins to abate in accordance with the condition $n \gg k_r^{-1} \sim 15$ (see Sec. 3). Notice also that, in the region of sufficiently high n values, the total quenching cross section σ^Q_{nl} may be due not only to transitions to the nearest levels, but also to an entire group of

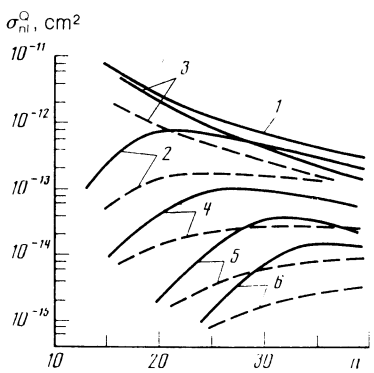

FIG. 1. Cross sections σ^Q_{nl} for quenching of the Rydberg levels nD (curve 1) and nS (curve 2) of lithium atoms Li (nl) as a result of $nl \to n + \Delta n (\Delta n = 0, \pm 1, \pm 2, \pm 3, \ldots)$ transitions induced in collisions with Li(2S) atoms at an energy $E = \mu V_E^2/2 = 900$ °K. The curves 3 are plots of the cross section for the quasielastic transition $nl \to n + \Delta n$, with $\Delta n = 0$, while the curves 4, 5, and 6 are respectively the plots of the cross sections for the inelastic transitions $nl \to n + \Delta n$ with $\Delta n = \pm 1, \pm 2$, and ± 3, as computed for the nl levels with $\delta_l \ll 1$ and $l \ll n$. The dashed curves correspond to the contribution σ^p_{nl} of the potential scattering ($L_{\mathrm{eff}} = 4.5$ a.u.) and the continuous curves are plots of the total cross sections $\sigma^Q_{nl} = \sigma^p_{nl} + \sigma^r_{nl}$, i.e., the cross sections that take account of the contribution of the ^3P resonance ($\varepsilon_0 = 3.2 \times 10^{-3}$ a.u., $\gamma = 11.4$ a.u.).

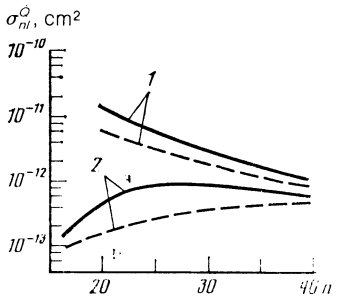

FIG. 2. Cross sections σ^Q_{nl} for quenching of the Rydberg levels nD (curve 1) and nS (curve 2) of sodium atoms Na(nl) as a result of $nl \to n + \Delta n (\Delta n = 1, \pm 1, \pm 2, \pm 3, \ldots)$ transitions induced in collisions with Na(3S) atoms at an energy $E = \mu V_E^2/2 = 430$ °K. The dashed curves correspond to the contribution σ^p_{nl} of the potential scattering ($L_{\mathrm{eff}} = 5$ a.u.) and the continuous curves are plots of the total quenching cross sections $\sigma^Q_{nl} = \sigma^p_{nl} + \sigma^r_{nl}$, i.e., the cross sections that take account of the contribuiton of the ^3P resonance ($\varepsilon_0 = 7 \times 10^{-3}$ a.u., $\gamma = 30$ a.u.).

levels n' (cf. the curves 1 and 3 in Fig. 1). The role of the ^3P resonance declines in the low n-value region [i.e., in the region $n \lesssim 15$ (see Figs. 1 and 2)] as well. This is explained by the fact that in this case the quenching process occurs with large energy defects $\Delta\varepsilon_{nS,n'}$, so that the electron energies close to the resonance energies, i.e., the energies $\varepsilon \sim E_r$, do not, in accordance with the condition $n \gg n_r$ [see (23)], contribute to the cross sections. Let us note that the estimation from the formula (23) of the quantities n_r for the quenching of the nS levels of lithium and sodium atoms in their own gases at relative-motion energies $E = \mu V_E^2/2$ equal respectively to 900 and 430 °K yields $n_r^{Li} \approx 15$ and $n_r^{Na} \approx 18$. This is in good agreement with the results obtained (Figs. 1 and 2).

As follows from the analysis carried out in the present paper, contrary to the assertions made in Ref. 22, the available experimental data[22] on the quenching of the Rydberg atoms Rb(nS) in collisions with Rb($5S$) atoms cannot be explained within the framework of the Fermi model with allowance made for only the potential scattering. The estimates obtained here with the aid of the formula (26) for the contribution of the potential scattering [with, in particular, the use of the same elastic e^--Rb($5S$) scattering data (Ref. 28)[2)] used in Ref. 22] show that the corresponding quenching cross sections σ_{nS}^p are an order of magnitude smaller than the experimental values reported in Ref. 22. It is natural to expect that, because the energies E_r of the ^3P resonance on the Rb ($5S$) atom are much smaller than the corresponding energies for the Li($2S$) and Na ($3S$) atoms, this resonance should play an even greater role in the quenching of the Rydberg levels of the Rb(nS) atom in its own gas than in the above-described cases (see Figs. 1 and 2). This is confirmed by the specific calculations carried out in the present paper (curve 1 in Fig. 3), which indicate that the experimental results for the $Rb(nS) + Rb \to Rb(\neq nS) + Rb$ quenching process occurring in the $34 \leqslant n \leqslant 43$ region[22] can be well described with the use of the above-obtained resonance-scattering formula (21) [see also (16) and (22)] and the ^3P-resonance parameter values $\varepsilon_0 = 4 \times 10^{-4}$ a.u. and $\gamma = 60$ a.u. The dominant contribution to the quenching cross section in this case is made by the transition $nS \to n-3$, $l' > 2$ (quantum defect $\delta_S^{Rb} = 3.15$), with the minimum energy defect $\Delta\varepsilon_{nS,n-3} \approx 0.15 n^{-3}$, although in the calculations we also took into account the transitions to the other levels n' (the contribution of which does not exceed 5 or 10% in the case when $n \lesssim 45$).

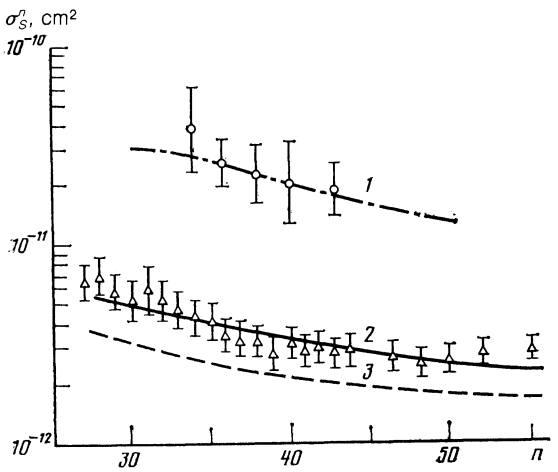

FIG. 3. Cross sections for quenching and collision broadening of the Rydberg nS levels of rubidium and potassium atoms in collisions with Rb($5S$) atoms. The curve 1 is a plot of the quenching cross sections σ_{nS}^Q for the Rb(nS) + Rb($5S$) process, as computed from the formula (21) with the parameters $\varepsilon_0 = 4 \times 10^{-4}$ a.u. and $\gamma = 60$ a.u. and energy $E = \mu_{Rb,Rb} V_E^2/2 = 400$ °K; the open circles indicate the experimental data obtained by Hugon *et al.*[22] at $T = 400$ °K. The curves 2 and 3 are plots of the broadening cross section σ_{nS}^b for the process K(nS) + Rb($5S$) at $E = \mu_{K,Rb} V_E^2/2 = 513$ °K, as computed from the formulas (21) and (30) with the following parameters: 2) $\varepsilon_0 = 8 \times 10^{-4}$ a.u., $\gamma = 30$ a.u.; 3) $\varepsilon_0 = 1 \times 10^{-3}$ a.u., $\gamma = 20$ a.u. (Ref. 21); the points Δ indicate the experimental data obtained by Heinke *et al.*[23] at $T = 513$ °K.

We can also furnish within the framework of the above-presented theory of inelastic transitions between highly excited atomic levels, which takes account of the presence of a resonance at a quasidiscrete level of the perturbing particle, a quantitative explanation of the available experimental data (see Ref. 23 and the references cited therein) on the broadening of the Rydberg nl levels of atoms in an atmosphere of alkali-metal atoms. In this case we should use the following well-known relation (see, for example, Ref. 29):

$$\sigma_{nl}^b = {}^1/_2(\sigma_{nl}^{inel} + \sigma_{nl}^{el}) = {}^1/_2(\sigma_{nl}^Q + \sigma_{BA^+}^{el} + \sigma_{Be^-}^{el}(nl \to nl)), \quad (30)$$

which relates the collision-broadening cross section σ_{nl}^b with the total cross section for all the inelastic $nl \to n'$ transitions (i.e., with the quenching cross section $\sigma_{nl}^Q \equiv \sigma_{nl}^{inel} = \Sigma_{n'} \sigma_{nl,n'}$ for the nl level in question) and the total cross section $\sigma_{nl}^{el} = \sigma_{BA^+}^{el} + \sigma_{Be^-}^{el}(nl \to nl)$ for elastic scattering of the perturbing particle B on the atom A(nl). Let us consider as an example, the broadening of the Rydberg levels of K(nS) atoms (quantum defect $\delta_S^K = 2.18$) in collisions with Rb($5S$) atoms, a process which has been experimentally investigated in the broad n-value range $9 \leqslant n \leqslant 55$ by Heinke *et al.*[23] The calculations carried out here with the formulas (21) and (30) (the curve 2 in Fig. 3) show that the experimental data obtained by Heinke *et al.*[23] are explained by the presence of the ^3P resonance on the rubidium atom, and are quantitatively well described (in the region $n \gtrsim 30$ of applicability of the theory) with the use of the following parameters[3)] of the quasidiscrete level of the negative ion Rb^-: $\varepsilon_0 = 8 \times 10^{-4}$ a.u. and $\gamma = 30$ a.u., which correspond to an energy $E_r = 1.8 \times 10^{-2}$ eV and a width at half-maximum $\Gamma_r = 2.3 \times 10^{-2}$ eV. The contribution of the elastic scattering of the Rb atom on the K^+-ion core to the broadening cross section is in this case $\sigma_{Rb,K^+}^b = 3.6(\alpha_{Rb}/V_E)^{2/3} \approx 10^{-12}$ cm², which does not exceed 30% of the cross section even at the high values of $n \sim 55$. The contribution $\sigma_{Be^-}^{el}(nl \to nl)$ of the elastic scattering of the perturbing Rb atom by the Rydberg electron e^- of the K(nS) atom in the n-value range under consideration is negligibly small.

The values found above for the parameters of the ^3P resonance at the quasidiscrete level of the negative ion Rb^- are in good agreement with the data obtained in Ref. 21 ($E_r = 2.3 \times 10^{-2}$ eV and $\Gamma_r = 2.5 \times 10^{-2}$ eV) through the extrapolation of the results obtained in a numerical calculation of the electron-on-rubidium atom scattering phases in the

region of very small energies. Our results therefore corroborate Fabrikant's[21] and Johnston and Burrow's[27] conclusions that the characteristic values of the energy and width of the ^3P resonance for the Rb(5S) atom are of the order of 10^{-2} eV, and not as low as the values found by Kaulakys[30] and Rabin and Rebentrost[31] ($E_r = 1.3\times10^{-3}$ eV, $\Gamma_r = 4.4\times10^{-4}$ eV), who determined the values from the oscillating (for n ranging roughly from 15 to 25) components of the measured widths and shifts of the Rydberg nS levels of the rubidium atom in its own gas. Also shown in Fig. 3 (curve 3) are the cross sections σ^b_{nS} for broadening of the Rydberg nS levels of potassium atoms in a rubidium gas in the region $n \gtrsim 30$, as computed from the formulas (21) and (30) with the use of Fabrikant's data[21] (which correspond to the parameters $\varepsilon_0 = 1\times10^{-3}$ a.u. and $\gamma = 20$ a.u.). It can be seen that the sensitivity of the computed cross sections to the resonance parameters is fairly high. At the same time, as follows from the approximate expression (25), in the region of high values of $n(>n_r)$ the slope of the plot of the $nl\to n'$ transition cross section against the principal quantum number n is determined first and foremost by the value of E_r, while the cross section values are proportional to the ratio $\Gamma_r E_r^{-3/2}$.

Thus, using the formulas obtained in the present paper for the cross sections for inelastic collisions of Rydberg atoms with perturbing neutral particles and the available (in a fairly broad range of n values) experimental data on the cross sections for quenching or broadening of highly excited atomic levels in a gas, we can determine the parameters E_r and Γ_r of the low-energy resonances occurring in the elastic scattering of ultralow-energy electrons by these particles. In doing this, we should naturally make sure in each specific case that the conditions of applicability (see Sec. 3) of the theory presented here are fulfilled. It should also be noted that, in the case when the contribution $\sigma^r_{nl}(B\to e^-)$ of the resonance to the cross sections for collisional quenching (broadening) of the Rydberg levels is significantly greater than both the contribution $\sigma^p_{nl}(B\to e^-)$ of the potential scattering of the perturbing atom B by the quasifree electron e^- and the contribution $\sigma_{nl}(B\to A^+)$ from the scattering on the A^+-ion core, the accuracy of this computation is largely determined by the quality of the experimental data themselves.

The authors are grateful to V. I. Kogan, L. P. Presnyakov, I. I. Sobel'man, and O. B. Firsov for a discussion of the results and to M. I. Chibisov for interest in the work and for fruitful discussions.

[1)]Note that the system of atomic units $e = m_e = \hbar = 1$ is used in all the formulas in the present paper.

[2)]Notice that Balling's computational data[28] for the region of low electron energies (where, as emphasized in the Ref. 20, the numerical calculations are much less accurate) are at variance with the results of the more recent theoretical[21] and experimental[27] investigations, which definitely indicate the existence of the ^3P resonance.

[3)]It should be noted that the broadening cross sections σ^b_{nS} computed with tha aid of the formula (30) from the experimental data[22] on the quenching of the nS levels of the rubidium atom in its own gas are approximately 2.5 times greater than the corresponding experimental results[23] obtained in direct collision-broadening cross section measurements. This cannot be explained by the insignificant difference in the gas temperatures $T = 400$ and 513 °K in these experiments. One of the possible causes of this may, apparently, be connected with the complexities of the measurement of the vapor pressure of the alkali-metal atoms in experiments of this kind (see, for example, Ref. 1, Chap. 7). Because of the indicated discrepancies in the experimental quenching[22] and broadening[23] data, the values obtained from these data for the parameters ε_0 and γ of the ^3P resonance on the rubidium atom differ slightly from each other.

[1]R. F. Stebbings and F. B. Dunning (editors), Rydberg States of Atoms and Molecules, Cambridge University Press, Cambridge, 1983.
[2]B. M. Smirnov, Usp. Fiz. Nauk **131**, 577 (1980) [Sov. Phys. Usp. **23**, 450 (1980)].
[3]O. B. Firsov, Zh. Eksp. Teor. Fiz. **21**, 627, 634 (1951).
[4]L. P. Pitaevskiĭ, Zh. Eksp. Teor. Fiz. **42**, 1326 (1962) [Sov. Phys. JETP **15**, 919 (1962)].
[5]V. A. Alekseev and I. I. Sobel'man, Zh. Eksp. Teor. Fiz. **49**, 1274 (1965) [Sov. Phys. JETP **2**, 882 (1966)].
[6]M. Matsuzawa, J. Chem. Phys. **55**, 2685 (1971); J. Phys. B **12**, 3743 (1979).
[7]A. Omont, J. Phys. (Paris) **38**, 1343 (1977).
[8]L. Petitgean and F. Gounand, Phys. Rev. A **30**, 2946 (1984).
[9]V. S. Lebedev and V. S. Marchenko, Zh. Eksp. Teor. Fiz. **88**, 754 (1985) [Sov. Phys. JETP **61**, 443 (1985)].
[10]B. Kaulakys, J. Phys. B **18**, L167 (1985).
[11]F. Gounand and L. Petitgean, Phys. Rev. A **30**, 61 (1984).
[12]K. Sasano, Y. Sato, and M. Matsuzawa, Phys. Rev. A **27**, 2471 (1983).
[13]Y. Sato and M. Matsuzawa, Phys. Rev. A **31**, 1366 (1985).
[14]V. S. Lebedev and V. S. Marchenko, Zh. Eksp. Teor. Fiz. **84**, 1623 (1983) [Sov. Phys. JETP **57**, 946 (1983)].
[15]V. S. Lebedev and V. S. Marchenko, Tr. Fiz. Inst. Akad. Nauk SSSR **145**, 79 (1984).
[16]F. Gounand and L. Petitgean, Phys. Rev. A **32**, 793 (1985).
[17]T. F. O'Malley, Phys. Rev. **130**, 1020 (1963).
[18]M. Matsuzawa, J. Phys. B **8**, L382 (1975); **10**, 1543 (1977).
[19]B. P. Kaulakis, L. P. Presnyakov, and P. D. Serapinas, Pis'ma Zh. Eksp. Teor. Fiz. **30**, 60 (1979) [JETP Lett. **30**, 53 (1979)].
[20]A. L. Sinfailam and R. K. Nesbet, Phys. Rev. A **7**, 1987 (1973).
[21]I. I. Fabrikant, Opt. Spektrosk. **53**, 223 (1982) [Opt. Spectrosc. (USSR) **53**, 131 (1982)].
[22]M. Hugon, F. Gounand, P. R. Fournier, and J. Berlande, J. Phys. B **16**, 2531 (1983).
[23]H. Heinke, J. Lawrenz, K. Niemax, and K. H. Weber, Z. Phys. A **312**, 329 (1983).
[24]M. L. Goldberger and K. M. Watson, Collision Theory, Wiley, New York, 1964 (Russ. Transl., Mir, Moscow, 1967).
[25]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems*, Springer Verlag, Berlin, 1958 (Russ. Transl., Fizmatgiz, Moscow, 1960).
[26]L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics), Nauka, Moscow, 1974 (Eng. Transl., Pergamon, Oxford, 1977).
[27]A. R. Johnston and P. D. Burrow, J. Phys. B **15**, L745 (1982).
[28]L. C. Balling, Phys. Rev. **179**, 78 (1969).
[29]L. A. Vaĭnshteĭn, I. I. Sobel'man, and E. A. Yukov, Vozbuzhdenie atomov i ushirenie spektral'nykh liniĭ (Excitation of Atoms and the Broadening of Spectral Lines), Nauka, Moscow, 1979.
[30]B. Kaulakys, J. Phys. B **15**, L719 (1982).
[31]Y. Rabin and F. Rebentrost, Opt. Commun. **40**, 257 (1982).

Translated by A. K. Agyei