Free electron model for inelastic collisions between neutral atomic particles and Rydberg atoms

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A model is developed which describes for the first time inelastic collisions of Rydberg atoms (RA) with complex neutral atomic particles, i.e., goes beyond the limits of the Fermi pseudopotential approximation. The model is based on an analysis of a binary collision of an RA electron with an incident particle. It is assumed that electron scattering by an atomic particle is described by the free-electron scattering amplitude, and the transitions between the RA states are due to the change of the kinetic energy and of the momentum of the electron colliding with the atomic particle. In this model, the cross sections of the processes are given by the amplitude of electron scattering by the incident atom, with allowance for the dependence of the scattering on the electron momentum and on the scattering angle. The general expressions obtained for the cross sections, rate constants, and diffusion coefficient of an electron in the energy space of the RA include, as particular cases, the results of known studies. These expressions account quantitatively for the experimentally observed dependences of the inelastic-transition cross sections on the energy defect of the transition, on the principal quantum number of the RA, and on the species and velocity of the perturbing particles, if the cross sections of the processes are smaller than the geometric cross section of the RA.

1. INTRODUCTION

Much attention is being paid at present to processes in which Rydberg atoms (RA) participate, including processes accompanying collisions between RA and neutral atomic particles (see the review[1]). The research into elastic collisions of RA with atoms and molecules is half a century old (see the review[2] and the references therein), whereas inelastic collisions that lead to transitions between RA levels have been intensively investigated only during the past decade.[1,3]

As a rule, theoretical description of such processes are based on the "free-electron" model proposed by Fermi,[4] and the interaction of a weakly bound RA electron with an incident neutral particle is described by a zero-radius pseudopotential. Within the framework of this approximation, the cross sections for $nl \to n'l'$ transitions were numerically calculated,[5–9] an approximation equation for the $nl \to n$ (l-mixing) transition applicable at small defects $\Delta E_{nl,n'}$ of the transition resonance was derived,[10] analytic expressions were obtained for the l-mixing cross sections of the elastic and all inelastic processes at $n^2 v \gg 1$ (v is the relative velocity of the colliding atoms),[11] and the adiabatic mechanism of l-mixing was investigated.[12] Quite recently, the Fermi pseudopotential model (the scattering-length approximation) was used to obtain analytic expressions for the transitions $n \to n'$,[13] $n \to n'$, and $nl \to n'$[14] on the basis of the impulse approximation and by a quasiclassical method[15]; these expressions are applicable for arbitrary resonance-transition defects.

The scattering-length approximation is valid when the amplitude for electron scattering by the perturbing particle is independent of the scattering angle and of the absolute value of the electron momentum within the limit of the permissible values of the electron momentum in the RA. This approximation holds strictly only for the helium atom. For heavier atoms, the scattering amplitude depends both on the electron momentum and on the scattering angle (since p scattering, and sometimes d scattering, are significant besides the s scattering). There is no theory of inelastic collisions of RA and neutral atomic particles with account taken of the dependences of the amplitude of the electron scattering by the incident atom on the electron momentum and on the scattering angle. (There is only a numerical analysis of inelastic collisions of RA with inert-gas atoms.[16–18] where account is taken of two terms in the expansion of the s-scattering amplitudes in the electron momenta.) Within the framework of the widely used approaches based on the quasiclassical method or the impulse approximation, it is hardly possible to obtain expressions for the cross sections for inelastic collisions of RA and netural particles with allowance for the dependences of the free-electron scattering amplitude on the momentum and on the scattering angle.

There exists, however, one more method of analyzing inelastic collisions of RA with neutral particles, a method based on a direct analysis of a binary collision of the RA electron with an incident atom. This approach was successfully used by Pitaevskiĭ[19] to calculate the coefficient of electron diffusion in the RA energy space. Pitaevskiĭ's method was generalized and developed in Refs. 20 and 21, but no analytic expressions were obtained for the inelastic-transition cross sections. We obtain in the present paper, on the basis of an analysis of a binary collision of an RA electron with an incident atom, analytic expressions for the cross sections and rate constants of the transitions $n \to n'$ and $nl \to n'$,

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and also of the coefficient of electron diffusion in the RA energy space. These expressions take full account of the amplitude of electron scattering by an incident atom as a function of the electron momentum and scattering angle, and also of the discrete character of the atomic states. This permits a rather simple calculation of the characteristics of the inelastic scattering of a complex neutral atomic particle by RA. From the expressions derived follows, as particular cases, all the known equations for the cross sections and rate constants of RA collisions with atoms in the ground state. In addition, an analysis of the expressions derived in this paper reveals the physical meaning and the applicability limits of the equations obtained by Alekseev and Sobel'man[22] for the cross sections for broadening and shifts of Rydberg levels. The analysis generalizes also the Pitaevskiĭ model[19] to include the discrete character of the RA states; this makes it possible to determine the coefficient of electron diffusion in the RA energy space in the region of small RA principal quantum numbers.

2. FREE-ELECTRON MODEL FOR THE TRANSITIONS $nl \to n'$ AND $n \to n'$

Consider the collision of an RA $A^{**}(nl)$ with a netural atomic particle B. The RA is large and the Rydberg electron has a high probability of being located at a distance $r \geqslant n^2$ from the core (ion) A^+. The interactions V_e and V_s of the neutral particle with the electron and the ion can therefore be considered independently. These interactions are jointly manifested only in the broadening and shift of the Rydberg levels,[23] whereas the inelastic processes are governed in almost all cases by the V_e interaction. Transitions due to collisions of neutral particles with the atomic core are caused by the inertia force that acts on the Rydberg electron as a result of the accelerated motion of the Coulomb center A^+ upon collision with a neutral. As seen from Refs. 24 and 25, the cross sections related to this transition mechanism can be comparable with those due to the V_e interaction only for very large principal quantum numbers ($n \geqslant 30$–50) and in some special cases (see the analysis of this question in Ref. 15). The present paper deals therefore with processes due to interaction of an incident particle with a Rydberg atom.

The model developed here for inelastic collisions of neutral particles with RA is close to the approach used in Refs. 19–21, i.e., it is assumed that the state of the RA changes when the RA-electron energy and momentum are changed by collision with the incident particle B. The electron is scattered by particle B as if it were free, with scattering amplitude $f_e(p,\theta)$, where p is the electron momentum and θ the scattering angle. The change of the electron coordinate in the e–B scattering is insignificant and does not alter substantially the potential energy of the RA electron. The last assumption means that the changes of the electron energy and momentum do not depend on the e–B collision point (at which the electron coordinate $\mathbf{r}$ coincides with the coordinate $\mathbf{R}$ of the atom B), but depends on the initial momentum of the electron and on the scattering angle. To calculate the inelastic-transition cross section it is therefore necessary to average over the electron momenta, the scattering angles, and the velocity directions of particle B, but there is no need to average over the coordinates of B.

We shall consider the transitions $nl \to n'$ and $n \to n'$, i.e., transitions with an undetermined electron orbital momentum in the final state of the RA. We determine first the cross section $d\sigma_{e-B}/d\varepsilon$, averaged over the velocity directions of the atom B, for the transfer of an energy ε to the electron in e–B scattering. We choose the coordinate frame such that the electron momentum $\mathbf{p}$ is directed along the z axis prior to the scattering by the atom B, and the electron radius vector $\mathbf{r}$ relative to A^+ is in the xz plane, i.e., $\mathbf{p}(p,0,0)$ and $\mathbf{r}(r,\chi,0)$ in a spherical coordinate system. After scattering, the coordinates of the electron momentum ($\mathbf{p}'$), of the momentum transfer ($\mathbf{Q}$), and of the velocity ($\mathbf{v}$) of the atom B are then $\mathbf{p}(p',\theta,\varphi)$, $\mathbf{Q}(Q,(\pi+\theta)/2,\varphi)$ and $\mathbf{v}(v,\theta_a,\varphi_a)$. Recognizing that the mass of the atom B is much larger than the electron mass, while the electron velocity is much larger than that of the atom B, the law of energy and momentum conservation in elastic e–B scattering yields for the electron energy after the scattering

$$\varepsilon = vQ\cos\gamma, \quad Q = 2p\sin(\theta/2)$$

(γ is the angle between $\mathbf{v}$ and $\mathbf{Q}$) or

$$\varepsilon = 2vp\sin(\theta/2)\cos\gamma, \quad \cos\gamma = -\sin(\theta/2)\cos\theta_a + \cos(\theta/2)\sin\theta_a\cos(\varphi-\varphi_a). \tag{2.1}$$

The differential cross section for the transfer of an energy ε to the electron in e–B scattering is obtained by integrating the squared e–B scattering modulus $|f_e(p,\theta)|^2$ over the scattering angles θ and φ, and averaging it over the angles θ_a and φ_a, under the condition that the electron had acquired an energy ε:

$$\frac{d\sigma_{e-B}(p)}{d\varepsilon} = \frac{1}{4\pi}\int |f_e(p,\theta)|^2\,\delta(\varepsilon - 2vp\sin(\theta/2)\cos\gamma) \times \sin\theta\sin\theta_a\,d\theta\,d\theta_a\,d\varphi\,d\varphi_a. \tag{2.2}$$

Integrating first over φ_a and φ and then over θ_a, we have

$$\frac{d\sigma_{e-B}(p)}{d\varepsilon} = \begin{cases} \dfrac{\pi}{vp}\displaystyle\int_{\theta_t}^{\pi} |f_e(p,\theta)|^2\cos\frac{\theta}{2}\,d\theta, & |\varepsilon| < 2vp, \\ 0, \quad |\varepsilon| \geqslant 2vp, & \theta_t = 2\arcsin(|\varepsilon|/2vp). \end{cases} \tag{2.3}$$

The rate constant of energy transfer to the electron, which is equal to the rate constant of energy transfer to the RA as a result of a collision of the Rydberg atom of momentum p with the atom B, is obtained by multiplying (2.3) by the electron velocity v_e (equal to p in atomic units). The cross section $d\sigma_{\text{PA}-B}/d\varepsilon$ for transfer of the RA energy as it collides with B will equal the rate constant divided by the collision velocity v and averaged over the momenta of the Rydberg electron in the initial nl state:

$$\frac{d\sigma_{\text{PA}-B}}{d\varepsilon} = \frac{\pi}{v^2}\int_{p_t}^{\infty} |g_{nl}(p)|^2 p^2\,dp \int_{\theta_t}^{\pi} |f_e(p,\theta)|^2\cos\frac{\theta}{2}\,d\theta,$$

$$p_t = \frac{|\varepsilon|}{2v}. \tag{2.4}$$

We obtain the cross section for the $nl \to n'$ transition by multiplying the cross section by the distance $\Delta\varepsilon = n'^{-3}$ between the hydrogen levels:

$$\sigma_{nl,n'} = \frac{\pi}{v^2 n'^3} \int_{p_t}^{\infty} |g_{nl}(p)|^2 p^2 dp \int_{\theta_t}^{\pi} |f_e(p,\theta)|^2 \cos\frac{\theta}{2} d\theta$$

$$= \frac{\pi}{v^2 n'^3} \int_{p_t}^{\infty} |g_{nl}(p)|^2 p\, dp \int_{2p_t}^{2p} |f_e(p,Q)|^2 dQ, \quad p_t = \frac{|\Delta E|}{2v}. \qquad (2.5)$$

Equation (2.5) is the solution of the problem of expressing the cross section of the $nl \to n'$ transition in terms of the amplitude of the e–B scattering amplitude. Let us analyze this equation. If f_e is independent of the momenta p and Q, (2.5) agrees with the results obtained in the impulse approximation [Eq. (3) of Ref. 14] and by the quasiclassical method.[15] This agreement between the particular Eq. (2.5) and equations obtained by other methods justifies the assumptions on which it was derived. According to (2.5), in the case of a finite transition energy defect ($\Delta E \neq 0$) a contribution to the cross section $\sigma_{nl,n'}$ is made only by scattering of an electron having a momentum higher than the threshold momentum p_t, and through an angle exceeding the threshold angle θ_t.

The total cross section for scattering of the particle B by the electron cloud of A is obtained by summing the cross section (2.5) over n'. At $2vn^2 \gg 1$ the cross section $\sigma_{nl,n'}$ depends little on n' (see also Ref. 14) and summation of (2.5) over n' can be replaced by integrating (2.4) with respect to $d\varepsilon$. Changing the order of integration in (2.4) and integrating it by parts with respect to $d\varepsilon$, we get

$$\sigma_{B-\mathrm{PA}e} = \frac{2\pi}{v} \int_0^{\infty} \left(\int_0^{\pi} |f_e(p,\theta)|^2 \sin\theta\, d\theta \right) |g_{nl}(p)|^2 p^3 dp$$

$$= v^{-4} \int_0^{\infty} \sigma_e(p) |g_{nl}(p)|^2 p^3 dp, \quad 2vn^2 \gg 1. \qquad (2.6)$$

Equation (2.6) agrees with the result of Alekseev and Sobel'man.[22] It follows hence also that the connection found in Ref. 22 between the amplitude of forward scattering of atomic particle B by the RA electron cloud and the amplitude of forward scattering of an electron by B,

$$f_{B-\mathrm{PA}e}(0) = \mu \int_0^{\infty} f_e(p,0) |g_{nl}(p)|^2 p^2 dp, \qquad (2.7)$$

where μ is the reduced mass of the RA and of the atom B, is valid when the cross sections for transitions with change of the principal quantum number of the RA are large (contrary to the assumptions of Ref. 22). See also Refs. 2, 11, and 14 concerning this question.

We obtain now explicit expressions for the cross sections $\sigma_{nl,n'}$. Equation (2.5) can be written in the form

$$\sigma_{nl,n'} = \int_{p_t}^{\infty} \sigma_{nl,n'}(p) |g_{nl}(p)|^2 p^2 dp, \qquad (2.8)$$

$$\sigma_{nl,n'}(p) = \frac{\pi}{v^2 n'^3} \int_{\theta_t}^{\pi} |f_e(p,\theta)|^2 \cos\frac{\theta}{2} d\theta. \qquad (2.9)$$

We express the e–B scattering amplitude and cross section in terms of the partial amplitudes

$$f_e(p,\theta) = \sum_L (2L+1) f_L(p) P_L(\cos\theta),$$

$$\sigma_e(p) = 4\pi \sum_L (2L+1) |f_L(p)|^2, \qquad (2.10)$$

where P_L is a Legendre polynomial.

We analyze first the cross section for mixing degenerate nl states ($\Delta E = 0$). Substituting (2.10) in (2.9) and integrating at $\theta_t = 0$ we obtain according to (Ref. 26, Vol. 2, p. 447)

$$\sigma_{nl,n}(p) = \frac{2\pi}{v^2 n^3} \sum_{L,L'} (2L+1) f_L(p) f_{L'}^*(p)\, {}_4F_3\Big(-L, L+1, \frac{1}{2}, \frac{1}{2}; 1, L'+\frac{3}{2}, -L'+\frac{1}{2}; 1\Big). \qquad (2.11)$$

Here ${}_4F_3$ is a generalized hypergeometric (Ref. 26, Vol. 2, p. 745). Averaging (2.11) in accordance with (2.8), we obtain the total cross section for orbital-angular-momentum mixing of degenerate nl states. The Rydberg electron is slow (its characteristic momentum is $p \sim n^{-1}$), therefore the main contribution to e–B scattering is made as a rule only by s and p scattering. According to (2.8) and (2.11) we have then

$$\sigma_{nl,n} = \frac{2\pi}{v^2 n^3} \Big[\overline{|f_s(p)|^2} + 2\,\mathrm{Re}\,(\overline{f_s(p) f_p^*(p)}) + \frac{3\cdot 7}{5} \overline{|f_p(p)|^2} + \ldots \Big], \qquad (2.12)$$

where the ellipsis stands for the contributions of $d, f,\ldots$ scattering and the superior bar denotes averaging over the momenta of the Rydberg electron, in analogy with (2.8), at $p_t = 0$. Comparison of (2.12) and (2.10) shows that in the general case the cross section $\sigma_{nl,n}$ [in contrast to the total cross section σ_{nl} (2.6)] is not expressed in terms of the e–B scattering cross section. The amplitudes f_L of the e–B scattering enter in the expression for $\sigma_{nl,n}$ with different weights, and interference of the amplitudes sets in. The following approximate relation, however, is satisfied:

$$\sigma_{nl,n} \approx \overline{\sigma_e(p)}/2v^2 n^3, \quad \Delta E = 0. \qquad (2.13)$$

The cross section $\sigma_{nl,n'}$ has an even more complicated dependence on the partial e–B scattering amplitudes at a finite energy defect $\Delta E = (2n^{*2})^{-1} - (2n'^2)^{-1}$ of the transition (n^* is the effective principal quantum number of the initial nl state). Thus, substituting (2.10) and (2.9) in (2.8) we obtain

$$\sigma_{nl,n'} = \frac{2\pi}{v^2 n'^3} \Big[\overline{|f_s(p)|^2 I^s(p_t,p)} + 2\,\mathrm{Re}\,\overline{(f_s(p) f_p^*(p)) I^{sp}(p_t,p)} + 3\overline{|f_p(p)|^2 I^p(p_t,p)} + \ldots \Big], \qquad (2.14)$$

$$I^s(p_t,p) = 1 - p_t/p, \quad I^{sp}(p_t,p) = 1 - 3p_t/p + 2(p_t/p)^2,$$

$$I^p(p_t,p) = {}^7/_5 - 3p_t/p + 4(p_t/p)^3 - {}^{12}/_5 (p_t/p)^5. \qquad (2.15)$$

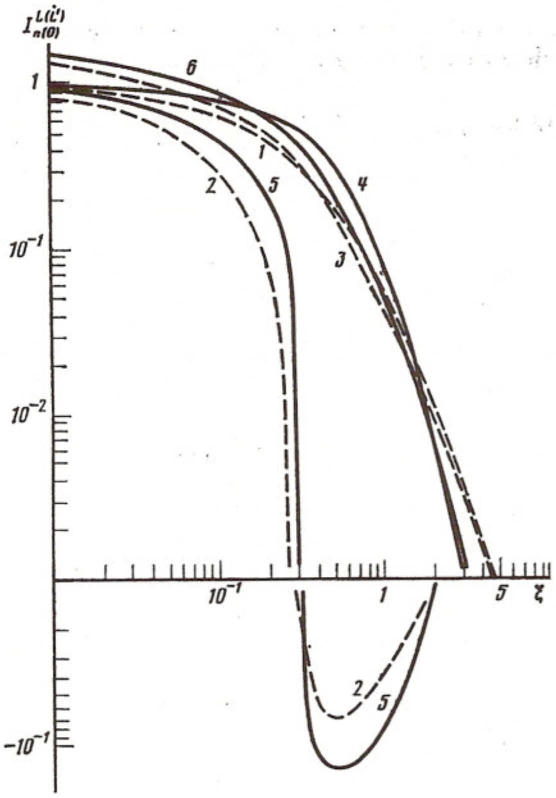

FIG. 1. Dependence of the integrals $I_{n(0)}^{L(L')}$ (A1) on the Massey parameter $\xi = |\Delta E| n^*/2v$. Curves 1, 2, and 3—the integrals I_{n0}^{s}, I_{n0}^{sp} and I_{n0}^{p} respectively according to (A3)–(A8); curves 4, 5, and 6—the integrals I_n^s, I_n^{sp} and I_n^p respectively according to (A10)–(A15).

The superior bar denotes here averaging in accordance with (2.8), i.e.,

$$\overline{|f_L(p)|^2 I^L(p_t,p)} = \int_{p_t}^{\infty} |f_L(p)|^2 I^L(p_t,p)\,|g_{nl}(p)|^2 p^2\,dp. \quad (2.16)$$

Using the approximate expressions for the distributions of $|g_{nl}(p)|^2$ averaged over the oscillations (see the Appendix), we can easily average in (2.16) if the functions $f_L(p)$ are known. The contribution to the integrals (2.16) is made by a relatively narrow range of electron momenta, viz., from p_t to approximately n^{*-1} if $p_t \lesssim n^{*-1}$, or in the vicinity of the point p_t if $p_t \geqslant n^{*-1}$. If there are no singularities (resonances) in the e–B scattering at $p \sim p_t$ or n^{*-1}, the scattering partial amplitudes $f_L(p)$ change little, as a rule, in the indicated momentum interval, and can therefore be taken outside the integral sign in (2.16). Thus,

$$\overline{|f_L(p)|^2 I^L(p_t,p)} \approx |f_L(\tilde p)|^2 \overline{I^L(p_t,p)} = |f_L(\tilde p)|^2 I_{nl}^L(\xi),$$
$$\tilde p = \max(n^{*-1}, p_t), \quad \xi = n^* p_t = |\Delta E| n^*/2v, \quad (2.17)$$

where ξ is the Massey parameter for the considered transition[11] (see also the Appendix). Note that in this case the characteristic internuclear distance is $n^*/2$, half the de Broglie length of the Rydberg electron. The Appendix contains expressions for the integrals $I_{nl}^L(\xi)$, which are plotted in Fig. 1. This makes it easy to determine the cross sections $\sigma_{nl,n'}$ by using (2.14) and (2.17). Note that $I_{nl}^{sp}(\xi)$ becomes negative at $\xi \geqslant 0.3$.

It follows from the foregoing analysis that if the e–B scattering amplitude changes little with change of the electron momentum is in the interval $p_t < p \lesssim n^{*-1}$, the cross section of the transition $nl \to n'$ is described with good accuracy by the expression

$$\sigma_{nl,n'} \approx \sigma_e(\tilde p) I_{nl}^s(\xi)/2v^2 n'^3. \quad (2.18)$$

In this approximation, the behavior of the cross sections of the transitions $nl \to n'(l \ll n)$ and $n \to n'$ follows respectively from (2.18), (A3), (A4) and (2.18), (A10), (A11). In particular, the cross section $\sigma_{n0,n'}$ as a function of n^* with v and $\Delta N^* = n' - n^*$ constant reaches a maximum value

$$\sigma_{n0,n'}^{max} = 0.095\sigma_e(\tilde p)/|\Delta n|^{4/3} v^{2/3}$$

at $n^*_{max} = 1.31(|\Delta n^*|/2v)^{1/2}$, while the cross section $\sigma_{n,n'}$ reaches a maximum

$$\sigma_{n,n'}^{max} = 0.16\sigma_e(\tilde p)/|\Delta n|^{4/3} v^{2/3}$$

at $n^*_{max} = 1.36(|\Delta n^*|/2v)^{1/2}$. Analysis of the behavior of the cross section $\sigma_{n0,n'}$ as a function of the collision velocity v shows that, with accuracy not worse than 22%, the rate constant of the transition $nl \to n'(l \ll n)$ is

$$K_{n0,n'} \equiv \langle \sigma_{n0,n'}(v) v \rangle \approx \sigma_{n0,n'}(\langle v \rangle)\langle v \rangle, \quad (2.19)$$

where the angle brackets denote averaging over the Maxwellian distribution of the collision velocities.

To calculate the rate constant of the transition $n \to n'$ we express the cross section $\sigma_{n,n'}$ in accordance with (2.18), (A1), and (A9), after integrating by parts, in the form

$$\sigma_{n,n'} = \frac{8\sigma_e(\tilde p)}{3\pi v^2 n'^3} \int_{\xi}^{\infty} \frac{dx}{(1+x^2)^3}. \quad (2.20)$$

Averaging (2.20) over the Maxwellian distribution of the collision velocities we obtain by integrating by parts and in accordance with Ref. 26 (Vol. 1, p. 324) the rate constant of the $n \to n'$ transition ($n > n'$)

$$K_{n,n'} = \frac{2\sigma_e(\tilde p)}{\pi v_T n'^3} U\left(\frac{5}{2}, \frac{1}{2}; \xi_T^2\right)$$
$$= \frac{2^{7/4}\sigma_e(\tilde p)}{\pi v_T n'^3} \exp(\xi_T^2/2)\, U\left(\frac{9}{2}, 2^{1/2}\xi_T\right), \quad (2.21)$$
$$K_{n',n} = (n^2/n'^2) K_{n,n'} \exp(-\Delta E/T).$$

Here $\xi_T = |\Delta E| n/2v_T$, $v_T = (2T/\mu)^{1/2}$ is the thermal velocity of the colliding atoms, $U(a,b;z)$ is a confluent hypergeometric function, and $U(a,z)$ is a Whittaker function tabulated in Ref. 27 (Chap. 19). From (2.21) follow limiting expressions for the rate constants:

$$K_{n,n'} = \sigma_e(\tilde p)/\pi^{3/2} v_T n^3, \quad \xi_T \ll 1,$$
$$K_{n,n'} = 2^6 \sigma_e(\tilde p) v_T^4/\pi n^5 n'^3 |\Delta E|^5, \quad \xi_T \gg 1. \quad (2.22)$$

At $n_{max} = 1.3(|\Delta n|/2v_T)^{1/2}$ the rate constant $K_{n,n'}$ as a function of n has a maximum at constant v and Δn:

$$K_{n,n'}^{max}=0{,}14\sigma_e(\tilde{p})v_T^{1/2}/|\Delta n|^{4/3}. \qquad (2.23)$$

Note that at $\xi_T \gg 1$ we have

$$K_{n,\,n'}\approx 2{,}3\sigma_{n,\,n'}(\langle v\rangle)\langle v\rangle.$$

If the e–B scattering amplitude $f_e(p,\theta)$ depends strongly on the momentum p at $p_r < p \lesssim n^{*-1}$, the cross section for the inelastic transition must be calculated from (2.14)–(2.16). It follows hence also that in the vicinity of the resonant scattering of slow electrons by atoms (which we have in fact predicted before[28–30] for alkali-metal atoms) the amplitude influences only transitions with $|\Delta n^*| \lesssim 2vn^{*3}(2E_r)^{1/2}$, where E_r is the position of the resonance, with $E_r \sim 0.1$ to 0.0011 eV for alkali-metal atoms.[30] Consequently, such resonances contribute mainly only to the cross sections for elastic and quasielastic scattering ($|\Delta n^*| \ll 1$).

3. ELECTRON DIFFUSION COEFFICIENT IN THE RA ENERGY SPACE

Having now an expression for the rate constant of the $n \to n'$ transition, we can calculate also the electron diffusion coefficient in the RA energy space, due to collisions of the RA with neutral particles of type B. Quantities expressed in terms of the diffusion coefficient are the ionization and recombination coefficients in a low-temperature plasma,[19,31,32] and the efficiency and time of collisional ionization of the RA.[33,34] The diffusion coefficient was calculated in Refs. 19 and 31 without allowance for the discrete character of the atomic states. We obtain now an expression for the diffusion coefficient $B(E)$, with full allowance for the discrete character of the atomic states, and for the transitions between all the RA levels. By definition,[19,31–34]

$$B(E)=\frac{N_B}{2}\sum_{n'}K_{n,n'}(\Delta E_{n,n'})^2, \quad E=(2n^2)^{-1}, \qquad (3.1)$$

where N_B is the density of the atoms B. Using (2.20), we can write

$$B(E)=\frac{32N_B\sigma_e}{3\pi^{3/2}n^9}\int_0^\infty \exp(-v^2/v_T^2)\,v\,dv\sum_{k=1}^\infty k^2\int_{k/2vn^2}^\infty \frac{dx}{(1+x^2)^3}. \qquad (3.2)$$

After integration by parts with respect to dv, expression (3.2) takes the form

$$B(E)=\frac{2^7N_B\sigma_e nv_T^2}{3\pi}\left\langle\sum_{k=1}^\infty \frac{v^2k^3}{[(2vn^2)^2+k^2]^3}\right\rangle, \qquad (3.3)$$

where the angle brackets denote averaging over the Maxwellian distribution of the collision velocities. The sum in (3.3) is of the form

$$\sum_{k=1}^\infty \frac{k^3}{(a^2+k^2)^3}\approx\int_b^\infty \frac{k^3\,dk}{(a^2+k^2)^3}=\frac{a^2+2b^2}{4(a^2+b^2)^2}. \qquad (3.4)$$

The lower integration limit must be chosen here to have (3.4) yield the exact result as $a \to 0$ (Ref. 26, Vol. 1, p. 651):

$$S_3=\sum_{k=1}^\infty k^{-3}=\int_b^\infty k^{-3}\,dk=(2b^2)^{-1}=1.202, \qquad (3.5)$$

i.e., $b=(2S_3)^{-1/2}=0.645$. At $a \gg 1$ (3.4) depends little on b, and is therefore a good approximation of the sum at all a. Averaging in (3.3), with allowance for (4.4) over the Maxwellian distribution of the velocities, we have

$$B(E)=(2^{9/2}/\pi b^{4/3})N_B\sigma_e v_T^{7/2}\xi_d^{3/2}\exp(\xi_d^2/2)[(4\xi_d^2+1)U(7/2,2^{1/2}\xi_d)$$
$$+2^{5/2}\xi_d U(9/2,2^{1/2}\xi_d)], \qquad (3.6)$$

where $\xi_d=bE/v_T$. Averaging separately the numerator and denominator of (3.3), we obtain from (3.4) an approximate for the diffusion coefficient

$$B(E)=(2^{9/2}/\pi b^{4/3})N_B\sigma_e v_T^{7/2}\xi_d^{3/2}(3+4\xi_d^2)(3+2\xi_d^2)^{-2}, \qquad (3.7)$$

which has the correct asymptotic values and differs from the exact result (3.6) by less than 15% for all ξ_d.

We compare now (3.7) with Pitaevskiĭ's result,[19] which is likewise obtained by changing the order of integration in (2.4) and integrating it by parts with respect to $d\varepsilon$, i.e.,

$$B_P(E)=\frac{N_B}{2}\left\langle v\int_{-\infty}^{\infty}\frac{d\sigma_{PA-B}}{d\varepsilon}\varepsilon^2\,d\varepsilon\right\rangle$$
$$=\frac{2\pi N_B}{3}\left\langle v^2\int_0^\infty\left[\int_0^\pi |f_e(p,\theta)|^2(1-\cos\theta)\sin\theta\,d\theta\right]\times|g_n(p)|^2p^5\,dp\right\rangle$$
$$=N_B\langle v^2\rangle\overline{\sigma_t(p)p^3}/3. \qquad (3.8)$$

Here σ_t is the e–B scattering transport cross section. At constant σ_t averaging of (3.8) yields in accordance with (A9)

$$B_P(E)=(2^{9/2}/3\pi)N_B\sigma_t v_T^2E^{3/2}. \qquad (3.9)$$

Since $\sigma_t \approx \sigma_e$, expression (3.7) differs from (3.9) mainly only by a factor $(1+4\xi_d^2/3)(1+2\xi_d^2/3)^{-2}$. It follows therefore that the Pitaevskiĭ expression (3.9) is valid only for $\xi_d \ll 1$, i.e., for $n \gtrsim n_P = 0.5(\mu/T)^{1/4}$. At thermal velocities, $n_P \sim 20$–40. At $n \lesssim n_P$ one must use the expression (3.7) above for the diffusion coefficient. Allowance for the discreteness of the atomic states at $n \lesssim n_P$ leads to a decrease of the electron diffusion coefficient in the RA energy space, to a decrease of the ionization and recombination coefficients in a low-temperature plasma, and to a longer time and less effective ionization of the RA by collisions.

4. LIMITS OF APPLICABILITY OF THE MODEL AND COMPARISON WITH THE EXPERIMENTAL DATA

It is assumed in the here-developed model of a free electron that the processes are due to collisions of the quasifree Rydberg atom with the perturbing atom B during the entire time that the atom B remains in the inside the RA. Inverse transitions are not taken into account. The free-electron model in this sense is therefore applicable when the investigated processes are not highly effective. This means that the cross sections for the processes described by the free-electron model must be much smaller than the geometric cross section of the RA. Thus, for mixed degenerate states we have according to (2.13) $8\pi v^2n^7 \gg \overline{\sigma_e(p)}$, which is an inverse criterion for the validity of the adiabatic mechanism.[12] For

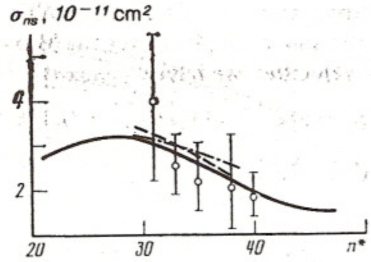

FIG. 2. Cross section for quenching of the *ns* states of rubidium by collisions with rubidium atoms in the ground state, at temperature $T = 400$ K, vs the effective principal quantum number n^*. Circles—experimental data[35], solid curve—calculation according to (2.18) at $\sigma_e = 2900\pi a_0^2$, dashed and dash-dot curves, respectively—numerical calculation[35] in the impulse approximation at $\sigma_e = 4\pi|f_e|^2 = 2900\pi a_0^2$ and with allowance for the dependence of the cross section $\bar{\sigma}_e$, averaged over the electron momenta in the *ns* state, on n.

transitions from an isolated level with large defect of the transition resonance, the free-electron model is applicable at smaller principal quantum numbers of the RA, i.e., according to (2.18), at $8\pi v^2 n^7 \gg \sigma_e(\tilde{p}) I_{nl}{}^s(\xi)$.

At $2vn^2 \gg 1$, transitions to a large number of states with $n' \sim n$ are effective. For the model to be valid in this case it is necessary that the summary cross section (2.6) likewise be smaller than the geometric cross section of the RA, i.e., $4\pi n^4 \gg \sigma_{B\text{-PA}e} \approx \sigma_e(\tilde{p})/vn$. According to the optical theorem, $\sigma_e(\tilde{p}) \lesssim 4\pi\tilde{p}^{-2} \approx 4\pi n^2$. It follows therefore that at $2vn^2 \gg 1$ the free-electron model and the theory of Alekseev and Sobel'man[22] can be used to describe collisions of RA with any neutral atomic particle.

In experiment one measures most frequently the cross sections for quenching nl states with small $l = 0,1,2,3$. According to our present results, such cross sections are determined at $2vn^2 \gg 1$ by transitions to the nearest n' level with the smallest transition-energy defect

$$|\Delta E| = \min(\{\delta_l\} n^{*-3},\ [1 - \{\delta_l\}] n^{*-3}),$$

where $\{\delta_l\}$ is the fractional part of the quantum defects. [at $\{\delta_l\} \approx 0.5$, transitions to two groups of states with $n' \approx n^* \pm 0.5$ are significant, and the cross section for the quenching such an nl state is equal to the sum of two cross sections of type (2.18).]

By way of example, Figure 2 shows a comparison of the experimental[35] cross sections for quenching the RA Rb (ns) by rubidium atoms in the ground state Rb(5*S*), on the one hand, with the cross section (2.18) obtained in the free electron model, on the other. Since the quantum defect of the *ns* series of Rb is $\delta_s = 3.13$, the principal channel of Rb(ns) quenching is the transition with the smallest transition-energy defect $\Delta E = 0.13 n^{*-3}$, i.e., the transition $ns \to (n-3) f,g,h,\ldots$. The cross section used by us for electron scattering by Rb(5*S*) was $\sigma_l = 2900\pi a_0^2$, obtained in Ref. 35 after averaging the theoretical cross section for electron scattering by the Rb atom[36] over the momenta of the Rydberg electron. Note that the cross sections for RA quenching by alkali atoms are very large, so that the free-electron model is applicable here at relatively large RA principal quantum numbers, $n \gg 20$–25. For RA collisions with inert gases, our model is applicable also at smaller n^* (~ 10–20).[14]

5. CONCLUDING REMARKS

A model was developed with which it was possible, for the first time ever, to describe theoretically inelastic collisions of RA with neutral atomic particles, without resorting to the Fermi-pseudopotential approximation. The model is based on an analysis of a binary collision of a Rydberg electron with an incident particle. In this approximation, the transition cross sections are expressed very simply in terms of the amplitude of the scattering of the electron by the atomic particle, with allowance for the dependence of this amplitude on the electron momentum and on the scattering angle. Measurement of the cross sections of processes that occur in collisions of an RA with a neutral particle permits a determination of the characteristics of scattering of a very slow electron by an atomic particle. This model can be generalized to describe $nl \to n'l'$ transitions, where it is necessary to consider also the changes of the angular momentum of the Rydberg atom as it collides with the atomic particles, as well as for the description of RA collisions with molecules, when scattering by a Rydberg atom takes a molecule into another vibrational-rotational state. Furthermore, in view of our present results, it is necessary to revise the physical meaning and the limits of applicability of the Rydberg-level broadening theory based on the impulse approximation.[2,22,28–30,37]

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APPENDIX

Calculation of the integrals $I_{n(l)}^{L(L')}(\xi)$.

From (2.16) and (2.17) we have

$$I_{n(l)}^{L(L')}(\xi) = \overline{I_{n(l)}^{L(L')}(p_t, p)} = \int_{p_t}^{\infty} I^{L(L')}(p_t, p)\,|g_{n(l)}(p)|^2 p^2\,dp. \qquad \text{(A1)}$$

At $l \ll n$ we use the radial part, averaged over the oscillations, of the Rydberg-electron *ns*-state wave function in the momentum representation[11,14,22]:

$$|g_{n0}(p)|^2 = 4n^*/\pi p^2(1 + n^{*2}p^2)^2, \quad (2n^{*2})^{-1} \ll p \ll l + 1/2. \qquad \text{(A2)}$$

Substituting (2.15) and (A2) in (A1) we get

$$I_{n0}{}^s = (2/\pi)[\operatorname{arcctg}\xi - \xi\ln(1 + \xi^{-2})], \qquad \text{(A3)}$$

$$I_{n0}{}^s \approx \begin{cases} 1 - (2/\pi)\xi(2\ln\xi^{-1} + 1) + \ldots, & \xi \ll 1, \\ 1/3\pi\xi^3 - 4/15\pi\xi^5 + \ldots, & \xi \gg 1, \end{cases} \qquad \text{(A4)}$$

$$I_{n0}{}^{sp} = (2/\pi)[\operatorname{arcctg}\xi + 4\xi - (4\xi^3 + 3\xi)\ln(1 + \xi^{-2})], \qquad \text{(A5)}$$

$$I_{n0}^{sp} \approx \begin{cases} 1 - (6/\pi)\xi(2\ln\xi^{-1} - 1) + \ldots, & \xi \ll 1, \\ -1/3\pi\xi^3 + 2/5\pi\xi^5 + \ldots, & \xi \gg 1, \end{cases} \qquad \text{(A6)}$$

$$I_{n0}{}^p = (2/5\pi)[7\operatorname{arcctg}\xi + 36\xi^3 + 22\xi - (36\xi^5 + 40\xi^3 + 15\xi)\ln(1 + \xi^{-2})], \qquad \text{(A7)}$$

$$I_{n0}{}^{p} \approx \begin{cases} 7/5-(6/\pi)\xi(2\ln\xi^{-1}-1)+\ldots, & \xi\ll 1, \\ 1/3\pi\xi^{3}-8/25\pi\xi^{5}+\ldots, & \xi\gg 1. \end{cases} \quad (A8)$$

We can similarly calculate the integrals of (A1) for transitions from the level n for equiprobable population of the nl states. In this case[11,14]

$$|g_n(p)|^2=\frac{1}{n^2}\sum_{l=0}^{n-1}(2l+1)|g_{nl}(p)|^2=\frac{32n^2}{\pi(1+n^2p^2)^4}. \quad (A9)$$

Substitution of (2.15) and (A9) in (A1) yields

$$I_n{}^{s}=(2/\pi)[\operatorname{arcctg}\xi-(3\xi^3+5\xi)/3(1+\xi^2)^2], \quad (A10)$$

$$I_n{}^{s} \approx \begin{cases} 1-16\xi/3\pi+\ldots, & \xi\ll 1, \\ 16/15\pi\xi^5-16/7\pi\xi^7+\ldots, & \xi\gg 1, \end{cases} \quad (A11)$$

$$I_n{}^{sp}=(2/\pi)[\operatorname{arcctg}\xi+16\xi^3\ln(1+\xi^{-2}) -(16\xi^5+25\xi^3+7\xi)/(1+\xi^2)^2]. \quad (A12)$$

$$I_n{}^{sp} \approx \begin{cases} 1-16\xi/\pi+\ldots, & \xi\ll 1, \\ -8/5\pi\xi^5+144/35\pi\xi^7+\ldots, & \xi\gg 1, \end{cases} \quad (A13)$$

$$I_n{}^{p}=(2/5\pi)[7\operatorname{arcctg}\xi+(384\xi^5+160\xi^3)\ln(1+\xi^{-2}) -(384\xi^7+736\xi^5+375\xi^3+33\xi)/(1+\xi^2)^2], \quad (A14)$$

$$I_n{}^{p} \approx \begin{cases} 7/5-16\xi/\pi+\ldots, & \xi\ll 1, \\ 32/25\pi\xi^5-16/5\pi\xi^7+\ldots, & \xi\gg 1. \end{cases} \quad (A15)$$

In (A3)–(A8) we have $\xi=p_t n^*\ll n^*$; $\xi\ll 1$ means actually that $\xi\lesssim 0.1$, while $\xi\gg 1$ means that $\xi\gtrsim 3$. Plots of $I_{n(l)}^{L(L')}(\xi)$ are shown in Fig. 1.

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