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Resonant ionization in slow-atom–Rydberg-atom collisions

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The process of ionization in slow-atom–Rydberg-atom collisions is investigated. A resonant energy exchange mechanism is considered responsible for the electron transition into the continuum. Both symmetrical and asymmetrical systems are considered. The ionization probabilities and cross sections for a number of Rydberg states in the colliding systems H* (n) + H, Li* (n) + Li, H* (n) + Li are calculated.

I. INTRODUCTION

The process of ionization of highly excited (Rydberg) atoms in slow collisions with ground-state atoms and molecules is of considerable interest in many fields of research, involving nonthermal and nonstationary laboratory and astrophysical plasmas.[1,2] Experimental investigations of this process have recently been performed[3,4] or are under way in several laboratories.[5] The theoretical studies of atom–Rydberg-atom ionizing collisions have been performed so far either within the classical[6] and semiclassical[7] approximations or by using the Fermi pseudopotential model.[8] In the present paper we consider the atom–Rydberg-atom ionization process within the framework of a resonant energy exchange mechanism recently developed for the inelastic transitions in the discrete spectrum of an atom–Rydberg-atom colliding system.[9] A limiting case of our problem has previously been treated by Zhdanov and Chibisov.[10]

In Sec. II we formulate the ionization problem in the slow-atom–Rydberg-atom collision in terms of the resonant energy exchange mechanism. In Sec. III we calculate the autoionization widths of the Rydberg states in both symmetrical and asymmetrical systems. In Sec. IV we present the results of our calculations on the ionization probabilities and cross sections of some Rydberg states in H*-H, Li*-Li, and H*-Li systems. In Sec. V we give some concluding remarks. Atomic units ($e=m_e=\hbar^2=1$) are used throughout this work, unless otherwise indicated.

II. RESONANT ENERGY EXCHANGE MECHANISM FOR ATOM-RYDBERG-ATOM IONIZATION PROBLEM

Let us consider a slow collision of a Rydberg atom $A^*(n)$ (n being the principal quantum number of the highly excited electron) with a ground-state atom B (or A) leading to the reaction

$$A^*(n)+B\rightarrow A+B^+ + e\,. \qquad (1)$$

We assume that the excitation energy $E_{\mathrm{ex},A}$ of the atom $A^*(n)$ is higher than the ionization potential I_B of atom B, and that $n\gg 1$. The reaction (1) differs from the usual Penning ionization process in two aspects. First, the state of the excited atom is not supposed to be a metastable one, and second, the decay of the autoionizing state leading to reaction (1) is dominated by the motion of the perturbing atom deeply inside the orbit of the excited (Rydberg) electron. If the transition $A^*(n)\rightarrow A(0)$ (where 0 refers to the ground state) is optically allowed, then at large internuclear distances $R\gg r_n, r_0$ [r_n, r_0 being the characteristic dimensions of atoms $A^*(n)$ and B (or A), respectively] the "direct" channel of reaction (1) is operative. However, owing to the small oscillator strength for such a transition (for $n\gg 1$), the efficiency of this channel is extremely small.

At low collision velocities ($v\ll n^{-1}$) and for impact parameters $\rho\ll r_n$, the perturbing atom B spends a good deal of time in the region inside the orbit of the Rydberg electron, so that inelastic electronic processes within the inner quasimolecular subsystem AB^+ are possible. The electronic transitions between the states of the subsystem AB^+ induce transitions of the outer Rydberg electron without any change in the electronic energy of the total system (i.e., in a resonant manner). If this resonant energy exchange between the inner subsystem and the outer electron is sufficient to bring the Rydberg electron into the continuum, then the ionization reaction occurs. In particular, the electronic transition in the inner quasimolecular ion AB^+ may lead to formation of a state which asymptotically correlates to the configuration $A+B^+$. In this case the Rydberg electron becomes unstable against autoionization. In the present paper we consider in more detail just this case [i.e., the "exchange" channel of reaction (1)].

It has been shown in Ref. 9 that the main contribution to the inelastic collision effects in atom–Rydberg-atom collisions at $v\ll n^{-1}$ gives the region $r_n\gg R\gg r_0$. If $\vec{r}_1$, $\vec{r}_2$ and $\vec{r}_{1b}$, $\vec{r}_{2b}$ are the position vectors of the Rydberg and the inner active electrons with respect to the atomic cores A^+ and B^+, then in the region $\vec{r}_1 \gg R \gg \vec{r}_2$ the Hamiltonian of our two-electron system can be written in the form

$$H = H_1 + H_2 + V_{\text{int}}\,, \tag{2}$$

$$H_1 = -\tfrac{1}{2}\nabla_1^2 - 1/r_1\,,$$

$$H_2 = -\tfrac{1}{2}\nabla_2^2 + V_A(r_2) + V_B(r_{2b})\,, \tag{2a}$$

$$V_{\text{int}} = -1/r_{1b} + 1/r_{12}\,, \tag{2b}$$

where $V_A(r)$ and $V_B(r)$ are the potentials of the cores A^+ and B^+, having Coulomb behavior for large r.

Let us denote by $\phi_{n(\epsilon)}(\vec{r}_1)$ and $\chi_j(\vec{r}_2;\vec{R})$ the eigenfunctions of the Hamiltonians H_1 and H_2, respectively (ϵ refers to the continuum states of H_1). The wave functions χ_j describe the adiabatic states of the system AB^+, with the corresponding energies $U_j(R)$. Let $\chi_1(\vec{r}_2, \vec{R})$ and $\chi_2(\vec{r}_2, \vec{R})$ be the wave functions of the two low-lying states of the molecular ion AB^+ such that $\omega(R) = U_2(R) - U_1(R)$ is positive for each R. [For $R \to \infty$ this assumption is consistent with the condition $I(A) > I(B)$ imposed on reaction (1).] For simplicity, we assume that the states described by χ_1 and χ_2 are Σ-molecular states. The initial- and final-state wave functions for reaction (1) are now (l denotes the orbital angular momentum quantum number)

$$\Psi_i = \phi_{nl}(\vec{r}_1)\chi_2(\vec{r}_2;\vec{R})\,, \quad \Psi_f = \phi_{\epsilon l'}(\vec{r}_1)\chi_1(\vec{r}_2;\vec{R})\,, \tag{3}$$

and the ionization rate is given by

$$W = 2\pi\,|\langle\Psi_i|V_{\text{int}}|\Psi_f\rangle|^2 g(\epsilon)\,, \tag{4}$$

where $g(\epsilon)$ is the statistical weight of the continuum state of the Rydberg electron. In Eq. (4) the equality of the initial- and final-state energies is presumed and in the wave functions Ψ_i and Ψ_f we have neglected the possibility of exchange of the Rydberg electron with the inner one. The main contribution to the matrix element (4) gives the region $r_1 \simeq n^2$, $r_2 \ll n^2$, so that for r_{12}^{-1} in V_{int}, one can use the expansion

$$\frac{1}{r_{12}} \simeq \frac{1}{r_1} + \frac{\vec{r}_1\vec{r}_2}{r_1^3} + \cdots\,. \tag{5}$$

Using the expansion (5) in Eq. (4) and the orthogonality of the initial- and final-state wave functions, one obtains

$$W = 2\pi M_1^2 D^2(R) g(\epsilon)\,, \tag{6}$$

where

$$M_1^2 = \sum_{l'm'} |\langle\phi_{nlm}(\vec{r}_1)|\vec{r}_1\hat{\lambda}/r_1^3|\phi_{\epsilon l'm'}(\vec{r}_1)\rangle|^2\,, \tag{6a}$$

$$D^2(R) = |\langle\chi_2(\vec{r}_2;\vec{R})|\vec{r}_2\hat{\lambda}|\chi_1(\vec{r}_2;\vec{R})\rangle|^2\,, \tag{6b}$$

and $\hat{\lambda}$ is a unit vector along the internuclear axis.

Using the Coulomb approximation for the functions $\phi_{nlm}(\vec{r}_1)$, we may transform the quantity M_1^2 to the form[11]

$$M_1^2 = \omega_{n\epsilon}^4 \sum_{l'm'} |\langle\phi_{nlm}|\vec{r}_1\hat{\lambda}|\phi_{\epsilon l'm'}\rangle|^2\,, \tag{7}$$

where $\omega_{n\epsilon}$ is the transition frequency. Further using the fact that M_1^2 can be expressed[11] in terms of the photoionization cross section σ_{ph}, we can put the decay probability $W(R)$ into the form

$$W = (\omega_{n\epsilon}^3 c/2\pi)\sigma_{\text{ph}} D^2(R)\,, \tag{8}$$

where c is the velocity of light.

For $n \gg 1$ and $\omega_{n\epsilon} \lesssim \frac{1}{2}$, the photoionization cross section can be represented by the quasiclassical expression of Kramers,[12] and for the decay probability, averaged over the initial-state quantum numbers, one obtains

$$W(R) = (4/3\sqrt{3}n^5)D^2(R)\,. \tag{9}$$

This expression for $W(R)$ is valid in the region of R in which the condition $\omega(R) = U_2(R) - U_1(R) \gtrsim |\epsilon_n|$ holds, where ϵ_n is the binding energy of the Rydberg electron.

The problem of the calculation of the transition probability $W(R)$ is thus reduced to the calculation of the dipole moment $D(R)$ of the quasimolecular ion AB^+.

III. CALCULATION OF DIPOLE MATRIX ELEMENT

In calculating the matrix element $D(R)$, we distinguish two cases: (a) $I_A - I_B \ll I_A, I_B$ $(I_A > I_B)$ and (b) $I_A - I_B \simeq I_A, I_B$ $(I_A > I_B)$, where I_A and I_B are the ground-state ionization potentials of the atoms A and B, respectively. We refer to case (a) as the "quasiresonant case" and to case (b) as the "strongly nonresonant case."

Since the region $r_n \gg R \gg r_0$ is of primary interest to us, in the calculation of $D(R)$ we may use the asymptotic methods of the low-energy atomic collision theory.[13]

A. Quasiresonant case: $I_A - I_B \ll I_A, I_B$

Let $\varphi_1(\vec{r}_2;\vec{R})$ and $\varphi_2(\vec{r}_2;\vec{R})$ be the molecular wave functions of the inner electron when it is dominantly localized around the cores A^+ and B^+, respectively. For $R \to \infty$ these functions go over into the corresponding atomic wave functions $\phi_A(\vec{r}_2)$ and $\phi_B(\vec{r}_{2b})$. The adiabatic molecular wave functions χ_1 and χ_2 of the ion AB^+ are expressed in terms of φ_1 and φ_2 in the usual way[13]:

$$\chi_1 = a_1\varphi_1 + a_2\varphi_2\,, \quad \chi_2 = -a_2\varphi_1 + a_1\varphi_2\,, \tag{10}$$

$$a_{1,2} = (1/\sqrt{2})[1 \pm \kappa/(\kappa^2 + \Delta^2)^{1/2}]^{1/2}\,, \tag{11a}$$

$$\kappa = |H_{11} - H_{22}|, \quad \Delta = 2|H_{12} - SH_{11}|, \tag{11b}$$

$$H_{ij} = \langle \varphi_i | H_2 | \varphi_j \rangle, \quad S = \langle \varphi_1 | \varphi_2 \rangle, \quad i,j = 1, 2, \tag{11c}$$

and terms of order of $O(S^2)$ in (11a) are neglected. The quantity $\Delta(R)$, defined by (11b), is known as an "exchange interaction" and can be calculated asymptotically exactly.[13] Inserting the wave functions (10) and (11) into Eq. (6b), we obtain asymptotically

$$D(R) = \frac{R}{2} \frac{\Delta}{(\kappa^2 + \Delta^2)^{1/2}} + z_{12}(R) \frac{\kappa}{(\kappa^2 + \Delta^2)^{1/2}}, \quad R \gg 1, \tag{12}$$

$$z_{12}(R) = \langle \varphi_1 | \vec{r}_2 \cdot \hat{\lambda} | \varphi_2 \rangle. \tag{13}$$

For $\kappa \equiv 0$ one obtains $D(R)$ from Eq. (12) for the pure resonant case ($B = A$):

$$D_{\text{res}}(R) = \tfrac{1}{2} R, \quad R \gg 1. \tag{14}$$

The functions χ_1 and χ_2 in this case describe the symmetrical (g) and antisymmetrical (u) low-lying states of the ion A_2^+, whereas $\Delta(R) = \Delta_{\text{res}}(R) \equiv E_u(R) - E_g(R)$ is the energy splitting of these states. The resonant ionization process in this case occurs only for $R \leqslant R_{\text{on}}$, where R_{on} is defined by the equation $\Delta_{\text{res}}(R_{\text{on}}) = |\epsilon_n|$, ϵ_n being the binding energy of the Rydberg electron. For $R \gg R_{\text{on}}$ resonant transitions occur only in the discrete spectrum.[9] Explicit expressions for $\Delta(R)$ are published elsewhere.[13] Using the above expression for $D_{\text{res}}(R)$ in Eq. (9), one has

$$W_{\text{res}}(R) = R^2 / 3\sqrt{3} n^5, \quad R \leqslant R_{\text{on}}. \tag{15}$$

If κ is not identically equal to zero ($B \neq A$), both terms in Eq. (12) should be retained. However, for small values of κ (near- or quasiresonance) and owing to the strong exponential dependence[13] of $\Delta(R)$, there exists a narrow region ($R_c + \delta R$, $R_c - \delta R$), with $\delta R \ll R_c$, such that when $R > R_c + \delta R$, $\kappa \gg \Delta$, and when $R < R_c - \delta R$, $\Delta \gg \kappa$. In the small region δR around R_c the character of the electronic wave functions changes drastically; i.e., a Demkov's nonadiabatic coupling of the states takes place. The critical internuclear distance R_c is determined by the equation $\Delta(R_c) = \kappa$. Bearing this in mind, we can represent $D(R)$ in the form

$$D(R) = \begin{cases} \tfrac{1}{2} R, & R \leqslant R_c, \quad \text{(16a)} \\ z_{12}(R), & R \geqslant R_c. \quad \text{(16b)} \end{cases}$$

The corresponding transition probability for $\kappa(\infty) = I_A - I_B > |\epsilon_n|$ has the form

$$W(R) = (4/3\sqrt{3} n^5) \times \begin{cases} \tfrac{1}{4} R^2, & R \leqslant R_c, \quad \text{(17a)} \\ z_{12}^2, & R \geqslant R_c. \quad \text{(17b)} \end{cases}$$

Since for values of κ not too large the critical distance R_c has a large value, one can neglect the contribution to $W(R)$ from the region $R > R_c$ as being exponentially small $[z_{12} \sim R^2 \Delta(R)]$. Therefore the transition probability for this case is dominantly determined by Eq. (17a). In writing expressions (17) for $W(R)$ we assume that in the region of interest the exchange interaction terms at adiabatic energies prevail over the multipole ones. In the case where $\kappa(\infty) < |\epsilon_n|$ and $\kappa(R)$ increases with decreasing R, the ionization process is energetically inaccessible until the distance R_n, at which $\omega(R_n) = |\epsilon_n|$, is reached. In this case the transition probability is again given by expression (17a), where the critical distance should be taken as $\min(R_c, R_n)$.

B. Strongly nonresonant case: $I_A - I_B \simeq I_A, I_B$

In the case of asymmetrical systems with a large resonance defect $\kappa(\infty)$, two limiting situations can be distinguished: (a) the first excitation level $E_{\text{ex},A}^{(1)}$ of atom A lies well above the ground-state level of atom B (so that $I_A - E_{\text{ex},A}^{(1)} \ll I_B$) and (b) there exists a low-lying excitation level (or a group of energetically close levels) $E_{\text{ex},A}$ in atom A such that its binding energy is close to the ionization potential of atom B ($I_A - E_{\text{ex},A} \approx I_B$). The first case has been considered by Zhdanov and Chibisov.[10] The characteristic feature of this case is that the hybridization of the states describing the localized electronic motion is energetically inappropriate. In this way one has $\chi_1 \simeq \varphi_1$ and $\chi_2 \simeq \varphi_2$, where φ_1 is close to ϕ_A. The dipole matrix element $D(R)$ in this case becomes

$$D(R) = \langle \phi_A | \vec{r}_2 \cdot \hat{\lambda} | \varphi_1 \rangle \equiv z_{12}^{(0)}, \tag{18}$$

where $z_{12}^{(0)}$ is calculated in Ref. 10. The transition probability $W^{(0)}(R)$ for this case consequently is given by

$$W^{(0)}(R) = (4/3\sqrt{3} n^5)(z_{12}^{(0)})^2. \tag{19}$$

Since $z_{12}^{(0)}$ exponentially decreases with increasing R, the decay rate (18) acquires considerable values only for relatively small R, i.e., when the perturbing atom is deeply inside the orbit of the Rydberg electron. Note that the result $D(R) \simeq z_{12}^{(0)}$ can be formally obtained from the expression (12) for $D(R)$, assuming that $\kappa \gg \Delta(R)$ in the whole region of R and replacing φ_1 by ϕ_A.

Let us consider now case (b), i.e., when there exists in the atom A an excited state (or a group of energetically close excited states) which has a binding energy ϵ_1 close to I_B, or more precisely,

$\tilde{\kappa}_1(\infty) \equiv |\epsilon_1 - I_B| \ll \kappa(\infty)$. We denote this state by $\tilde{A}$ and assume that it is just the first excited state of atom A. We introduce a function $\tilde{\varphi}_1$, analogous to the functions φ_1 and φ_2, which describes the electronic motion when the electron is dominantly localized in $\tilde{A}$. For $R \to \infty$ the wave function $\tilde{\varphi}_1$ tends to the atomic excited-state wave function $\tilde{\phi}_A$. (In the case of a group of energetically close excited states, $\tilde{\phi}_A$ represents a linear combination of the wave functions of these states.) Owing to the condition $\tilde{\kappa}_1(\infty) \ll \kappa(\infty)$ for the molecular wave function χ_1, as in case (a),

$$\chi_1 \simeq \varphi_1 \simeq \phi_A \, . \qquad (20)$$

This wave function correlates asymptotically to the configuration $A + B^+$. By χ_1 and χ_2 we denote the adiabatic molecular wave functions which correlate asymptotically to the configurations $A + B^+$ and $A^+ + B$, respectively. As in the quasiresonance case, χ_1 and χ_2 are expressed in terms of $\tilde{\varphi}_1$ and φ_2 by the linear combinations

$$\chi_1 = b_1 \tilde{\varphi}_1 + b_2 \varphi_2 \, , \quad \chi_2 = - b_2 \tilde{\varphi}_1 + b_1 \varphi_2 \, , \qquad (21)$$

where the coefficients $b_{1,2}$ are given by the same expressions (11a), in which, however, $\kappa(R)$ and $\Delta(R)$ should be replaced by $\tilde{\kappa}_1(R)$ and $\tilde{\Delta}_1(R)$ defined by (11b) and (11c) with the functions $\tilde{\varphi}_1$ and φ_2. In constructing the functions (21) we have taken into account the orthogonality of $\tilde{\chi}_1$ and χ_2 with respect to χ_1, which in the present case reduces to $\langle \tilde{\varphi}_1 | \phi_A \rangle \simeq 0$ and excludes the hybridization of φ_2 and ϕ_A.

Hereafter it is convenient to distinguish between three cases: (a) $\epsilon_1 < I_B$, (b) $\epsilon_1 > I_B$, $\tilde{\kappa}_1(R) \geqslant |\epsilon_n|$, and (c) $\epsilon_1 > I_B$, $\tilde{\kappa}_1(R) < |\epsilon_n|$. In case (a) the direct transitions $\chi_2 \to \tilde{\chi}_1$ lead not to ionization of the Rydberg electron, but rather to its deexcitation. Therefore, from the point of view of the resonant ionization, only the $\chi_2 \to \chi_1$ transitions should be considered. The corresponding dipole matrix element is given by

$$D_a(R) = - b_2 \tilde{z}_A(R) + b_1 z_{12}^{(0)}(R) \, , \qquad (22)$$

where $\tilde{z}_A = \langle \phi_A | \vec{r}_2 \cdot \hat{\lambda} | \tilde{\varphi}_1 \rangle$ and $z_{12}^{(0)}$ is defined by Eq. (18). For large values of R, $\tilde{z}_A$ is close to the value of the matrix element $z_{A\tilde{A}}$ for the atomic $A \to \tilde{A}$ transition. We see from Eq. (22) that, contrary to the strongly nonresonant case (b), where $D(R)$ is determined only by the "direct" transition term $z_{12}^{(0)}$, in the present case a new, "exchange-induced" transition term appears, as the result of the electron-density-delocalization effects in the quasiresonant condition. As we shall see below, the "exchange-induced" decay channel is the dominant one when $\tilde{\kappa}_1(\infty)$ is sufficiently small.

In case (b) [$\epsilon_1 > I_B$ and $\tilde{\kappa}_1(R) \geqslant |\epsilon_n|$] the transition $\chi_2 \to \tilde{\chi}_1$ is possible and is much more favored than the $\chi_2 \to \chi_1$ transition. The dipole matrix element for the $\chi_2 \to \tilde{\chi}_1$ transition is analogous to that of the already investigated quasiresonant case [see Eq. (12)], namely,

$$D_b(R) = \frac{R}{2} \frac{\tilde{\Delta}_1}{(\tilde{\kappa}_1^2 + \tilde{\Delta}_1^2)^{1/2}} + \tilde{z}_{12}(R) \frac{\tilde{\kappa}_1}{(\tilde{\kappa}_1^2 + \tilde{\Delta}_1^2)^{1/2}} \, , \qquad (23)$$

where $\tilde{z}_{12} = \langle \tilde{\varphi}_1 | \vec{r}_2 \cdot \hat{\lambda} | \varphi_2 \rangle$. The excited state created, $\tilde{\chi}_1$, which asymptotically goes over into the atomic excited state $\tilde{\phi}_A$, can decay radiatively (if the corresponding transition is allowed); i.e., this resonant ionization channel of the Rydberg electron can be identified by monitoring the radiation from the decay $\tilde{A} \to A + h\nu$.

In case (c) [$\tilde{\kappa}_1(R) < |\epsilon_n|, \epsilon_1 > I_B$] the transition $\chi_2 \to \tilde{\chi}_1$ leads only to resonant excitation of the Rydberg electron into a state $\tilde{\chi}_2$, which correlates asymptotically with the configuration $\tilde{A} + \tilde{B}$ [$\tilde{B}$ represents an excited state of the atom B with a binding energy of $\epsilon_{2B} = \epsilon_n - \tilde{\kappa}_1(\infty)$]. However, the doubly excited state created in this way relaxes via the resonant transition $(\chi_1, \tilde{B}) \to (\chi_1, B^+ + e)$. The dipole matrix element for the $\tilde{\chi}_1 \to \chi_1$ transition in this case is given by

$$D_c(R) = b_1 \tilde{z}_A(R) + b_2 z_{12}^{(0)} \, , \quad R \leqslant R_1 \, , \qquad (24)$$

where R_1 is the characteristic distance for the $\chi_2 \to \tilde{\chi}_1$ transition and $\tilde{z}_A$, $z_{12}^{(0)}$ have already been defined. If we designate by p_1 the probability for the $\chi_2 \to \tilde{\chi}_1$ transition, then during the collision the system will stay on the state χ_2 with a probability $1 - p_1$ until it eventually reaches the distance R_{n1} ($< R_1$), at which $\tilde{\kappa}_1(R_{n1}) = |\epsilon_n|$. In the region $R < R_{n1}$, $\tilde{\kappa}_1(R)$ becomes larger than $|\epsilon_n|$, so that the transition $\chi_2 \to \tilde{\chi}_1$ again leads directly to ionization, and the corresponding dipole matrix element is given by Eq. (23).

The characteristic distance R_1 is defined by the equation $\tilde{\Delta}_1(R_1) = \tilde{\kappa}_1(R_1)$. When $R < R_1$, $\tilde{\Delta}_1(R) \gg \tilde{\kappa}_1$, and when $R > R_1$, $\tilde{\kappa}_1 \gg \tilde{\Delta}_1(R)$. Bearing this in mind and using the explicit expressions for the coefficients b_1 and b_2, we see that the transition probabilities $W_\alpha(R)$ for the three cases discussed above have the form

$$W_\alpha(R) = (4/3\sqrt{3}\, n^5) D_\alpha^2(R) p_\alpha \, , \quad \alpha = a, b, c \, , \qquad (25)$$

where

$$D_a^2(R) = \begin{cases} \frac{1}{2} \tilde{z}_A^2 [1 - (2 z_{12}^{(0)} / \tilde{z}_A) + (z_{12}^{(0)} / \tilde{z}_A)^2], & R \leqslant R_1 \, , \qquad (26a) \\ (z_{12}^{(0)})^2, & R \geqslant R_1 \, , \qquad (26b) \end{cases}$$

$$D_b^2(R) = \begin{cases} \frac{1}{4} R^2, & R \leqslant R_1 \, , \qquad (27a) \\ \tilde{z}_{12}^2, & R \geqslant R_1 \, , \qquad (27b) \end{cases}$$

$$D_c^2(R)=\begin{cases}\frac{1}{4}R^2, \quad R\leqslant R_{1n}(<R_1), & (28a)\\ \frac{1}{2}\tilde{z}_A^2[1+(2z_{12}^{(0)}/\tilde{z}_A) \\ \qquad +(z_{12}^{(0)}/\tilde{z}_A)^2], \quad R\leqslant R_1, & (28b)\\ 0, \quad R>R_1, & (28c)\end{cases}$$

and

$$p_a=p_b=1\,,$$

$$p_c=\begin{cases}1-p_1, \quad R\leqslant R_{1n}(<R_1),\\ p_1, \quad R\leqslant R_1\,.\end{cases}$$

The probability p_1 defines the nonadiabatic $\chi_2\rightarrow\chi_1$ transition due to the raidal Demkov-type coupling, and its expression is given elsewhere.[13] Since for small $\tilde{\kappa}_1$ the critical distance R_1 is large and since the matrix elements z_{12} and $z_{12}^{(0)}$ are exponentially small for large R, the main contribution to $W(R)$ in all three cases comes from the region $R\leqslant R_1$. In this region either a symmetric-resonance-type ($D\simeq\frac{1}{2}R$) or an electron exchange-induced atomiclike ($D\simeq\tilde{z}_A$) transition dominates the resonant ionization probability. Both of the above-mentioned transitions are strong and provide a very efficient resonant ejection of the Rydberg electron into the continuum.

In order to complete our analysis of the electron transition probability in the ionization reaction (1), we give now the explicit expressions for the matrix elements $z_{12}^{(0)}$ and z_{12} (and $\tilde{z}_{12}$). Since in this paper we are considering only Σ states of the inner subsystem AB^+, the corresponding expressions for $z_{12}^{(0)}$ and z_{12} have somewhat simpler forms.

The matrix element $z_{12}^{(0)}$ has the form[10]

$$z_{12}^{(0)}(R)=C^{(0)}R^{2/\gamma_B-1}e^{-\gamma_B R}\,, \tag{29}$$

$$C^{(0)}=N_B(2l_B+1)^{1/2}(2\gamma_B/e)^{1/\gamma_B}(1+\gamma_B)^{-5} \times[(1-\gamma_B)/(1+\gamma_B)]^{1/\gamma_B-2}\Gamma(1-1/\gamma_B)\,, \tag{30}$$

where $\frac{1}{2}\gamma_B^2=I_B$, l_B is the angular momentum quantum number of the electron in atom B, and N_B is a "normalization" constant in the asymptotic form of the atomic wave function ϕ_B. The matrix element z_{12} can be calculated easily, since the expressions for the functions φ_1 and φ_2 are known.[13] The result is

$$z_{12}(R)=C(\tfrac{1}{2}R)^{1/\gamma_A+1/\gamma_B+1}e^{-(\gamma_A+\gamma_B)R/2}\,, \tag{31}$$

$$C=N_AN_B[(2l_A+1)(2l_B+1)]^{1/2}(4/e)^{(1/\gamma_A+1/\gamma_B)/2} \times\frac{\Gamma(1-1/\gamma_A+1/\gamma_B)\Gamma(2+1/\gamma_A-1/\gamma_B)}{(\gamma_A+\gamma_B)}\,, \tag{32}$$

where the quantities γ_A, l_A, and N_A have the same meaning as γ_B, l_B, and N_B, but refer to the atomic state ϕ_A. The expression for $\tilde{z}_{12}(R)$ is of the same form as (31) and (32), the only difference being that the parameters of the wave function ϕ_A should be replaced by those of the excited-state wave function $\tilde{\phi}_A$. The expressions for $\Delta(R)$ and $\tilde{\Delta}_1(R)$ are given elsewhere.[13]

IV. IONIZATION PROBABILITY AND CROSS SECTION CALCULATIONS

Within the classical trajectory description of nuclear motion the ionization probability $P_n(\rho, v)$ for a given impact parameter ρ and Rydberg state n is given by[13]

$$P_n(\rho, v)=1-\exp[-J_n(\rho, v)]\,, \tag{33}$$

$$J_n(\rho, v)=\frac{2}{v}\int_{R_m}^{\infty}\frac{qW(R)\,dR}{[1-\rho^2/R^2-U_2(R)/E]^{1/2}}\,, \tag{34}$$

where $U_2(R)$ is the upper-molecular-state energy, $E=\frac{1}{2}\mu v^2$ is the kinetic energy of collision, R_m is the distance of closest approach, and $q=\frac{1}{2}$ and 1 for the symmetrical (resonance) and the asymmetrical systems, respectively. When calculating the integral $J_n(\rho, v)$, one should take the limits in accordance with the validity region of the particular expression for the $W(R)$ under consideration. In addition, the collision energy E must be such that R_m satisfies the condition $R_m<R_s$, where R_s is the upper limit of the integral $J_n(\rho, v)$(i.e., satisfies the threshold condition for ionization).

In the case of symmetrical systems the energy $U_2(R)$ of the decaying molecular state χ_2 for large R can be taken in the form

$$U_2(R)=\tfrac{1}{2}\,|\Delta_{\text{res}}(R)|-\alpha/2R^4\,, \tag{35}$$

where α is the polarizability of the ground-state atom. In the case of asymmetrical systems, $U_2(R)$ must be obtained by molecular-structure calculations.

Having determined $P_n(\rho, v)$, we see that the ionization cross section is given by

$$\sigma_n=2\pi\int_0^{\infty}P_n(\rho, v)\rho\,d\rho\,. \tag{36}$$

We now calculate P_n and σ_n for some specific ionization processes.

A. $H^*(n)+H\rightarrow H+H^++e$ and $Li^*(n)+Li\rightarrow Li+Li^++e$ reactions

By using Eqs. (33)–(35) and (15), we have calculated the ionization probability $P_n(\rho,v)$ for the $H^*(n)+H$ and $Li^*(n)+Li$ colliding systems at $E=0.3$ eV and for $n=10$, 15, 20, and 25. The results of the calculations are given in Fig. 1. We can see from Fig. 1 that up to some impact parameter ρ_n^* the ionization probability is almost constant and afterward it rapidly decreases to zero. The impact parameter ρ_n at which $P_n(\rho_n)=0$ corresponds to the critical internuclear dis-

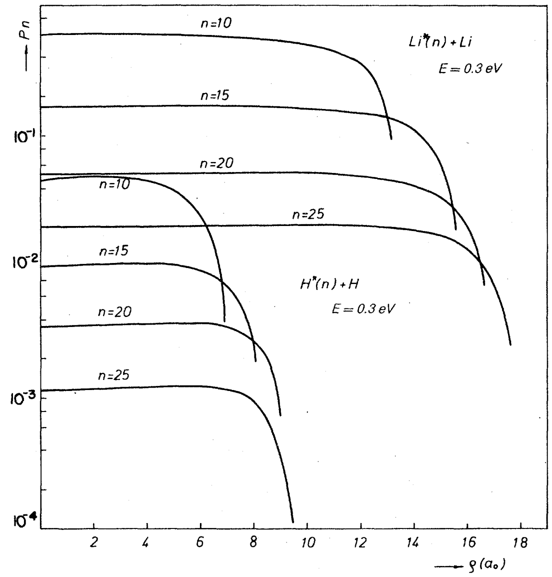

FIG. 1. Probability for $H^*(n)+H\rightarrow H+H^+ + e$ and $Li^*(n)+Li\rightarrow Li+Li^+ + e$ reactions ($n=10$, 15, 20, and 25) at $E=0.3$ eV.

tance R_n at which the ionization becomes energetically possible. In order to understand the behavior of the function $P_n(\rho)$, we approximate the classical trajectory of the particle moving in the potential $U_2(R)$ by a parabola. Then integral (34) can be calculated in the following form:

$$J_n(\rho, v)=\frac{2R_m^2}{3\sqrt{3}\,n^5 v}\left(\frac{R_n-R_m}{R_m^2-\rho^2+2\rho^2/R_m}\right)^{1/2} \times\left[1+\frac{2}{3}\frac{R_n-R_m}{R_m}+\frac{1}{5}\left(\frac{R_n-R_m}{R_m}\right)^2\right], \qquad (37)$$

where R_n and R_m are determined by the equations $\Delta(R_n)=|\epsilon_n|$ and $U_2(R_m)=E(1-\rho^2/R_m^2)$, respectively.

The parabolic trajectory approximation (37) for the ionization probability is justified for energies not too high, such that $R_n-R_m \lesssim R_m$. Further, if v and n are such that $\exp[-J_n(\rho, v)]$ can be represented well by the first two terms of its power-series expansion, then $P_n(\rho, v)$ is simply given by $J_n(\rho, v)$. All curves in Fig. 1 [except that for the Li* ($n=10$) + Li case] are reproduced by the expression $P_n(\rho, v)\simeq J_n(\rho, v)$ to within a 10% accuracy, with the excpetion of the region of very small ρ (for $\rho=0$ the error is about 30%). The critical impact parameter ρ_n at which P_n equals zero is given in the parabolic trajectory approximation by

$$\rho_n \simeq R_n[1-|\epsilon_n|/2E-V_p(R_n)/E]^{1/2}, \qquad (38)$$

where $V_p(R)$ is the polarization (or, generally, the long-range) interaction in the subsystem AB^+.

As seen from the expression (37) for $J_n(\rho, v)$, the ρ dependence of $J_n(\rho, v)\simeq P_n(\rho, v)$ in the region $\rho \lesssim \rho_n^* \simeq 2^{-1/2}\rho_n$ is fairly weak, since ρ never reaches R_m, and R_m depends logarithmically on ρ. In physical terms, the almost constant value of $P_n(\rho, v)$ for $\rho \lesssim \rho_n^*$ is the result of the mutual compensation of the following two effects: with decreasing ρ the mean collision path does not increase considerably in the reaction zone ($R \lesssim R_n$) due to the repulsive interaction $U_2(R)$ acting between the particles, but at the same time the mean value of the square of the dipole moment does not decrease either. Note that the expression (37) for $J_n(\rho, v)$ may also be used for the asymmetrical systems in the regions where $D(R)$ is given by $\frac{1}{2}R$.

The cross sections σ_n of the $H^*(n)+H\rightarrow H+H^+ + e$ and $Li^*(n)+Li\rightarrow Li+Li^+ + e$ reactions ($n=10$, 15, 20, and 25), calculated by using Eq. (36), are given in Fig. 2. In the low-energy region the cross sections rapidly increase with energy and beyond a fairly broad maximum they decrease approximately as $E^{-1/2}$ with increasing energy. In the high-energy region, where $P_n(\rho, v)\simeq J_n(\rho, v)$, the n dependence of σ_n is given by $\sigma_n \simeq n^{-5}$. As seen in Fig. 2, in the low-energy region this behavior breaks down, and σ_n may become larger than σ_{n-1}. Therefore, for sufficiently low energies (e.g., in the thermal region), σ_n as a function of n would have a maximum at some n^* defined by $J_{n^*}(\rho_n^*, v)\simeq 1$.

B. $H^*(n)+Li\rightarrow H+Li^+ + e$ reaction

In the case of the $H^*(n)+Li\rightarrow H+Li^+ + e$ reaction the $n=2$ hydrogenic energy level for $\tilde{\kappa}_1(\infty)$

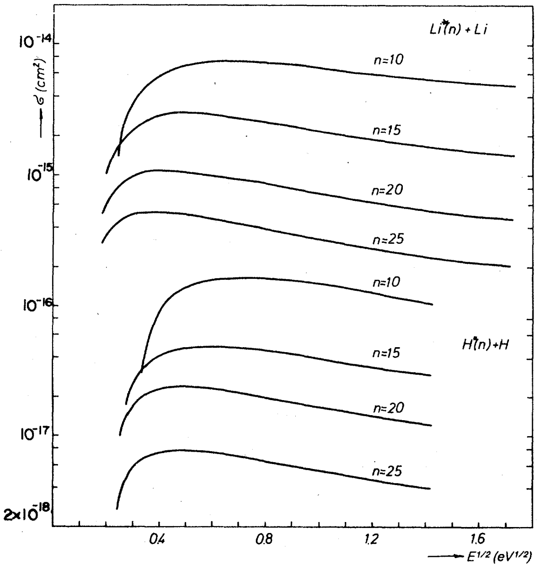

FIG. 2. Cross sections for $H^*(n)+H\rightarrow H+H^+ + e$ and $Li^*(n)+Li\rightarrow Li+Li^+ + e$ reactions ($n=10$, 15, 20, and 25).

$=2.0$ eV lies above the ground-state lithium level, whereas the ground states of these two atoms are energetically separated by $\kappa(\infty)=8.17$ eV. The transition probability in this case is thus given by Eq. (25) and by one of the expressions (26)–(28). For $n>10$ the corresponding dipole matrix element is D_a, as given by Eq. (26).

We have calculated the ionization probability for this reaction for $n=10$, 15, 20, and 25 at $E=0.3$ eV, and the results are presented in Fig. 3. In these calculations the potential-energy curve $U_2(R)$ was first calculated in the linear-combination-of-atomic-orbitals approximation by substituting for $\tilde{\phi}_A$ and ϕ_B linear combinations of the wave functions of the $2s$ and $2p$ states of H $(n=2)$ and Li atoms. The wave function of the Li $2p$ state has been included in ϕ_B in order to describe correctly the long-range polarization part of the $U_2(R)$ potential. The matrix elements $\tilde{z}_A$ and $z_{12}^{(0)}$ have, however, been calculated only with the $2s$ wave function of Li. Expression (29) has been used for $z_{12}^{(0)}$. The matrix element $\tilde{z}_A$ has been approximated by $\xi z_{2p,1s}(\mathrm{H})$, where the factor ξ is the statistical weight of the $2p$ hydrogen state.

The shape of the ionization probability $P_n(\rho,v)$ as a function of ρ is dominantly determined by the polarization part of the $U_2(R)$ potential. Up to $\rho=\rho_p$, where ρ_p is the radius of the polarization capture $[\rho_p=(2\alpha_B/E)^{1/4}]$, the ionization probability may be considered constant. Its value is given approximately by $\overline{P}_n=P_n(0,v)$. In the low-energy region, where the inequality $U_2(R)\gg E$ is satisfied, $\overline{P}_n$ is given by

$$\overline{P}_n \simeq (4\xi z_{A\tilde{A}}^2 R_1^3/9\sqrt{3}\,n^5)(\mu/\alpha_B)^{1/2}\,, \tag{39}$$

where μ is the reduced mass of the colliding particles and α_B is the polarizability of the lithium atom. In this energy region the cross section σ_n can be represented in the form

$$\sigma_n \simeq \pi\rho_p^2\overline{P}_n \simeq 8\pi z_{A\tilde{A}}^2 R_1^3/9\sqrt{3}\,n^5 v\,. \tag{40}$$

In Fig. 4 the cross sections σ_n $(n=10$, 15, 20, and 25) for the reaction $\mathrm{H}^*(n)+\mathrm{Li}\rightarrow\mathrm{H}+\mathrm{Li}^++e$, calculated for the energy range from 0.01 to ≈2 eV, are presented. They all have an approximate $E^{-1/2}$ behavior in the energy range under consideration, which indicates the validity of the polarization capture approximation in this energy range.

V. CONCLUDING REMARKS

In the present paper we have considered the process of ionization in the slow collisions of Rydberg atoms with ground-state atoms. A resonant energy exchange within the electronic part of the system is assumed to be responsible for the ionization process. This assumption is justified for $v\ll n^{-1}$. The basic approximation made in our collision model is the neglect of the higher-order transitions. For example, the resonant ionization in the symmetrical systems can, in principle, occur in two steps, starting from the ground Σ_g state of the AB^+ subsystem: a $\Sigma_g\rightarrow\Sigma_u$ transition at large distances may lead to a resonant deexci-

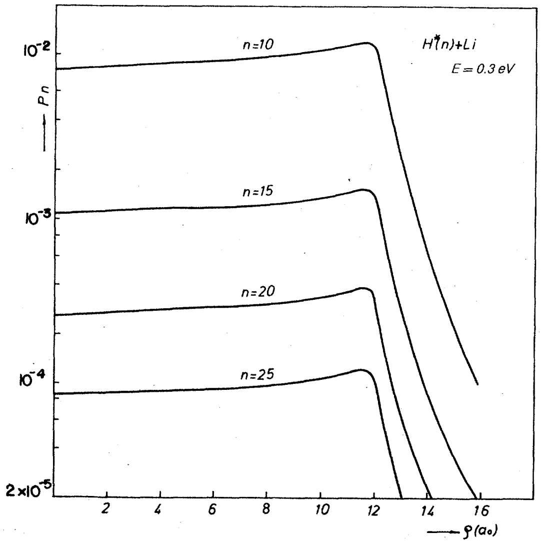

FIG. 3. Probability for $\mathrm{H}^*(n)+\mathrm{Li}\rightarrow\mathrm{H}+\mathrm{Li}^++e$ reaction $(n=10$, 15, 20, and 25) at $E=0.3$ eV.

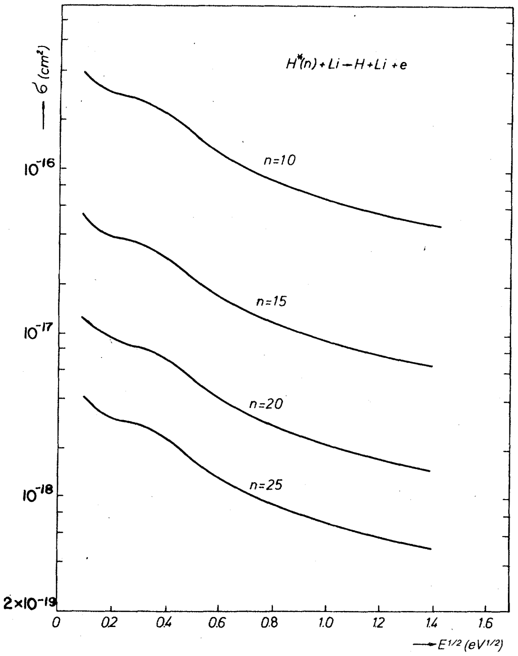

FIG. 4. Cross sections for $\mathrm{H}^*(n)+\mathrm{Li}\rightarrow\mathrm{H}+\mathrm{Li}^++e$ reaction $(n=10$, 15, 20, and 25).

tation of the Rydberg electron; however, a second reverse $\Sigma_u \rightarrow \Sigma_g$ transition in the later stage of the collision may lead to ejection of the Rydberg electron into the continuum. Such second-order (or higher) processes have been neglected in our treatment. In other words, the resonant ionization model investigated in the present paper introduces from the beginning the "decay approximation."[9] Another approximation, introduced in Sec. II to help derive explicit expressions for the transition probability $W(R)$, is the Kramers approximation for the photoionization cross section. This approximation, however, can always be removed if necessary (e.g., for values of n not too large).

In the real $A^*(n)+B$ collisions, besides the reaction (1) there may occur also the ion-pair formation $A^*+B \rightarrow A^+ + B^-$ and the associative ionization $A^*+B \rightarrow AB^+ + e$ reactions. The ion-pair formation process is possible (if B^- can exist at all) if the potential-energy curve of the covalent configuration $A^*(n)+B$ has a crossing (pseudocrossing) with the Coulomb potential of the ionic configuration at a not too large internuclear distance, at which the corresponding nonadiabatic coupling can still effectively cause transitions. For Rydberg states with $n \geq n_0 + 4$, where n_0 is the principal quantum number of the ground-state parent atom, this possibility is excluded. The associative ionization channel is, however, very probable. Its description requires an accurate quantum-mechanical treatment of nuclear motion. The simplest way to do this is to multiply the transition probability $W(R)$ by the corresponding Franck-Condon factor. Since high vibrational states are expected to be dominantly populated in the resonant associative ionization, one can use the quasiclassical approximation in treating the nuclear motion. This will be done in a future paper.[14]

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