PHYSICAL REVIEW A VOLUME 20, NUMBER 5 NOVEMBER 1979

Excitation and deexcitation processes in slow collisions of Rydberg atoms with ground-state parent atoms

R. K. Janev and A. A. Mihajlov
Institute of Physics, P. O. Box 57, 11001 Belgrade, Yugoslavia

(Received 8 March 1979; revised manuscript received 26 July 1979)

The excitation and deexcitation processes in slow collisions of highly excited (Rydberg) atoms with ground-state parent atoms are considered. A mechanism, based on the quasiresonant energy transfer within the electronic part of the colliding system, is proposed for these processes. Both direct and exchange reaction channels are included into the treatment. Expressions for the $n \rightarrow n'$ transition probabilities are obtained in closed form. Probability and cross section calculations for some transitions and level decays in the $H^*(n)$-H system are presented.

I. INTRODUCTION

The inelastic processes of highly excited (Rydberg) atoms with ground-state neutral particles (atoms and molecules) have recently received great attention in connection with their important role in various nonthermal and nonstationary laboratory and astrophysical plasmas.[1-3] The study of these processes has been particularly stimulated in the last several years by research in the field of laser isotope separation[4] as well as the development of the neutral injection method for additional heating (and refueling) of thermonuclear fusion plasmas in mirror devices.[5]

Accurate experimental investigations of the inelastic collisions between Rydberg atoms and ground-state neutral particles have become possible because of the development of several efficient and reliable methods for production and detection of highly excited atoms in strictly determined quantum states. The results of the experimental studies of these collisions have been recently reviewed by Stebbings.[2] We note that most of these data are related to the process of collisional depopulation and ionization of Rydberg atoms.

Most of the theoretical studies of atom (molecule)–Rydberg-atom inelastic collisions generally follow two main approaches. One of them is based on Fermi's model,[6] in which the inelastic effects in the colliding system are described in terms of the scattering parameters of the weakly bound (Rydberg) electron on the ground-state atom. Within this approach the neutral (perturbing) particle is treated as a short-range (δ-function) potential and the Rydberg electron is considered to be quasifree.[7-9]

The other theoretical approach to the inelastic collision process of Rydberg atoms is based on the semiclassical approximation.[3,11,12] The inelastic transition within this approximation results from the energy and momentum transfer from the perturbing atom to the Rydberg electron.

One can show that both the Fermi pseudopotential approach and the semiclassical approximation provide appreciable cross sections for inelastic processes involving a considerable change of Rydberg-electron binding energy only for collision velocities v which are close to the classical velocity v_n of the Rydberg electron.[10,12,13] However, for $v \ll v_n$, neither the Fermi electron scattering mechanism nor the classical atom-to-Rydberg electron momentum transfer mechanism can produce inelastic cross sections which exceed the cross section for the elastic electron scattering on the perturbing atom.[12,13] (We note however that for the sublevel mixing processes the Fermi mechanism provides cross sections of the order of the geometrical atom–Rydberg-atom cross section.[8,14])

In order to complete the presentation of the existing methods for calculating inelastic processes in atom-Rydberg-atom collisions, we should mention here also the quantum-mechanical two-state close-coupling calculations of Olson[15] on the l-mixing depopulation of $\mathrm{Na}(n^2D)$ by rare-gas atoms and the calculations of the n-changing processes in the field of an oscillating dipole[16] (n and l are the principal and angular momentum quantum numbers of the Rydberg electron).

In all of the above-mentioned theoretical methods for treating the atom (molecule)–Rydberg-atom inelastic collisions, the interaction of the loosely bound electron with the perturbing atom (molecule) is considered to be dominant in the system and responsible for the inelastic transitions. In the present paper we consider the opposite situation, in which the dominant interaction in the system is that between the perturbing ground-state atom and the ionic core of the Rydberg atom. This situation occurs at low collision velocities $v \ll v_n$ and for impact parameters much smaller than the characteristic dimension of the Rydberg atom.

Thus during the effective time of the collision the perturbing atom and the ionic core of the Rydberg atom may be considered a quasimolecular system lying inside the orbit of the loosely bound electron. The Rydberg electron interacts with this quasimolecular ion as with a whole. For such collisions of Rydberg atoms with neutral particles we propose a new mechanism of inelastic electron transitions in the system. This mechanism is based on the quasiresonant energy exchange within the electronic part of the colliding system, thus providing large cross sections. Although this mechanism of internal energy conversion is operative for a large class of inelastic processes occurring in the slow collisions of Rydberg atoms with composite neutral particles, in the present paper we confine ourselves to the excitation and deexcitation processes in symmetrical systems (n-changing collisions). The process of ionization and the inelastic processes in asymmetrical systems will be considered elsewhere.

In Sec. II we qualitatively formulate the quasiresonant internal energy conversion mechanism for inelastic processes in slow-atom–Rydberg-atom collisions. In Sec. III we give a quantum-mechanical formulation of the problem of excitation and deexcitation processes in symmetrical-atom–Rydberg-atom systems. In Sec. IV we introduce a "decay approximation" which enables us to obtain a formal solution of the coupled differential equations for the problem. In Sec. V expressions for the transition probabilities are derived in closed form. Probability and cross-section calculations for the excitation and deexcitation processes in the hydrogenic case are presented in Sec. VI. Finally, in Sec. VII some concluding remarks are given.

Atomic units ($m_e = \hbar = e^2 = 1$) will be used throughout this work, unless otherwise indicated.

II. QUASIRESONANT INTERNAL ENERGY CONVERSION MECHANISM FOR INELASTIC PROCESSES IN SLOW-ATOM-RYDBERG-ATOM COLLISIONS

In order to demonstrate the main features of the quasiresonant internal-energy conversion mechanism, let us consider processes of the following type:

$$A^*(\tilde{n}) + A \to A^*(\tilde{n}') + A\ , \qquad (1)$$

$$\to A + A^*(\tilde{n}')\ , \qquad (2)$$

where A and $A^*(\tilde{n}')$ are the ground state and the Rydberg atom [in the quantum state $\tilde{n} \equiv (n, l, m)$], respectively. For $\tilde{n}' \neq \tilde{n}$ channel (1) describes the direct inelastic processes, whereas channel (2) describes processes involving an excitation transfer. For $\tilde{n}' = \tilde{n}$ channels (1) and (2) describe the elastic scattering and the resonant excitation transfer, respectively. We consider processes (1) and (2) assuming that n is sufficiently high ($n \gg 1$, $v_n \sim 1/n \ll 1$), so that the energy difference $|\omega_{\tilde{n}\tilde{n}'}| = |\omega_{\tilde{n}'} - \omega_{\tilde{n}}|$ between any two states with $n' \neq n$ is much larger than the sublevel splitting of a given n level. The binding energy $\omega_{\tilde{n}}$ of the Rydberg electron is assumed to be smaller than the electron affinity of atom A. This assumption excludes the possibility that processes (1) and (2) can occur owing to nonadiabatic ionic-covalent coupling transitions. We further assume that the collision time $\tau_c \sim n^2/v$ is much longer than the characteristic time $\tau_t \sim n^3/|\Delta n|$ ($\Delta n = n' - n \neq 0$) for an inelastic transition, i.e., that the collision has an adiabatic character. Under this condition ($v \ll |\Delta n|/n \sim |\Delta n| v_n$), neither the Fermi mechanism nor any direct energy transfer (from the incident atom to the Rydberg electron) mechanism can produce considerable inelastic transition probabilities. Finally we assume that the collision energy E is much larger than the internal energy changes involved in the inelastic process, so that a classical description of the relative nuclear motion is allowed.

With the above conditions of the atom–Rydberg-atom collision, another approach to the inelastic processes (1) and (2) can be proposed. Owing to the long collision time, for impact parameters $\rho \ll r_{\tilde{n}}$ ($r_{\tilde{n}} \sim n^2$ is the characteristic dimension of the Rydberg atom) the perturbing atom A spends a lot of time deeply within the orbit of the Rydberg electron, forming with the ionic core A^+ of the Rydberg atom a quasimolecular ion $A^+ + A$. The Rydberg electron interacts with the subsystem $A^+ + A$ as with a whole. Owing to this interaction, any transition in the subsystem $A^+ + A$ leading to a change of its electronic energy will induce an inelastic transition of the Rydberg electron. This energy exchange process within the electronic part of the atom–Rydberg-atom system can take place in a resonance manner. In order to simplify mathematical derivations, let us assume that atom A possesses an s-electron outside a closed shell. Given that $r_{\tilde{n}} \sim n^2 \gg 1$ (so that the valence electron of atom A weakly interacts with the Rydberg electron) and that the collision is slow ($v \ll 1/n$), the state of the subsystem $A^+ + A$ can be described as a superposition of the first two low-lying states, Σ_g^+ and Σ_u^+, of the molecular ion A_2^+. The molecular states Σ_g^+ and Σ_u^+ are described by the corresponding adiabatic wave functions Ψ_g and Ψ_u, respectively. The energy separation $\omega(R) = \omega_u(R) - \omega_g(R)$ of these two molecular states is known,[10] and it exponentially decreases with increasing R. The condition for a resonant energy exchange between the Rydberg electron and the inner subsystem $A^+ + A$ is given by

$$\omega(R_{\tilde{n}\tilde{n}'}) = |\omega_{\tilde{n}\tilde{n}'}| , \tag{3}$$

where $\omega_{\tilde{n}\tilde{n}'} = \omega_{\tilde{n}'} - \omega_n$ and $\omega_{\tilde{n}}$ is the energy of the Rydberg state. Owing to the quantum-mechanical character of the process, transitions occur also in a narrow region around the resonance at $R = R_{\tilde{n}\tilde{n}'}$. The transitions $(\tilde{n},g) \rightarrow (\tilde{n}',u)$, $n' < n$ correspond to the deexcitation processes, whereas the transitions $(\tilde{n},u) \rightarrow (\tilde{n}',g)$, $n' > n$ correspond to the excitation processes of the Rydberg atom. (In the latter case, when $\tilde{n}'$ represents a state in the continuum, the transition $\tilde{n} \rightarrow \epsilon_{\tilde{n}'}$ describes an ionization process.) Owing to the exponential behavior of $\omega(R)$ and to $|\omega_{\tilde{n}\tilde{n}'}| \approx |\Delta n|/n^3$ being small for $n \gg 1$, it follows from condition (3) that the resonance energy exchange within the atom–Rydberg-atom system occurs at large internuclear distances $R_{\tilde{n}\tilde{n}'} \gg r_0$, where r_0 is the characteristic dimension of the neutral atom A. This implies that in describing the electronic motion of the quasimolecular subsystem $A^+ + A$ we can use the asymptotic methods of atomic collision theory.[10] Starting again from Eq. (3) and using the exponential dependence of $\omega(R)$, one can see that the region where the quasiresonance condition is satisfied in fairly narrow: $|R - R_{\tilde{n},\tilde{n}'}| \ll R_{\tilde{n}\tilde{n}'}$. Having in mind this discussion and the general assumption $R \sim \rho \ll r_n$, we can define the region of internuclear distances and impact parameters where the quasiresonant energy exchange mechanism is operative by the following inequalities:

$$\gamma R_{\tilde{n}\tilde{n}'} \gg 1 , \tag{4}$$

$$R_{\tilde{n},\tilde{n}'} \ll n[n(l + \tfrac{1}{2})]^{1/2} \equiv \langle r^{-2} \rangle_{nl} , \tag{5}$$

$$|\vec{R} - \vec{\rho}| \ll \rho , \tag{6}$$

where $-\frac{1}{2}\gamma^2$ is the binding energy of the inner s electron and $\langle r^{-2} \rangle_{nl}$ is calculated using the hydrogenlike wave functions.

Condition (5) allows us to use the dipole approximation in describing the interaction of the Rydberg electron with the subsystem $A^+ + A$. In the reaction zone (6) for $\gamma R \gg 1$ the dipole moment occurring because of the coupling of the Σ_g^+ and Σ_u^+ states of A_2^+ molecular ion can be well represented as $\frac{1}{2}R$, and hence has large values. Therefore the induced Rydberg-electron transitions are expected to be very intense. Outside the region (6) the Rydberg electron interacts with atom A, which is weakly perturbed by the field of ion A^+. We assume that for $v \ll v_n$ this interaction is weak and that it does not generate inelastic $\tilde{n} \rightarrow \tilde{n}'$ transitions with $n' \neq n$.

We finally note that the conditions $\gamma R \sim \gamma\rho \gg 1$ and $E \gg |\omega_{\tilde{n}\tilde{n}'}|$ allow us to use a straight-line trajectory description of the nuclear motion.

At this point we would like to add the following remark. Although demonstrated on inelastic processes within the discrete spectrum, the internal energy conversion mechanism may control many other inelastic processes in an atom (molecule)–Rydberg-atom system, including ionization and electron rearrangement processes. The resonance (or internal energy conservation) condition (3) may easily be generalized to include transitions involving changes of the vibrational energy. The restriction to Rydberg levels above the ionic $A^+ + A^-$ configuration, made at the beginning of this section, is also unessential to the mechanism itself. Being operative in the region when the perturbing atom is inside the orbit of the Rydberg electron, this mechanism does not interfere with some other mechanisms which may cause inelastic electron transition in an earlier stage of the collision.

III. QUANTUM-MECHANICAL FORMULATION OF PROBLEM OF INELASTIC TRANSITIONS

A. General considerations

Let us place the center of mass of the Rydberg atom $A^*(\tilde{n})$ in the origin of a fixed coordinate system and take the z axis to be parallel to the vector $\vec{v}$ of the collision velocity and the x axis to be perpendicular to $\vec{v}$ (see Fig. 1). Let us associate the indices a and b with the centers of the Rydberg and the ground-state atoms respectively and designate by $\vec{r}_1$ and $\vec{r}_2$ the position vectors of the Rydberg (outer) and inner electron, respectively (see Fig. 1). The electronic motion in this system is described by the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\vec{r}_1, \vec{r}_2, t) = H\Psi(\vec{r}_1, \vec{r}_2, t) , \tag{7}$$

where the electronic Hamiltonian H parametrically depends on time through $R^2 = \rho^2 + (vt)^2$ and is given by

$$H = H_1 + H_2 + V , \tag{8}$$

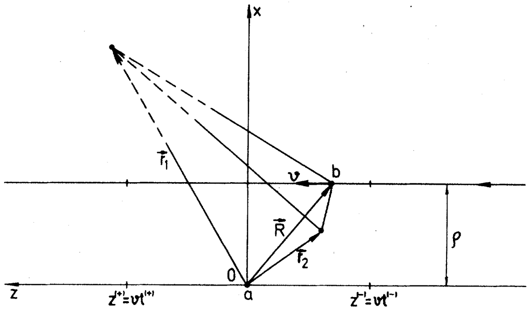

FIG. 1. Geometry of $A^*(n) + A$ collision.

$$H_1=-\tfrac{1}{2}\nabla_1^2-1/r_1,\quad H_2=-\tfrac{1}{2}\nabla_2^2+U_b(r_2)+U_a(|\vec{r}_2-\vec{R}|)\,, \tag{9a}$$

$$V=1/|\vec{r}_1-\vec{r}_2|-1/|\vec{r}_1-\vec{R}|\,. \tag{9b}$$

The potentials $U_{a,b}(r)$ describe the interactions of the inner electron with the corresponding atomic cores and asymptotically behave as $-1/r$.

Let us divide the trajectory into three parts by two points: $t^{(+)}(>0)$ and $t^{(-)}(<0)$, located on the time axis symmetrically with respect to the point $t=0$.

For $t\leqslant t^{(-)}$ the inner electron 2 is dominantly localized around the atomic core b, and the interaction of the Rydberg electron 1 with the atom A is so weak that no inelastic transitions $n\to n'(\neq n)$ can occur. The eventual l transitions within the same n are disregarded in our treatment, since we average the transition amplitude for the $n\to n'$ transition over the l,m quantum numbers. One can expect that this averaging procedure will significantly reduce the errors introduced in the transition amplitude by neglecting the perturbation in the region $t<t^{(-)}$. The function $\Psi(t\leqslant t^{(-)})\equiv\Psi^{(-)}$, which will be determined below, can serve as an initial condition in solving Eq. (7).

For $t\geqslant t^{(+)}$ the inner electron 2 can be dominantly localized either around the atomic core b [in reaction (1)] or around the core a [in reaction (2)]. However, analogous to the previous case, we neglect the perturbations of the Rydberg electron by the potential of the ground-state atom A. The function $\Psi(t\geqslant t^{(+)})\equiv\Psi^{(+)}$ describes the system when all relevant $n\to n'(\neq n)$ transitions are already finished. The determination of the structure of the function $\Psi^{(+)}$ is the subject of our investigation.

In the region $t^{(-)}\leqslant t\leqslant t^{(+)}$, where the inelastic $n\to n'(\neq n)$ transitions effectively take place and where condition (6) is fulfilled, we represent the solution of Eq. (7) in the form

$$\begin{aligned}\Psi=\;&\Psi_g\sum_{\tilde{n}'}a_{\tilde{n}'}^{(g)}\psi_{\tilde{n}'}\exp\{-i[\omega_{\tilde{n}'}t-\tfrac{1}{2}\eta(t)-\tfrac{1}{2}\eta_0]\}\\&+\Psi_u\sum_{\tilde{n}'}a_{\tilde{n}'}^{(u)}\psi_{\tilde{n}'}\exp\{-i[\omega_{\tilde{n}'}t+\tfrac{1}{2}\eta(t)+\tfrac{1}{2}\eta_0]\}\,,\end{aligned} \tag{10}$$

where $\psi_{\tilde{n}}(r_1)$ is the wave function of the Rydberg electron and

$$\eta(t)=\int_0^t\omega(t)dt,\quad \eta_0=\int_{-\infty}^0\omega(t)dt=\int_0^\infty\omega(t)dt\,. \tag{11}$$

In the asymptotic region $\gamma R\gg 1$ the function $\Psi_{g,u}(\vec{r}_2,\vec{R})$ can be represented in the form[10]

$$\Psi_{g,u}=2^{-1/2}(\varphi_b\pm\varphi_a)\,, \tag{12}$$

where $\varphi_{a(b)}(\vec{r}_2,\vec{R})$ is the wave function of the inner electron, dominantly localized on the center $a(b)$ and perturbed by the Coulomb field of the atomic core $b(a)$. For $R\to\infty$ the functions $\varphi_{a,b}(\vec{r}_2,\vec{R})$ go over into the unperturbed atomic wave functions $\varphi_{a,b}^{(0)}(\vec{r}_2)$. We assume that the process of delocalization of the inner electron takes place already at $t=t^{(-)}-\delta t$ (δt is a small positive number), so that the previously defined wave function $\Psi^{(-)}$ has the form

$$\begin{aligned}\Psi^{(-)}=2^{-1/2}&[\Psi_g e^{(i/2)\Delta\eta^{(-)}(t)}+\Psi_u e^{-(i/2)\Delta\eta^{(-)}(t)}]\\&\times\psi_{\tilde{n}}e^{-i\omega_{\tilde{n}}t}\,,\end{aligned} \tag{13}$$

where

$$\Delta\eta^{(-)}(t)=\int_{-\infty}^t\omega(t)dt,\quad t\leqslant t^{(-)}\,. \tag{14}$$

Given that $|\Delta\eta^{(-)}|\ll 1$ (see Appendix A), the continuity condition for the wave function Ψ at $t=t^{(-)}$ gives

$$a_{\tilde{n}'}^{(g,u)}=2^{-1/2}\delta_{\tilde{n}\tilde{n}'},\quad(\delta_{\tilde{n}\tilde{n}'}\equiv\delta_{nn'}\delta_{ll'}\delta_{mm'})\,. \tag{15}$$

Let us now turn to the function $\Psi^{(+)}\equiv\Psi(t\geqslant t^{(+)})$. Since at $t\geqslant t^{(+)}$ the inner electron is dominantly localized on either of the atomic centers, we represent $\Psi^{(+)}$ in the form

$$\Psi^{(+)}=\Psi_{(\mathrm{I})}^{(+)}+\Psi_{(\mathrm{II})}^{(+)}\,, \tag{16}$$

where

$$\Psi_{(\mathrm{I})}^{(+)}=\varphi_b\sum_{\tilde{n}'}B_{\tilde{n}'}^{(\mathrm{I})}(t)\psi_{\tilde{n}'}e^{-i\omega_{\tilde{n}'}t},\quad t\geqslant t^{(+)}\,, \tag{17a}$$

$$\Psi_{(\mathrm{II})}^{(+)}=\varphi_a\sum_{\tilde{n}'}B_{\tilde{n}'}^{(\mathrm{II})}(t)\psi_{\tilde{n}'}e^{-i\omega_{\tilde{n}'}t},\quad t\geqslant t^{(+)}\,, \tag{17b}$$

$$\begin{aligned}B_{\tilde{n}'}^{(\mathrm{I},\mathrm{II})}=2^{-1/2}&[a_{\tilde{n}'}^{(g)}e^{i[\eta_0-(1/2)\Delta\eta^{(+)}]}\\&\pm a_{\tilde{n}'}^{(u)}e^{-i[\eta_0-(1/2)\Delta\eta^{(+)}]}]\,,\end{aligned} \tag{18}$$

where

$$\Delta\eta^{(+)}(t)=\int_t^\infty\omega(t)dt\,, \tag{19}$$

with $|\Delta\eta^{(+)}|\ll 1$ (see Appendix A) and the signs + and − are associated with the indices I and II, respectively. As it can be seen from Eq. (17a) the amplitude $B_{\tilde{n}'}^{(\mathrm{I})}(t\to\infty)\equiv A_{\tilde{n}\tilde{n}'}^{(\mathrm{I})}$ for $\tilde{n}'\neq\tilde{n}$ describes the inelastic processes in reaction (1) and for $\tilde{n}'=\tilde{n}$ describes the elastic scattering channel.

In the case of the rearrangement channel (2), the coefficients $B_{\tilde{n}'}^{(\mathrm{II})}(t\to\infty)$ cannot be interpreted as transition amplitudes. The reason is that the functions $\psi_{\tilde{n}'}$, which appear in $\Psi_{(\mathrm{II})}^{(+)}$ (see Eq. 17b), are centered on the fixed center a, while in reaction (2) the Rydberg electron is bound to the moving center b. In order to determine the transition amplitudes in the rearrangement channel (2), one has to reexpand the function $\Psi_{(\mathrm{II})}^{(+)}$ over an electronic basis set in the coordinate system comoving with the center b, i.e., over the functions

$$\varphi_a \psi_{\tilde{n}'}[\vec{r}_1 - \vec{R}(t)] \exp(i\vec{v}\vec{r}_1) .$$

The corresponding coefficients $A^{(II)}_{\tilde{n}\tilde{n}'}$ in such an expansion, taken at $t = t^{(+)}$, can be then interpreted as proper transition amplitudes in channel (2). For $\tilde{n}' = \tilde{n}$ the amplitude $A^{(II)}_{\tilde{n}\tilde{n}'}$ describes the process of the resonant excitation transfer. However, under the conditions for which the quasiresonant energy exchange mechanism is expected to be efficient, there is no strict necessity to perform the re-expansion procedure. Namely one can show that under the simultaneous fulfillment of the conditions $v \ll v_n$ and $R_{\tilde{n}\tilde{n}'} \lesssim n$ [the latter is consistent with condition (5)], the transfer of the Rydberg electron to the other center takes place in an adiabatic manner, i.e., without change of the principal quantum number. The condition $R_{\tilde{n}\tilde{n}'} \lesssim n$ provides that the characteristic distance at which the resonant process dominantly occurs does not exceed the characteristic distance of the change of the Rydberg electron wave function.

If the amplitudes $A^{(I)}_{\tilde{n}\tilde{n}'}$ and $A^{(II)}_{\tilde{n}\tilde{n}'}$ for the $\tilde{n} \to \tilde{n}'$ transitions in channels (1) and (2) respectively are known, then one can define the probabilities $P^{(I,II)}_{nn'}$ for the $n \to n'$ transition in the corresponding channel by the relation

$$P^{(I,II)}_{nn'} = \frac{1}{n^2} \sum_{\substack{l\,m \\ l'\,m'}} |A^{(I,II)}_{\tilde{n}\tilde{n}'}|^2 . \tag{20}$$

For $n' = n$, $P^{(I)}_{nn}$ and $P^{(II)}_{nn}$ are the averaged probabilities for the elastic scattering in channel (1) and for the resonant excitation transfer, respectively. One can infer that for $n' \neq n$ the probabilities $P^{(I,II)}_{nn'}$, within the adiabatic approximation, should be close to one another. This fact will be proved in Sec. V.

B. Coupled equations for expansion coefficients

By substituting Eq. (10) into the Schrödinger equation (7) one gets the following system of coupled differential equations for the coefficients $a^{(g)}_{\tilde{n}'}$ and $a^{(u)}_{\tilde{n}'}$:

$$\begin{aligned} i\frac{\partial a^{(g)}_{\tilde{n}'}}{\partial t} &= \sum_{\tilde{n}''} \langle \tilde{n}', g | V | \tilde{n}'', g \rangle \exp(i\omega_{\tilde{n}''\tilde{n}'} t) a^{(g)}_{\tilde{n}''} \\ &\quad + \sum_{\tilde{n}''} \langle \tilde{n}', g | V | \tilde{n}'', u \rangle \\ &\qquad \times \exp[i(\omega_{\tilde{n}''\tilde{n}'} t - \eta(t) - \eta_0)] a^{(u)}_{\tilde{n}''} , \end{aligned} \tag{21a}$$

$$\begin{aligned} i\frac{\partial a^{(u)}_{\tilde{n}'}}{\partial t} &= \sum_{\tilde{n}''} \langle \tilde{n}', u | V | \tilde{n}'', u \rangle \exp(i\omega_{\tilde{n}''\tilde{n}'} t) a^{(u)}_{\tilde{n}''} \\ &\quad + \sum_{\tilde{n}''} \langle \tilde{n}', u | V | \tilde{n}'', g \rangle \\ &\qquad \times \exp[i(\omega_{\tilde{n}''\tilde{n}'} t + \eta(t) + \eta_0)] a^{(g)}_{\tilde{n}''} , \end{aligned} \tag{21b}$$

with the initial conditions in the form of (15). Within an accuracy of $O(1/\gamma R)$ one can, using the dipole approximation, transform the matrix elements of Eq. (21) into the form

$$\langle \tilde{n}', g | V | \tilde{n}'', g \rangle = \langle \tilde{n}', u | V | \tilde{n}'', u \rangle \simeq \tfrac{1}{2} \langle \tilde{n}' | \vec{r}_1 \vec{R} / r_1^3 | \tilde{n}'' \rangle , \tag{22a}$$

$$\langle \tilde{n}', g | V | \tilde{n}'', u \rangle = \langle \tilde{n}', u | V | \tilde{n}'', g \rangle \simeq -\tfrac{1}{2} \langle \tilde{n}' | \vec{r}_1 \vec{R} / r_1^3 | \tilde{n}'' \rangle , \tag{22b}$$

$$\langle \tilde{n}' | \vec{r}_1 \vec{R} / r_1^3 | \tilde{n}'' \rangle = \mathcal{R}_{\tilde{n}'\tilde{n}''} (\rho C^{(x)}_{\tilde{n}'\tilde{n}''} + vt C^{(z)}_{\tilde{n}'\tilde{n}''}) , \tag{23}$$

where the geometry of Fig. 1 and expression (9b) for V have been taken into account. By $\mathcal{R}_{\tilde{n}'\tilde{n}''}$ and $C_{\tilde{n}'\tilde{n}''}$ in Eq. (23) we have denoted the radial and angular parts of the matrix element, respectively. Note that $C_{\tilde{n}'\tilde{n}''}$ provide the fulfillment of the dipole selection rules: $l'' = l' \pm 1$, $C^{(x)}_{\tilde{n}'\tilde{n}''} \neq 0$ for $m'' = m' \pm 1$, $C^{(z)}_{n'n''} \neq 0$ for $m'' = m'$. Inserting Eqs. (22) and (23) into Eq. (21) the system of coupled equations becomes

$$\begin{aligned} i\frac{da^{(g,u)}_{\tilde{n}'}}{dt} &= \sum_{\tilde{n}''} \frac{1}{2} \rho \mathcal{R}_{\tilde{n}'\tilde{n}''} \left(C^{(x)}_{\tilde{n}'\tilde{n}''} + \frac{vt}{\rho} C^{(z)}_{\tilde{n}'\tilde{n}''}\right) e^{i\omega_{\tilde{n}''\tilde{n}'} t} \\ &\qquad \times (a^{(g,u)}_{\tilde{n}''} - a^{(u,g)}_{\tilde{n}''} e^{\mp i(\eta(t)+\eta_0)}) , \end{aligned} \tag{24}$$

with the initial conditions in the form of Eq. (15).

The system of coupled differential equations for the expansion coefficients $a^{(g,u)}_{\tilde{n}'}(t)$ (where $\tilde{n}'$ may be also $\tilde{n}$) completely defines our problem in the dipole approximation of the interaction potential. We note that the equations of system (24) are coupled with respect to the indices $(\tilde{n}', \tilde{n}'')$ and (g, u). Our next task is to simplify this system of coupled equations on the basis of some physical grounds.

IV. APPROXIMATE SOLUTION OF SYSTEM OF COUPLED EQUATIONS

The use of the dipole approximation implies that the matrix elements in Eq. (24) are different from zero only for those $\tilde{n}''$ which are optically coupled with $\tilde{n}'$. On the other hand, within the proposed mechanism of the process, the strongest coupling takes place between those $(\tilde{n}', \tilde{n}'')$ pairs of states for which the condition $\omega(t) = |\omega_{\tilde{n}''\tilde{n}'}|$ is fulfilled. For different $\tilde{n}''$ levels this condition is satisfied at different characteristic internuclear distances $R_{\tilde{n}'\tilde{n}''}$. Keeping in mind the initial condition (i.e., the fact that at the beginning of the collision process only the level $\tilde{n}$ is populated) and the abovementioned resonant selectivity of the $(\tilde{n}', \tilde{n}'')$ coupling, as well as the dipole selection rules, it follows that the main contribution to amplitudes $a^{(g,u)}_{\tilde{n}'}$ in Eq. (24) comes from the term $\tilde{n}'' = \tilde{n}$. This means that during the collision (or effectively for

$t^{(-)} \leq t \leq t^{(+)}$) each of the $\tilde{n}'$ states can be resonantly coupled either with the initial state $\tilde{n}$ or with states which are optically not coupled with $\tilde{n}$ (and therefore little populated during the collision). These arguments show that if the total decay probability P_n of the initial state is not too large, then the cascading (or other higher-order) transitions can be neglected. On the basis of this discussion the system of equations (24) is reduced to

$$i\frac{da^{(g,u)}_{\tilde n'}}{dt} = \tfrac{1}{2}\rho\mathcal{R}_{\tilde n'\tilde n}\left(C^{(x)}_{\tilde n'\tilde n} + \frac{vt}{\rho}C^{(z)}_{\tilde n'\tilde n}\right)\exp(i\omega_{\tilde n\tilde n'}t) \times\left(a^{(g,u)}_{\tilde n} - a^{(u,g)}_{\tilde n}\exp\{\mp i[\eta(t)+\eta_0]\}\right), \quad \tilde n' \neq \tilde n, \tag{25a}$$

$$i\frac{da^{(g,u)}_{\tilde n}}{dt} = \sum_{\tilde n'\neq\tilde n}\frac{1}{2}\rho\mathcal{R}_{\tilde n\tilde n'}\left(C^{(x)}_{\tilde n\tilde n'} + \frac{vt}{\rho}C^{(z)}_{\tilde n\tilde n'}\right)\exp(i\omega_{\tilde n'\tilde n}t) \times\left(a^{(g,u)}_{\tilde n'} - a^{(u,g)}_{\tilde n'}\exp\{\mp i[\eta(t)+\eta_0]\}\right), \tag{25b}$$

with the initial conditions (15). The approximation (25) of the system of coupled equations (24) shall be referred to as "decay approximation." Note that if we neglect the changes of the coefficients $a^{(g,u)}_{\tilde n}$, which corresponds to the first Born approximation, then the system of Eqs. (25) completely decouples and can be solved exactly. Our aim is however to go beyond the first Born approximation, and therefore we shall follow another procedure in solving Eqs. (25). To proceed along this direction and to make more explicit the role of the resonant energy exchange mechanism in producing inelastic transitions, let us transform the system of coupled differential equations (25) into the form of coupled integral equations. Differentiating Eq. (25a) by part in the interval $(t^{(-)}, t^{(+)})$ and taking into account the relation [which follows from Eq. (25b)]

$$\frac{da^{(g,u)}_{\tilde n}}{dt} = -\frac{da^{(u,g)}_{\tilde n}}{dt}e^{\pm i(\eta(t)+\eta_0)}, \tag{26}$$

we obtain [up to $O(\frac{1}{2}\Delta\eta^{(\mp)})$]

$$a^{(g,u)}_{\tilde n'}(t^{(+)}) = \mp ie^{\mp i(\eta_0-\Delta\eta^{(+)}/2)}\frac{\rho\mathcal{R}_{\tilde n\tilde n'}}{\omega_{\tilde n\tilde n'}}\left(C^{(x)}_{\tilde n\tilde n'}(\Omega^{(g,u)}_{\tilde n\tilde n'} + \mathcal{J}^{(u,g)}_{\tilde n\tilde n'}) - \frac{iv}{\rho}C^{(z)}_{\tilde n\tilde n'}\frac{\partial}{\partial\omega_{\tilde n\tilde n'}}(\Omega^{(g,u)}_{\tilde n\tilde n'} + \mathcal{J}^{(u,g)}_{\tilde n\tilde n'})\right), \quad \tilde n' \neq n, \tag{27a}$$

$$a^{(g,u)}_{\tilde n}(t^{(+)}) = 2^{-1/2} \mp ie^{\mp i(\eta_0-\Delta\eta^{(+)}/2)}\sum_{\tilde n'\neq n}\frac{\rho\mathcal{R}_{\tilde n'\tilde n}}{\omega_{\tilde n'\tilde n}}\left(C^{(x)}_{\tilde n'\tilde n}(\Omega^{(g,u)}_{\tilde n'\tilde n} + \mathcal{J}^{(u,g)}_{\tilde n'\tilde n}) - \frac{iv}{\rho}C^{(z)}_{\tilde n'\tilde n}\frac{\partial}{\partial\omega_{\tilde n'\tilde n}}(\Omega^{(g,u)}_{\tilde n'\tilde n} + \mathcal{J}^{(u,g)}_{\tilde n'\tilde n})\right), \tag{27b}$$

where

$$\Omega^{(g,u)}_{\tilde n\tilde n'} = e^{i\omega_{\tilde n\tilde n'}t^{(+)}}\left[\left(\frac{a^{(g,u)}_{\tilde n} + a^{(u,g)}_{\tilde n}}{2}\right)\sin\eta_0 \mp i\left(\frac{a^{(g,u)}_{\tilde n} - a^{(u,g)}_{\tilde n}}{2}\right)\cos\eta_0\right]_{t=t^{(+)}}, \tag{28}$$

$$\mathcal{J}^{(u,g)}_{\tilde n\tilde n'} = -\tfrac{1}{2}\int_{t^{(-)}}^{t^{(+)}} a^{(u,g)}_{\tilde n}\left(1 \mp 2i\frac{d\ln a^{(u,g)}_{\tilde n}}{d\eta}\right)\eta'\exp[i(\omega_{\tilde n\tilde n'}t \mp \eta(t))]\,dt, \tag{29}$$

and

$$\Omega^{(g,u)}_{\tilde n'\tilde n} = \Omega^{(g,u)}_{\tilde n\tilde n'}(\tilde n' \leftrightarrow \tilde n, g \leftrightarrow u).$$

In Eqs. (27) the effects of the $(g,\tilde n)\to(u,\tilde n')$ and $(u,\tilde n)\to(g,\tilde n')$ transitions are separated from those corresponding to the $(g,\tilde n)\to(g,\tilde n')$ and $(u,\tilde n)\to(u,\tilde n')$ transitions. The latter are included only in the $\Omega^{(g,u)}_{\tilde n\tilde n'}$ terms, and, as will be seen later on, this term contributes to the resonant excitation transfer amplitude only. The transitions $(g,\tilde n)\to(u,\tilde n')$ and $(u,\tilde n)\to(g,\tilde n')$ are included both in $\Omega^{(g,u)}_{\tilde n\tilde n'}$ and $\mathcal{J}^{(u,g)}_{\tilde n\tilde n'}$. However, only the $\mathcal{J}^{(u,g)}_{\tilde n\tilde n'}$ term contributes dominantly to the inelastic amplitudes, a fact which will be proved later on too. Let us therefore examine in more detail the structure of the integrals $\mathcal{J}^{(u,g)}_{\tilde n\tilde n'}$. Since $\omega_{\tilde n\tilde n'} = \omega_{\tilde n'} - \omega_{\tilde n}$ may be both positive and negative, two groups of inelastic $(g) \rightleftarrows (u)$ processes are described by Eqs. (27): (i): $(g,\tilde n)\to(u,\tilde n')$, $\omega_{\tilde n\tilde n'} < 0$, $(u,\tilde n)\to(g,\tilde n')$, $\omega_{\tilde n\tilde n'} > 0$ and (ii): $(g,\tilde n)\to(u,\tilde n')$, $\omega_{\tilde n\tilde n'} > 0$, $(u,\tilde n)\to(g,\tilde n')$, $\omega_{\tilde n\tilde n'} < 0$. For these two groups of transitions the phase $\varphi = \omega_{\tilde n\tilde n'}t \mp \eta(t)$ appearing in $\mathcal{J}^{(g,u)}_{\tilde n\tilde n'}$ can be represented as $\varphi_{(\text{i})} = \pm(|\omega_{\tilde n\tilde n'}|t - \eta)$ and $\varphi_{(\text{ii})} = \pm(|\omega_{\tilde n\tilde n'}|t + \eta)$, respectively. Since $\eta(t)$ is positive [see Eqs. (11) and (A3)] and since the region where $\varphi' \simeq 0$ gives the main contribution to the integral $\mathcal{J}^{(u,g)}_{\tilde n\tilde n'}$, it is obvious that the integrals containing $\varphi_{(\text{ii})}$ are always negligibly small with respect to those containing $\varphi_{(\text{i})}$. (An exception is the region only of very large impact parameters, where η is extremely small and therefore all integrals are exponentially small. This region is obviously of no practical interest.) We have thus shown that the processes of group (i) for which the resonance condition $\varphi' = 0$ can be fulfilled are the dominant inelastic processes occurring in the system. The processes of group (ii) are strongly nonresonant; for their occurrence a considerable amount of energy transfer from the nuclear to the electronic motion is required. In our further consideration these processes will be neglected.

Within the decay approximation the coefficients $a_{\tilde{n}}^{(g,u)}$ are not allowed to vary strongly with time. Using this fact, one can represent the integral $\mathcal{J}_{\tilde{n}\tilde{n}'}^{(u,g)}$ in the form (we replace φ by $\varphi_{(\mathrm{i})}$)

$$\mathcal{J}_{\tilde{n}\tilde{n}'}^{(u,g)}=-\tfrac{1}{2}\alpha_{\tilde{n}\tilde{n}'}^{(u,g)}\int_{t^{(-)}}^{t^{(+)}}\eta'\exp\{\pm i[\,|\omega_{\tilde{n}\tilde{n}'}|t-\eta(t)]\}dt\,, \tag{30}$$

where $\alpha_{\tilde{n}\tilde{n}'}^{(u,g)}$ has a finite value. The representation (30) is valid only if the integral on the right-hand side does not vanish. This, however, can always be achieved by slightly changing the integration limits, for instance. It can be easily verified that, within the decay approximation, $\alpha_{\tilde{n}\tilde{n}'}^{(u,g)}$ depends on $\omega_{\tilde{n}\tilde{n}'}$ only weakly. If, further, the variation of $\eta(t)$ on time is such that the relation $|\eta'| \gg |\ln a_{\tilde{n}}^{(u,g)}|$ holds, then the coefficient $\alpha_{\tilde{n}\tilde{n}'}^{(u,g)}$ has the meaning of a certain mean value of $a_{\tilde{n}}^{(g,u)}$ from the interval $(t^{(-)},t^{(+)})$ [see Eq. (29)]. Therefore $\alpha_{\tilde{n}\tilde{n}'}^{(u,g)}$ cannot exceed the initial value of $a_{\tilde{n}}^{(u,g)}$. In the case in which the decay of the initial state is so small that the Born approximation is valid, the following identity holds:

$$\alpha_{\tilde{n}\tilde{n}'}^{(u,g)}\equiv a_{\tilde{n}}^{(u,g)}(t^{(-)})=2^{-1/2}\,. \tag{31}$$

The introduced set of time-independent coefficients $\alpha_{\tilde{n}\tilde{n}'}^{(u,g)}$ is equivalent to the initial-state amplitude $a_{\tilde{n}}^{(u,g)}$. Their determination, of course, should be done simultaneously with the determination of $a_{\tilde{n}'}^{(g,u)}$. However, the advantage of their introduction into the treatment is that Eqs. (27) are reduced to a system of algebraic equations. Instead of going into a procedure of direct solving such an obtained system of algebraic equations, we shall first calculate the transition amplitudes of the processes involved in reactions (1) and (2), considering $\alpha_{\tilde{n}\tilde{n}'}^{(u,g)}$ known. The determination of $\alpha_{\tilde{n}\tilde{n}'}^{(u,g)}$ will be postponed to the end of Sec. V and will be performed by using the detailed-balance principle and the probability-normalization relation. With these remarks in mind we can consider Eqs. (27) as being a formal solution to the system of differential equations (25).

V. CALCULATION OF TRANSITION AND DECAY PROBABILITIES

A. Calculation of transition amplitudes

All our previous considerations are of a quite general form and allow one to take into account the deviations of the atomic field from the pure Coulomb one. In particular, one can use the previous results to treat the l-mixing collisions. In the rest of the present paper, however, we shall confine ourselves to the case in which the abovementioned deviations are small and in which the states of the Rydberg electron may be considered hydrogenlike. The matrix element $\mathcal{R}_{\tilde{n}\tilde{n}'}$ then can be transformed as[17]

$$\mathcal{R}_{\tilde{n}\tilde{n}'}=\omega_{nn'}^{2}r_{\tilde{n}\tilde{n}'}\,,\quad r_{\tilde{n}\tilde{n}'}\equiv\langle n'l'|r|nl\rangle\,, \tag{32}$$

where the radial matrix element $r_{\tilde{n}\tilde{n}'}$ can be exactly calculated by Gordon's formula.[17] Using Eqs. (32) and (30) and expression (27) for $a_{\tilde{n}'}^{(g,u)}$ in Eq. (18), we obtain the following expression for the inelastic amplitude in reaction (1):

$$B_{\tilde{n}'}^{(\mathrm{I})}\equiv A_{\tilde{n}\tilde{n}'}^{(\mathrm{I})}=\pm i2^{-1/2}\rho\omega_{nn'}r_{\tilde{n}\tilde{n}'}\alpha_{\tilde{n}\tilde{n}'}^{(u,g)}\times\left[C_{\tilde{n}\tilde{n}'}^{(x)}\mathcal{J}_{nn'}+i\frac{v}{\rho}C_{\tilde{n}\tilde{n}'}^{(z)}\left(\frac{\mathcal{J}_{nn'}}{\omega_{nn'}}-\frac{\partial\mathcal{J}_{nn'}}{\partial\omega_{nn'}}\right)\right],\quad \tilde{n}'\neq\tilde{n}\,, \tag{33}$$

where

$$\mathcal{J}_{nn'}=\tfrac{1}{2}\int_{t^{(-)}}^{t^{(+)}}\eta'\exp[\,|\omega_{nn'}|t-\eta(t)]\,dt\,. \tag{34}$$

The amplitude of the elastic scattering in the direct channel (1) can be obtained directly from Eq. (18) (by setting there $\tilde{n}'=\tilde{n}$) and reads

$$B_{\tilde{n}}^{(\mathrm{I})}\equiv A_{\tilde{n}\tilde{n}}^{(\mathrm{I})}=2^{1/2}\left[\left(\frac{a_{\tilde{n}}^{(g)}+a_{\tilde{n}}^{(u)}}{2}\right)\cos\eta_0+i\left(\frac{a_{\tilde{n}}^{(g)}-a_{\tilde{n}}^{(u)}}{2}\right)\sin\eta_0\right]_{t=t^{(+)}}\,. \tag{35}$$

To obtain the transition amplitudes in the rearrangement channel (2), one, in principle, has to reexpand the function $\Psi_{(\mathrm{II})}^{(+)}$ of Eq. (17b) over the Coulomb basis set associated with the moving atom. Within the dipole approximation, it is not necessary, owing to the adiabatic character of the collision, to perform such a reexpansion procedure. By inserting Eqs. (27) and (18) into Eq. (17b) [and keeping in mind Eqs. (30) and (32)], one obtains

$$\Psi_{(\mathrm{II})}^{(+)}=\varphi_a\left\{\sum_{\tilde{n}'(\neq\tilde{n})}A_{\tilde{n}\tilde{n}'}^{(\mathrm{II})}\psi_{\tilde{n}'}e^{-i\omega_{\tilde{n}'}t}+B_n^{(\mathrm{II})}e^{-i\omega_{\tilde{n}}t}\sum_{\tilde{n}'}K_{\tilde{n}\tilde{n}'}\psi_{\tilde{n}'}\right\}_{t\geq t^{(+)}}, \tag{36}$$

where

$$A^{(\mathrm{II})}_{\tilde{n}\tilde{n}'}=i2^{-1/2}\rho\omega_{nn'}r_{\tilde{n}\tilde{n}'}\alpha^{(u,g)}_{\tilde{n}\tilde{n}'}\left[C^{(x)}_{\tilde{n}\tilde{n}'}\mathcal{J}_{nn'}+i\frac{v}{\rho}C^{(z)}_{\tilde{n}\tilde{n}'}\left(\frac{\mathcal{J}_{nn'}}{\omega_{nn'}}-\frac{\partial\mathcal{J}_{nn'}}{\partial\omega_{nn'}}\right)\right],\quad \tilde{n}'\neq\tilde{n}\,, \tag{37}$$

$$B^{(\mathrm{II})}_{\tilde{n}}=2^{1/2}\left[\left(\frac{a^{(g)}_{\tilde{n}}-a^{(u)}_{\tilde{n}}}{2}\right)\cos\eta_0+i\left(\frac{a^{(g)}_{\tilde{n}}+a^{(u)}_{\tilde{n}}}{2}\right)\sin\eta_0\right]_{t=t^{(+)}}, \tag{38}$$

$$K_{\tilde{n}\tilde{n}'}=r_{\tilde{n}\tilde{n}'}[\omega_{nn'}(\rho C^{(x)}_{\tilde{n}\tilde{n}'}+vt^{(+)}C^{(z)}_{\tilde{n}\tilde{n}'})+ivC^{(z)}_{\tilde{n}\tilde{n}'}]. \tag{39}$$

The first term in Eq. (36) describes the inelastic processes in the rearrangement reaction (2) ($A^{(\mathrm{II})}_{\tilde{n}\tilde{n}'}$ being the corresponding transition amplitudes), whereas the second term describes the "elastic scattering" (i.e., the resonant excitation transfer process). It is important to note that the amplitudes $A^{(\mathrm{I})}_{\tilde{n}\tilde{n}'}$ and $A^{(\mathrm{II})}_{\tilde{n}\tilde{n}'}$ for the direct and rearrangement inelastic processes are essentially equal. This fact is a consequence of the adiabaticity of the collision and was asserted at the end of Sec. III A on the basis of general arguments. It is also worthwhile to note that the same expression [Eq. (39)] for the coefficient $K_{\tilde{n}\tilde{n}'}$ can be obtained if one expands

$$\langle\psi_{\tilde{n}}(\vec{r}-\vec{R}(t^{(+)})e^{i\vec{v}\vec{r}}\,|\,\psi_{\tilde{n}}(\vec{r})\rangle$$

in a power series (over $z=vt^{(+)}$ and ρ) and retains only the first two terms. Such an expansion gives us the condition for the adiabaticity of the electronic transfer from the fixed to the moving Coulomb center in a more precise form: $v\lesssim(2/n)^2$, which is consistent with our general condition $v\ll v_n$.

Let us now examine in more detail the elastic and resonant excitation transfer amplitudes. Note first that the phase η_0 [see Eq. (11)] is the same as that which determines the elastic and charge exchange processes in the slow A^++A collisions.[10] In the Born approximation ($a^{(g)}_{\tilde{n}}=a^{(u)}_{\tilde{n}}=2^{-1/2}$) the amplitudes of the elastic and the resonant excitation transfer channels are respectively given by $A^{(\mathrm{I})}_{\tilde{n}\tilde{n}}=\cos\eta_0$ and $A^{(\mathrm{II})}_{\tilde{n}\tilde{n}}\sim B^{(\mathrm{II})}_{\tilde{n}}=i\sin\eta_0$. We see from here that in the Born approximation the elastic and the resonant excitation transfer processes in atom–Rydberg-atom slow collisions are essentially determined by the elastic and the charge exchange processes in the subsystem A^++A. The same remains true also in the case for which $a^{(g)}_{\tilde{n}}(t^{(+)})\neq a^{(u)}_{\tilde{n}}(t^{(+)})$, with the difference that a lowering of the corresponding elastic and charge transfer amplitudes takes place and that some interference effects appear. Thus the decay of the initial Rydberg state both decreases and mixes the amplitudes of the elastic and charge exchange processes in the subsystem A^++A.

B. Expressions for transition probabilities

Having the expressions for the amplitudes $A^{(\mathrm{I})}_{\tilde{n}\tilde{n}'}$ and $A^{(\mathrm{II})}_{\tilde{n}\tilde{n}'}$ at hand, one can immediately construct the transition amplitudes $P^{(\mathrm{I})}_{\tilde{n}\tilde{n}'}=P^{(\mathrm{II})}_{\tilde{n}\tilde{n}'}$ or the averaged (over l and m) amplitudes $P^{(\mathrm{I})}_{nn'}=P^{(\mathrm{II})}_{nn'}$ [see Eq. (20)]. Before doing this we make the following remark. Owing to the adiabaticity condition $v\lesssim n^{-2}$ and conditions (5) and (6) (or $\rho\ll n^2\sim r_n$), on which our quasiresonant energy exchange model is based, it follows that the inequality $v/\rho\ll|\omega_{nn'}|$ always holds. Therefore the terms in expressions (33) and (37) for $A^{(\mathrm{I,II})}_{\tilde{n}\tilde{n}'}$ connected with the component $C^{(z)}_{\tilde{n}\tilde{n}'}$ of the angular matrix element are much smaller than the other terms and can be neglected with respect to them. We have retained them in the structure of $A^{(\mathrm{I,II})}_{\tilde{n}\tilde{n}'}$ only to indicate that, although not important within our model, the transitions connected with $C^{(z)}_{\tilde{n}\tilde{n}'}$ do exist and, for small impact parameters or very large n or both, they can give an appreciable contribution to the transition amplitude. The integral $\mathcal{J}_{nn'}$ [Eq. (34)], which also appears in the transition amplitudes $A^{(\mathrm{I,II})}_{\tilde{n}\tilde{n}'}$, can be evaluated analytically (see Appendix B), and the result is

$$\mathcal{J}_{nn'}=\pi^{3/4}|\chi_{nn'}|^{1/2}\mathcal{J}^{(0)}_{nn'}\,, \tag{40}$$

$$\mathcal{J}^{(0)}_{nn'}=\pi^{1/4}|\chi_{nn'}|^{1/2}\mu^{1/3}\exp(\tfrac{2}{3}\mu^2)$$

$$\times\mathrm{Ai}(\mu^{4/3}-\mu^{1/3}\Delta\chi^{2/3}),\quad \Delta\chi\geqslant 0\,, \tag{41a}$$

$$=\pi^{1/4}\frac{\chi_\rho^{2/3}}{|\chi_{nn'}|^{1/2}}\exp\left(\frac{2}{3}\frac{1}{\chi_\rho^2}-\frac{\Delta\chi}{\chi_\rho}\right)$$

$$\times\mathrm{Ai}\left(\frac{1}{\chi_\rho^{4/3}}-\frac{\Delta\chi}{\chi_\rho^{1/3}}\right),\quad \Delta\chi\leqslant 0\,, \tag{41b}$$

where the following notations have been introduced:

$$\chi_{nn'}\equiv\left(\frac{2\rho}{\gamma}\right)^{1/2}\frac{\omega_{nn'}}{v},\quad \chi_\rho\equiv\left(\frac{2\rho}{\gamma}\right)^{1/2}\frac{\omega(\rho)}{v}\,, \tag{42a}$$

$$\Delta\chi=\chi_\rho-|\chi_{nn'}|,\quad \mu=\ln(\chi_\rho/|\chi_{nn'}|)/\Delta\chi\,, \tag{42b}$$

and Ai(z) is the Airy function. We note that $\mathcal{J}^{(0)}_{nn'}\leqslant 1$ for all values of $\chi_{nn'}$ and χ_ρ. The equation $\Delta\chi=0$ defines a critical impact parameter $\rho_{nn'}$ such that for $\rho\leqslant\rho_{nn'}$ the inelastic $n\to n'$ transition is energetically allowed and for $\rho>\rho_{nn'}$ it is energetically forbidden. The behavior of $\mathcal{J}^{(0)}_{nn'}$ as function of ρ is illustrated in Fig. 2.

Using the above results one can write explicit expressions for the probabilities $P^{(\mathrm{I})}_{\tilde{n}\tilde{n}'}=P^{(\mathrm{II})}_{\tilde{n}\tilde{n}'}$.

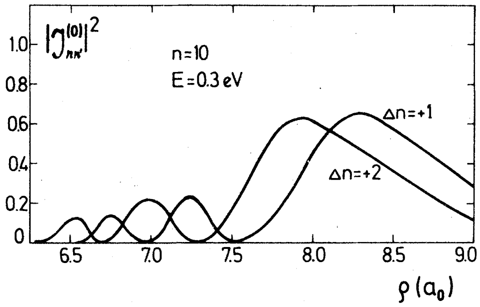

FIG. 2. Behavior of $|\mathcal{J}^{(0)}_{nn'}|^2$ as function of impact parameter ρ.

Summing them over the quantum numbers l', m' of the final state and averaging them over the quantum numbers l, m of the initial state, we obtain the probability for the $n\to n'(\neq n)$ transition in both reaction channels (1) and (2) in the form

$$P_{nn'}=\pi^{3/2}\left(\frac{2}{\gamma}\right)^{1/2}\frac{|\omega_{nn'}|^3\rho^{5/2}}{v}L_{nn'}|\mathcal{J}^{(0)}_{nn'}|^2 d^{(u,g)}_{nn'}, \tag{43}$$

$$L_{nn'}=\frac{1}{n^2}\left(\sum_{l=0}(l+1)(r^{n',l+1}_{n,l})^2+\sum_{l=1}l(r^{n',l-1}_{n,l})^2\right), \tag{44}$$

where $d^{(u,g)}_{nn'}$ is defined as the mean value of $|\alpha^{(u,g)}_{\tilde{n}\tilde{n}'}|^2$ over all the possible transitions within $\tilde{n}\to\tilde{n}'$, namely,

$$d^{(u,g)}_{nn'}=\frac{\sum\limits_{l\,m,\,l'm'}|\alpha^{(u,g)}_{\tilde{n}\tilde{n}'}|^2|r_{\tilde{n}\tilde{n}'}C^{(x)}_{\tilde{n}\tilde{n}}|^2}{\sum\limits_{l\,m,\,l'm'}|r_{\tilde{n}\tilde{n}'}C^{(x)}_{\tilde{n}\tilde{n}'}|^2} \tag{45}$$

and the indices u and g correspond to $n'>n$ and $n'<n$, respectively.

It is also useful to define the total decay probability of the initial state n due to all excitation and deexcitation processes,

$$P_n=\sum_{n'(\neq n)}P_{nn'}\,. \tag{46}$$

Thus our task is now reduced to the determination of the coefficients $d^{(u,g)}_{nn'}$. However, before proceeding to this goal, we note that these coefficients possess the following symmetry property:

$$d^{(u,g)}_{nn'}=d^{(g,u)}_{n'n}\,. \tag{47}$$

In other words, as a consequence of the detailed-balance principle for the $\tilde{n}\rightleftharpoons\tilde{n}'$ transitions, the coefficients $\alpha^{(u,g)}_{\tilde{n}\tilde{n}'}$ satisfy the equality $|\alpha^{(u,g)}_{\tilde{n}\tilde{n}'}|^2=|\alpha^{(g,u)}_{\tilde{n}'\tilde{n}}|^2$, from which relation (47) immediately follows.

Using relation (47) in Eq. (43), one concludes that the probabilities $P_{nn'}$ and $P_{n'n}$ also satisfy the detailed-balance principle: $P_{nn'}/P_{n'n}=n'^2/n^2$.

C. Determination of coefficients $d^{(u,g)}_{nn'}$

Let us first note that within the framework of the proposed model the following relation is valid:

$$|A^{(\mathrm{I})}_{\tilde{n}\tilde{n}}|^2+|A^{(\mathrm{II})}_{\tilde{n}\tilde{n}}|^2 =|a^{(g)}_{\tilde{n}}(t^{(+)})|^2+|a^{(u)}_{\tilde{n}}(t^{(+)})|^2, \tag{48}$$

where $A^{(\mathrm{I,II})}_{\tilde{n}\tilde{n}}$ are the elastic amplitudes in channels (1) and (2). It can be also easily verified that within our model the total $\tilde{n}_2\to\tilde{n}'$ $(n'>n)$ probability cannot exceed the change of $|a^{(u)}_{\tilde{n}}(t)|^2$ in the interval $(t^{(-)},t^{(+)})$. The same is true of the total $\tilde{n}\to\tilde{n}'$ $(n'<n)$ probability with regard to $|a^{(g)}_{\tilde{n}}(t)|^2$. With these remarks and relation (48) in mind, the normalization of the total probability to unity gives (after averaging over the l,m quantum numbers)

$$|a^{(u)}_n(t^{(+)})|^2+\sum_{n'>n}P_{nn'}=\tfrac{1}{2}, \tag{49a}$$

$$|a^{(g)}_n(t^{(+)})|^2+\sum_{n'<n}P_{nn'}=\tfrac{1}{2}, \tag{49b}$$

where

$$|a^{(g,u)}_n(t^{(+)})|^2=\frac{1}{n^2}\sum_{l\,m}|a^{(g,u)}_{\tilde{n}}(t^{(+)})|^2 \tag{50}$$

and $P_{nn'}$ is given by Eq. (43). Equations (49) show that in the decay approximation the excitation and deexcitation processes for a fixed initial state n are completely decoupled. If n is considered a variable, then the system of equations (49), together with condition (47), can serve to determine the coefficients $d^{(u,g)}_{nn'}$ and $|a^{(g,u)}_n(t^{(+)})|^2$. Solving such a system of equations is equivalent to solving the system of equations (27) after introducing in them the coefficients $\alpha^{(u,g)}_{\tilde{n}\tilde{n}'}$ by relation (30). However, within the decay approximation, one can avoid the solving of this difficult problem. Introducing the quantity

$$S^{(u,g)}_n=\sum_{n'}\frac{P_{nn'}}{d^{(u,g)}_{nn'}}, \tag{51}$$

where the index u (g) corresponds to summation over $n'>n$ $(n'<n)$, one can show that the most general and, at the same time, most physically meaningful representation of $d^{(u,g)}_{nn'}$ should be

$$d^{(u,g)}_{nn'}=\frac{1}{2}\,\frac{1}{1+\kappa^{(g,u)}_{nn'}S^{(u,g)}_n}, \tag{52}$$

$$\kappa^{(g,u)}_{nn'}=\frac{S^{(g,u)}_{n'}}{S^{(g,u)}_{n'}+S^{(u,g)}_n}\,. \tag{53}$$

Since in the decay approximation $S^{(g,u)}_{n(n')}$ cannot be greater than one, it follows from Eq. (53) that $0\leqslant\kappa^{(g,u)}_{nn'}\leqslant 1$. The coefficients $d^{(u,g)}_{nn'}$, chosen in the form (52), have the following properties: (i) they satisfy relation (47), which provides fulfillment of the detailed-balance principle; (ii) they have a correct upper limit ($d_{nn'}^{(u,g)}=\frac{1}{2}$) when either n or n' is sufficiently large [then $P_{nn'}\sim n^{-5}$; see Eq. (43)]; and (iii) they satisfy the inequality $|a_n^{(u,g)}(t^{(+)})|^2 \leqslant d_{nn'}^{(u,g)} \leqslant |a_n^{(u,g)}(t^{(-)})|^2$. Note that the values $\kappa_{nn'}^{(g,u)}=0$ (corresponding to the Born approximation) and $\kappa_{nn'}^{(g,u)}=1$ (corresponding to the so-called "normalized Born approximation") respectively give the highest and the lowest values of $d_{nn'}^{(u,g)}$ and consequently the upper and lower limit of $P_{nn'}$. One can show that for $n\gg 1$ and $|\Delta n|\ll n$ (which corresponds to considering the Rydberg spectrum as equidistant) $\kappa_{nn'}^{(g,u)}$ can be approximately given by

$$\kappa_{nn'}^{(g,u)}\approx\tfrac{1}{2}(1\mp\overline{\Delta n}/n)\,, \tag{54}$$

where $\overline{\Delta n}\,(\ll n)$ is a certain mean change of the initial state n due to the collision. If one calculates $P_{nn'}$ and P_n by setting $\kappa_{nn'}^{(g,u)}=\frac{1}{2}$ in Eq. (52), then the corresponding errors do not exceed $\frac{1}{3}(\overline{\Delta n}/n)$ and $O(\overline{\Delta n}/n)^2$, respectively, provided $S_n^{(g,u)}\leqslant 1$. Analogous estimates can be obtained also for the case of nonequidistant Rydberg spectrum. If $\overline{\Delta n}\lesssim n^{1/2}$ (which for $n\gg 1$ is practically always fulfilled), then the approximation $\kappa_{nn'}^{(g,u)}=\frac{1}{2}$ introduces an error in P_n of $O(1/n)$. Noting that the adiabatic character of the collision implies $R_{nn'}\sim\rho_{nn'}\lesssim n$, we see that the above accuracy is compatible with the general degree of accuracy of our method, which is $O(1/\gamma\rho_{nn'})$. However, in the calculations where one needs fulfillment of the detailed-balance principle [with an accuracy higher than $O(|n'-n|/n)$], one should use for $\kappa_{nn}^{(g,u)}$ expression (52). In our calculations of H*(n)-H inelastic collision processes, presented in Sec. VI, we have used the value $\kappa_{nn'}^{(g,u)}=\frac{1}{2}$ throughout.

VI. PROBABILITY AND CROSS SECTION CALCULATIONS FOR H*(n)-H COLLISIONS

In this section we give the results of our calculations on the probabilities $P_{nn'}$, P_n and the decay cross sections σ_n for the case of H*(n)-H collisions. Owing to the proper Coulomb character of the Rydberg states in this case and their angular degeneracy, no additional restrictions should be imposed on the theory developed in Secs. IV and V.

In calculating the transition probabilities $P_{nn'}$ we have used Gordon's formula[17] for evaluation of the radial matrix elements $r_{\bar{n}\bar{n}'}$. Figure 3 shows several typical examples of the dependence of $P_{nn'}$ on the impact parameter (for $n=10$; $\Delta n=\pm 1$, ± 2; and $E=0$, 3 eV). It can be seen from Fig. 3 that the probabilities $P_{nn'}$ have a strongly expressed maximum at $\rho=\rho_{n,n'}$, which corresponds to fulfillment of the resonance condition $\omega(R_{n,n'})=|\omega_{nn'}|$. For $\rho>\rho_{nn'}$, $P_{nn'}$ decreases exponentially, whereas for $\rho<\rho_{nn'}$, $P_{nn'}$ oscillates with decreasing amplitudes. The observed mutual displacement of the structures of $P_{n,n+|\Delta n|}$ and $P_{n,n-|\Delta n|}$ results from the nonequidistant character of the low-lying Rydberg states. For larger values of $|\Delta n|$ this displacement is more pronounced.

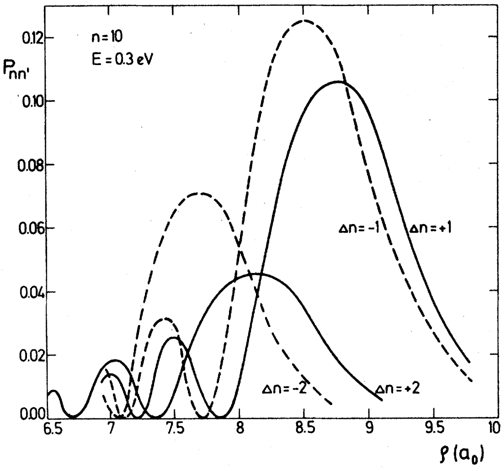

FIG. 3. Dependence of the $P_{nn'}$ transition probability on impact parameter ρ for $n=10$ ($\Delta n=\pm 1$, ± 2; $E=0.3$ eV).

It is also seen from Fig. 3 that for the same value of $|\Delta n|$ the magnitude of the transition probability for deexcitation, $P_{n,n-|\Delta n|}$, is bigger than that of the probability for excitation, $P_{n,n+|\Delta n|}$. This is a result of the properties of the $r_{\bar{n}\bar{n}'}$ matrix elements as well as the presence of the factor $|\omega_{nn'}|^3$ in expression (43) for $P_{nn'}$. For higher Rydberg states and for $|\Delta n|\ll n$ the dependence of $P_{nn'}$ on the sign of Δn should become negligible.

Figure 4 shows the total decay probability P_n of the levels $n=10,12,14,16$ at $E=0.3$ eV due to all $n\to n'$ transitions in the discrete spectrum. In the region of ρ shown in the figure, only the transitions with $|\Delta n|\leqslant 5$ contribute to P_n. For $\rho\lesssim 6a_0$

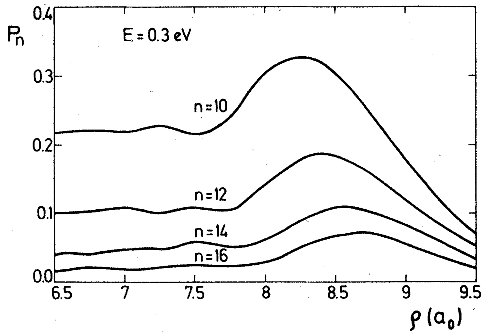

FIG. 4. Decay probability P_n of the Rydberg levels $n=10,12,14,16$ as function of impact parameter ρ ($E=0.3$ eV).

the transitions with $|\Delta n| \geq 6$ also become important. In this region, however, the main contribution to P_n comes from the transitions caused by the angular components $C^{(z)}_{nn'}$ of the dipole matrix elements. The contribution of the angular transitions to P_n (or $P_{nn'}$), as discussed previously, cannot be properly accounted for in our asymptotic treatment of the problem, and therefore the calculations of $P_{nn'}$ and P_n were restricted to the region $\rho \geq 6a_0$.

An important feature of the decay probability P_n is its oscillatory structure for $\rho < \rho_n^*$, where ρ_n^* is the impact parameter at which the biggest maximum of P_n occurs. The weak oscillations in P_n are a result of the superposition of the $P_{nn'}$ probabilities, and therefore their amplitudes do not change much with varying collision energy (see Fig. 5). As seen from Figs. 4 and 5, the weak variations of P_n with ρ in the region $\rho < \rho_n^*$ can be averaged and the decay probability can be represented by a certain mean value $\bar{P}_n$. A formal inclusion of the angular transitions in the calculation showed that the mean value $\bar{P}_n$ of the decay probability can be extended down to a few Bohr radii. On general physical grounds one cannot expect drastic changes in P_n in the region of small ρ in the considered energy range. In any case, this region of ρ does not contribute to the decay cross section to any considerable extent. Therefore we can represent the decay cross section

$$\sigma_n = 2\pi \int_0^\infty P_n \rho \, d\rho \tag{55}$$

in the form

$$\sigma_n = \pi \rho_{on}^2 \bar{P}_n + 2\pi \int_{\rho_{on}}^\infty P_n \rho \, d\rho \, . \tag{56}$$

In our calculations of σ_n we have used Eq. (56), determining ρ_{on} as the point in the region $\rho > \rho_n^*$ at which $P_n(\rho_{on}) = \bar{P}_n$. Since for $\rho > \rho_{on}$, P_n decreases exponentially, the second term on the right-hand side in Eq. (56) gives a negligible contribution to σ_n. The results of our calculations of σ_n for $n = 10, 12, 14$ are shown in Fig. 6. As seen in this figure, the magnitude of σ_n for n not too large and for $v \lesssim 10^6$ cm/sec is of the order of $10^{-15} - 10^{-16}$ cm^2. At this point we would like to make the following remark. Since for the hydrogen case ($\gamma = 1$) the function $\omega(R)$ decreases very rapidly at large R, the resonance for a given $|\omega_{nn'}|$ is reached at relatively small $R_{nn'}$, and the corresponding critical impact parameters ρ_{on} are also relatively small. For example, for $n = 12$ $\rho_{on} \approx 9a_0$ (at $E = 0.3$ eV; see Fig. 4). For atoms A with a smaller binding energy of the valence electron ($\gamma < 1$), the function $\omega(R) \sim \exp(-\gamma R)$ at large R decreases less rapidly, and consequently $R_{nn'}$ and ρ_{on} (for the same values of $|\omega_{nn'}|$ and E as in the hydrogen case) have larger values. This results in an increasing of the value of the decay cross section σ_n. The preliminary calculations of P_n and σ_n for the Li*(n)-Li system[18] ($\gamma \simeq 0.63$) have confirmed the above conclusion. For example, for $n = 12$ and $E = 0.3$ eV in this system, $\rho_{on} \approx 18a_0$ and σ_n is larger by more than one order of magnitude than in the case for hydrogen.

Another remark we would like to make now concerns the velocity dependence of σ_n. In the low-velocity region, when the phase $\eta(t)$ is comparable to $\omega_{nn'}t$, the dominant dependence of σ_n (or $P_{nn'}$) is given by the explicit v^{-1} factor in Eq. (43). In this velocity region the function $|\mathcal{J}^{(0)}_{nn'}|^2$ depends weakly on v (like $v^{-1/6}$). At higher velocities, however, the phase $\eta(t)$ can be neglected with respect to $\omega_{nn'}t$, so that $|\mathcal{J}^{(0)}_{nn'}|^2$ depends on v as v^{-1}, and the v dependence of σ_n is $\sigma_n \sim v^{-2}$. The charge

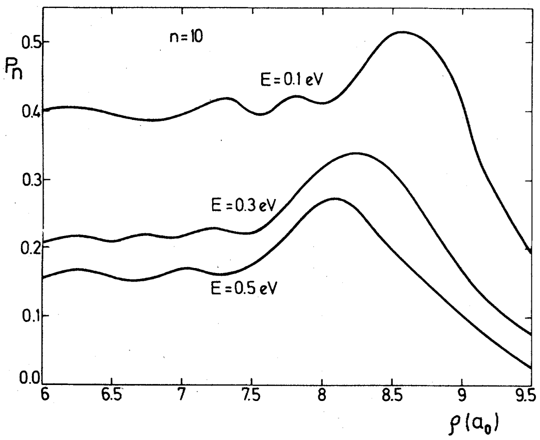

FIG. 5. Decay probability P_n ($n = 10$) for $E = 0.1, 0.3,$ and 0.5 eV as function of ρ.

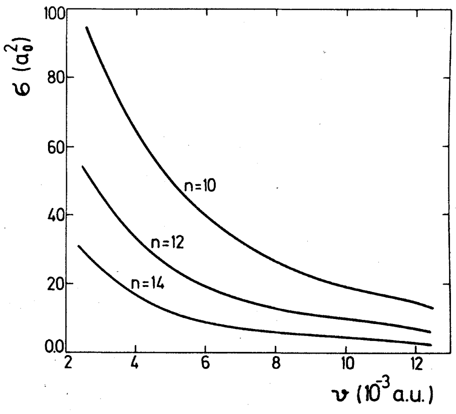

FIG. 6. Decay cross section σ_n ($n = 10, 12, 14$) as function of relative collision velocity.

of the velocity dependence of σ_n (or $|\mathcal{J}^{(0)}_{nn}|^2$) can be obtained directly from the corresponding asymptotic expansions of the Airy function, contained in $\mathcal{J}^{(0)}_{nn'}$. In Fig. 6, the change in the character of the velocity dependence of σ_n can be noticed at the end of the considered velocity range (at $v \approx 12.10^{-3}$ a.u.).

VII. CONCLUSIONS

In the present paper we have proposed a resonant-energy exchange mechanism for the inelastic transitions in the discrete spectrum which occur in slow collisions of Rydberg atoms with their parent ground-state atoms. The main idea of this mechanism lies in considering the transitions of the Rydberg electron as being resonantly coupled with the transitions in the quasimolecular subsystem $A^+ + A$. The nature of this coupling is radiative: photons emitted (absorbed) in the transitions between the states of the quasimolecular system are absorbed (emitted) by the Rydberg electron, which undergoes optical transitions. It is obvious that the internal-energy conversion mechanism should be also operative for many other inelastic processes in atom (molecule)–Rydberg-atom collisions (e.g., l mixing, ionization, electronic-to-vibrational energy transfer, etc.), provided the conditions for resonant energy exchange are met. We have considered in the present paper the n-changing processes in the discrete spectrum, since at $v \ll v_n$ they cannot be properly described either by the Fermi's mechanism or by using the semiclassical approximation. The physical conditions at which the quasiresonant-energy exchange mechanism efficiently produce inelastic transitions in the atom–Rydberg-atom systems are, in a certain sense, opposite to those at which the Fermi's mechanism works. Therefore these two mechanisms should be considered complementary.

We have succeeded in simplifying the problem of inelastic processes in atom–Rydberg-atom collisions by introducing the decay approximation, i.e., by neglecting the cascading and other higher-order transitions. In this approximation, which is essentially based on the dipole approximation for the interaction of the Rydberg electron with the inner subsystem $A^+ + A$, the excitation and deexcitation processes in the system become decoupled. The decay approximation presumes that the total decay probability of the initial state is not too high; i.e., we are not too far beyond the conditions where the Born approximation is valid. Our final results on the inelastic transition probabilities are in fact a sort of properly normalized Born approximation.

In our treatment, especially in the procedure of determination of the normalization coefficients $d^{(u,g)}_{nn'}$, we have essentially used the condition $|\Delta n|/n \ll 1$. This condition implies that the group of Rydberg levels around n, within which we calculate the transition probabilities, is considered part of an equidistant energy spectrum. This means that the initial Rydberg level should be rather high (in the case of hydrogen $n \gtrsim 15$, for example). The use of any unsymmetrized form of the normalization coefficients $d^{(u,g)}_{nn'}$ will introduce an error in the $P_{nn'}$ probabilities of the order of $|\Delta n|/n$. However, as we have seen at the end of Sec. V C, the errors introduced in the total decay probability P_n are only of $O(|\Delta n|^2/n^2)$, and therefore the total decay cross sections of the present theory can be reliable even for the low-lying part of the Rydberg spectrum. For nonhydrogenic atoms, however, the problem of the transitions between the low-lying Rydberg states becomes complicated by the effects of the quantum defect.

A concluding remark we would like to make concerns the efficiency of the inelastic transitions in the region of small impact parameters. For $\rho \ll \rho_{nn'} \sim R_{nn'}$ the asymptotic method, applied in the present paper for description of the electronic motion in the subsystem $A^+ + A$, loses its validity. In other words important contributions to the inelastic transition amplitude in this region come from the angular component of the dipole matrix element. Its inclusion in the treatment represents an overestimation of the accuracy of the asymptotic method. However, in the velocity region considered in the present work and for Rydberg states not particularly high (say, $n \lesssim 50$), it cannot be expected that the rotational transitions will prevail over those caused by the radial part of the dipole matrix element. Therefore, as in the theory of the resonant charge transfer at low energies, the introduction of a critical impact parameter ρ_{on} (the so-called "radius" of the inelastic process) such that for $\rho \leq \rho_{on}$ the process takes place with constant probability seems to be meaningful. This idea lies in the basis of the so-called "dense-target" approximation or "absorbing-sphere" models of atomic collision theory.

ACKNOWLEDGMENT

We would like to express our gratitude to Professor I. C. Percival for bringing to our attention the symmetry properties of the coefficients $d^{(g,u)}_{nn'}$ and their connection with the detailed-balance principle.

APPENDIX A

The adiabatic energy splitting of the symmetrical and antisymmetrical states Σ_g^+ and Σ_u^+ of the quasimolecular system $A^+ + A$ at large distances $(\gamma R \gg 1)$ has the form[10]

$$\omega(R) = C^2 R^{2/\gamma - 1} \exp(-\gamma R - 1/\gamma)\,, \tag{A1}$$

where C is a "normalization" constant in the asymptotic form of the radial part of the electron wave function.

For large values of the impact parameter $(\gamma\rho \gg 1)$ and for $R \sim \rho$ [see Eqs. (4) and (6)], the internuclear distance $R(t) = [\rho^2 + (vt)^2]^{1/2}$ can be expanded in a Taylor series around the distance of the closest approach. Retaining only the first two terms in such an expansion, $\omega(R)$ can be obtained in the form

$$\omega(\rho, t) = \omega_\rho \exp(-\gamma v^2 t^2 / 2\rho)\,, \tag{A2}$$

where

$$\omega_\rho \equiv \omega(\rho) = \omega(R)\,|_{R=\rho}\,.$$

The phases $\eta(t)$ and η_0 defined by Eqs. (11) can be now put in the form

$$\eta(t) = \omega_\rho \int_0^s \exp(-s^2) ds\,, \quad \eta_0 = \frac{\omega_\rho}{v}\left(\frac{\pi\rho}{2\gamma}\right)^{1/2}\,, \tag{A3}$$

where

$$s = vt(2\rho/\gamma)^{-1/2}\,. \tag{A4}$$

The phases $\Delta\eta^{(\mp)}(t)$, defined by Eqs. (14) and (19), can now be written in a unified form $(|t^{(-)}| = t^{(+)})$:

$$\Delta\eta^{(\pm)} = \chi_\rho \int_{|s|}^{\infty} \exp(-s^2) ds\,, \quad \chi_\rho = \frac{\omega_\rho}{v}\left(\frac{2\rho}{\gamma}\right)^{1/2}\,. \tag{A5}$$

Majorizing the erfc$(|s|)$ function appearing in (A5),[19] we obtain the following inequality:

$$\Delta\eta^{(\pm)} \leqslant \eta_0 \frac{\exp(-s^2)}{\pi^{1/2}[\,|s| + (s^2 + 4/\pi)^{1/2}]}\,. \tag{A6}$$

It can be easily verified that for $\rho_{\tilde{n}\tilde{n}'} \sim R_{\tilde{n},\tilde{n}'}$, defined by the condition $\omega(\rho_{\tilde{n}\tilde{n}'}) = |\omega_{\tilde{n},\tilde{n}'}|$, the inequality $\Delta\eta^{(\pm)} \ll 1/(\gamma\rho_{\tilde{n}\tilde{n}'})$ is satisfied already for $s \lesssim \sqrt{2}$ even for η_0 of the order of unity.

APPENDIX B

We estimate here the integral $\mathcal{J}_{nn'}$, defined by Eq. (34). In terms of the variable s [see (A4)] and using the notation

$$\chi_\rho = \frac{\omega_\rho}{v}\left(\frac{2\rho}{\gamma}\right)^{1/2}\,, \quad \chi_{nn'} = \frac{\omega_{nn'}}{v}\left(\frac{2\rho}{\gamma}\right)^{1/2}\,, \tag{B1}$$

$\mathcal{J}_{nn'}$ can then be written in the form

$$\mathcal{J}_{nn'} = \tfrac{1}{2}\chi_\rho \int_{s^{(-)}}^{s^{(+)}} \exp\{-s^2 \pm i[\,|\chi_{nn'}|s - \eta(s)]\} ds\,, \tag{B2}$$

where

$$\eta(s) = \chi_\rho \int_0^s \exp(-s^2) ds \tag{B3}$$

and $s^{(\pm)}$ corresponds to $t^{(\pm)}$. Since the integral in (B2) contains symmetrical limits $(|s^{(-)}| = s^{(+)})$, it is evident that the sign in front of the phase function $\varphi^{(-)}(s) = [\,|\chi_{nn'}|s - \eta(s)]$ plays no role in the calculations. Therefore we consider it as positive.

Taking into account that $\Delta\eta^{(\pm)} \ll 1$ for $s \gtrsim 1$, we may set $|s^{(-)}| = s^{(+)} \approx 1$. If we now expand the function $\eta(s)$ in a power series around $s = 0$ and keep the first two terms only, it becomes evident that the phase function $\varphi^{(-)}(s)$ can be replaced by an approximate one,

$$\tilde{\varphi}(s) = \alpha s + \tfrac{1}{3}\beta s^3\,. \tag{B4}$$

By appropriate choices for the constants α and β, the function $\tilde{\varphi}(s)$ can give a good representation of the true phase function in the interval $(s^{(-)}, s^{(+)})$. In the region outside of this interval, which does not contribute to $\mathcal{J}_{nn'}$, the function $\tilde{\varphi}(s)$ increases rapidly enough to allow one to expand the integration region in (B2) to infinity. Keeping these remarks in mind, expression (B2) for $\mathcal{J}_{nn'}$ can be written in the form

$$\mathcal{J}_{nn'} = \tfrac{1}{2}\chi_\rho \int_{-\infty}^{+\infty} \exp[-s^2 + i(\alpha s + \tfrac{1}{3}\beta s^3)] ds\,. \tag{B5}$$

Expanding the function $\exp(-s^2)$ into a Fourier integral and then changing the order of integration in (B5), we obtain

$$\mathcal{J}_{nn'} = \tfrac{1}{2}\pi^{1/2}\chi_\rho \int_{-\infty}^{+\infty} \exp(-a\lambda^2) \mathrm{Ai}[-(\lambda - b)] d\lambda\,, \tag{B6}$$

where

$$a = \tfrac{1}{4}\beta^{2/3}\,, \quad b = \alpha\beta^{-1/3}\,, \tag{B7}$$

and

$$\mathrm{Ai}(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \exp[i(tx + \tfrac{1}{3}t^3)] dt \tag{B8}$$

is the Airy function. The integral in (B6) can be calculated exactly,[20] and one gets

$$\mathcal{J}_{nn'} = \tfrac{1}{2}\pi a^{-1/2}\chi_\rho \exp\left[\frac{2}{3}\left(\frac{1}{4a}\right)^3 + \frac{b}{4a}\right] \mathrm{Ai}\left[\left(\frac{1}{4a}\right)^2 + b\right]. \tag{B9}$$

We choose the constants α and β in (B4) from the conditions

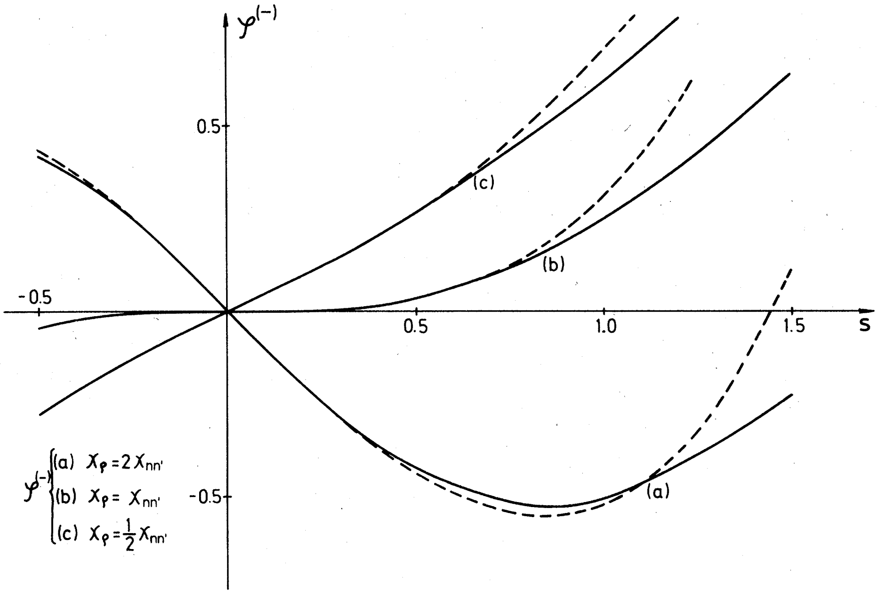

FIG. 7. Comparison of exact phase function $\varphi^{(-)}(s)$ (solid curves) and approximate phase function $\tilde{\varphi}(s)$ (dashed curves) for three values of $\chi_\rho/|\chi_{nn'}|$.

$$\tilde{\varphi}'(0)=\varphi'^{(-)}(0), \quad \tilde{\varphi}'(s_0)=\varphi'^{(-)}(s_0), \tag{B10}$$

where $s_0^2=\ln(\chi_\rho/|\chi_{nn'}|)$. These conditions provide a correct behavior of the phase function $\tilde{\varphi}$ in the region of $s=0$ and in the resonance region.

The values of α and β, determined from conditions (B10), have the form

$$\alpha=-(\chi_\rho-|\chi_{nn'}|)\equiv-\Delta\chi, \tag{B11}$$

$$\begin{aligned}\beta&=\frac{\Delta\chi}{\ln(\chi_\rho/|\chi_{nn'}|)}\equiv\frac{1}{\mu}, \quad \Delta\chi\geqslant 0\\ &=\chi_\rho, \quad \Delta\chi\leqslant 0.\end{aligned} \tag{B12}$$

Inserting (B11) and (B12) into (B7) and using then (B9), we obtain the expression for $\mathcal{I}_{nn'}$ given by Eqs. (40) and (41).

In order to investigate the degree of accuracy of the approximation (B4) with respect to the correct phase function $\varphi^{(-)}$ in the region $(s^{(-)},s^{(+)})$, we have numerically calculated $\varphi^{(-)}(s)$ for three values of the ratio $\chi_\rho/|\chi_{nn'}|$. ($\chi_{nn'}$ is taken to be unity.)

The comparison of $\varphi^{(-)}(s)$ with $\tilde{\varphi}(s)$ is given in Fig. 7 (the full curves represent $\varphi^{(-)}$), where it can be seen that in the region of s giving the main contribution to $\mathcal{I}_{nn'}$ the approximate phase $\tilde{\varphi}$ represents $\varphi^{(-)}$ quite well. We note that the maximum of the maximum of the $P_{nn'}$ probability corresponds to a phase function $\varphi^{(-)}$ lying somewhere between cases (a) and (b) in Fig. 7. For this phase function the approximation (B4) is even more successful than for the (a) and (b) cases. The phase function $\varphi^{(-)}$ (c) in Fig. 7 corresponds to the case of the energetically inaccessible region for the $n\to n'$ transition.

---

[1] J. E. Bayfield, in *The Physics of Electronic and Atomic Collisions: Invited Lectures and Progress Reports given at the 9th International Conference on the Physics of Electronic and Atomic Collisions*, edited by J. Risley and R. Geballe (University of Washington, Seattle, 1975), p. 726.

[2] R. F. Stebbings, in *Electronic and Atomic Collisions: Invited Papers*, edited by G. Watel (North-Holland, Amsterdam, 1978), p. 549.

[3] I. C. Percival, in *Electronic and Atomic Collisions: Invited Papers*, edited by G. Watel (North-Holland, Amsterdam, 1978), p. 569.

[4] N. V. Karlov and A. M. Prokhorov, Usp. Fiz. Nauk 118, 583 (1976) [Sov. Phys. Usp. 19, 285 (1976)].

[5] J. R. Hiskes, J. Nucl. Energy C 8, 577 (1966).

[6] E. Fermi, Nuovo Cimento 11, 157 (1934).

[7] M. Matsuzawa, J. Electron Spectrosc. Relat. Phenom. 4, 1 (1974).

[8] J. I. Gersten, Phys. Rev. A 14, 1354 (1976).

[9] A. Omont, J. Phys. (Paris) 38, 1343 (1977).

[10] B. M. Smirnov, *Asymptotic Methods in Theory of Atomic Collisions* (Atomizdat, Moscow, 1973) (in Russian).

[11] M. R. Flannery, Ann. Phys. (N.Y.) 61, 465 (1970); 79, 480 (1973).

[12] B. M. Smirnov, in *The Physics of Electronic and Atomic Collisions: Invited Lectures and Progress Reports given at the 9th International Conference on the Physics of Electronic and Atomic Collisions*, edited by J. Risley and R. Geballe (University of Washington, Seattle, 1975), p. 701.

[13] R. K. Janev, lecture delivered at the 7th All-Union Conference on Electronic and Atomic Collisions, Petrozavodsk, USSR, 1978 (unpublished).
[14] E. de Prunnele and J. Pascale, J. Phys. B (in press).
[15] R. E. Olson, Phys. Rev. A 15, 631 (1977).
[16] V. A. Smirnov and A. A. Mihailov, Opt. Spektrosk. 30, 984 (1971) [Opt. Spectrosc. (USSR) 5, 525 (1971)].
[17] H. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems* (Springer, Berlin, 1957).
[18] R. K. Janev, A. A. Mihailov, and G. S. Petrović, *The Physics of Ionized Gases* (Institute of Physics, Beograd, Yugoslavia, 1978), p. 115.
[19] M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).
[20] Y. B. Band and K. F. Freed, J. Chem. Phys. 63, 3382 (1975).