Stimulated electron-ion (-atom) recombination at a resonance

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The problem of stimulated recombination at a resonance is investigated by a time-dependent, nonperturbative approach. The number of pairs recombined by a laser pulse is computed as a function of the intensity, of the pulse duration, and of the initial electron-energy distribution (as well as of the parameters which characterize the atomic resonance and its field-induced coupling to the final bound state). The role of spontaneous emission (or other paths) from the recombined state (if it is excited) is also discussed. Numerical results are given including an example of recombination to the ground state in the Sr atom.

I. INTRODUCTION

The process of electron-ion (-atom) recombination has been traditionally considered as important for plasma physics and astrophysics.[1] It can be written as

$$A^+ (A)+e^-\rightarrow A\ (A^-)+h\nu$$

and the spontaneously emitted photon acts only as a third body for carrying out the excess energy. The initial and final states have not been indicated, since, in a plasma, ions (atoms) can be initially in a mixed state and even if the ions were in a pure initial state they can recombine to a variety of excited states. Furthermore, the electrons are usually far from being monoenergetic. In this situation one can only apply a kinetic treatment[2] using suitable rate constants to compare the relative importance of recombination with respect to other competing processes.

Spontaneous recombination is of crucial importance in astrophysics. However, the measurement of the isolated processes in a laboratory is difficult due to its small cross section. The consequences of utilizing lasers on stimulated processes are the motivation of this work. The availability of laser sources has recently produced renewed interest in photoionization experiments and in the study of the continuum part of the atomic spectrum. In this situation it seems natural to investigate the possibility of increasing the probability of the recombination process by laser stimulation. This has been the subject of a previous paper.[3] Here we extend the treatment and include the possibility of recombination via an autoionization resonance, which should significantly affect and further increase the probability of capture.

We study here a state-to-state recombination in the presence of a monochromatic and monomode laser field, assuming an initial electron-energy distribution. Our treatment is fully quantum mechanical (in the sense that we solve the Liouville equation of motion for the population of the recombined state), which is completely different from the traditional rate approach. It should be more adequate to describe the recombination in dilute systems, where the electron-ion (-atom) collision takes place undisturbed by other collisions in a coherent electromagnetic (e.m.) field.

II. THEORY

Let us first introduce the basic assumption of the present treatment. From now on we refer only to electron-ion recombination, keeping in mind that the treatment is also valid for electron-atom attachment.

(i) The monomode laser field is assumed to be a rectangular pulse of duration τ.

(ii) At time $t=0$, when the pulse is switched on, the electron-ion system is assumed to be described by a density-matrix diagonal in the basis set of eigenstates for the recombined system, i.e., for the neutral atom (in the following this point is discussed in more detail).

(iii) We assume that stimulated recombination takes place toward a single bound state $|b\rangle$, well separated from other bound states. Hence, from the point of view of the e-ion system, we must study a continuum-bound transition. The continuum supports a resonance, which is also supposed to be well separated from other resonances.

The Hamiltonian is written as (the notation is self-explaining; a.u. are used)

$$H=H_{\rm at}+H_{\rm rad}+V_L\ , \tag{1}$$

$$H_{\rm rad}=a^{\dagger}a\omega\ , \tag{2}$$

$$V_L=i\left[\frac{\omega}{2\epsilon_0 V}\right]^{1/2}(a-a^{\dagger})d_z\ . \tag{3}$$

(We have assumed that the radiation is linearly polarized along the z axis. The component of the dipole moment is d_z.) Due to assumption (ii) it is convenient to introduce directly the Hamiltonian for the atom, in place of the one for the interacting e-ion system. This distinction is immaterial at this level but becomes important when we go to a spectral representation of the Hamiltonian. In fact, in the resonant approximation and neglecting continuum-continuum transitions, one may write

$$H=|b,(n+1)\omega\rangle\langle b,(n+1)\omega|[E_b+(n+1)\omega]+\int|\vec{k},n\omega\rangle\langle\vec{k},n\omega|(E_k+n\omega)\rho(\vec{k})d\vec{k}$$
$$+\left[\int\langle\vec{k},n\omega|V_L|b,(n+1)\omega\rangle|\vec{k},n\omega\rangle\langle b,(n+1)\omega|\rho(\vec{k})d\vec{k}+\text{H.c.}\right] \tag{4}$$

[the resulting level and coupling scheme is schematized in Figs. 1(a) and 1(b)]. Here $|\vec{k}\rangle$ is a continuum eigenstate of $H_{\rm at}$.

In principle a complete set of scattering states can be used here. It is, however, more convenient to choose the same set here as is used in expressing the initial conditions. This has not been specified in (ii). The natural choice is a set having an incoming-wave behavior characterized by the momentum $\vec{k}$. Hence one can make the identification $|\vec{k}\rangle\equiv|\vec{k}_+\rangle$.

The expression for the number of recombined pairs at time t is (see Appendix A for the derivation)

$$N_{\rm rec}(t)=\frac{n_i n_e}{V}\int P_{b\vec{k}}(t)p(\vec{k})d\vec{k}\ , \tag{5}$$

where

$$P_{b\vec{k}}(t)\equiv|\langle b,(n+1)\omega|U(t)|\vec{k},n\omega\rangle|^2\ . \tag{6}$$

In Eq. (5) n_i (n_e) is the number of ions (electrons) in the interaction volume V and $p(\vec{k})$ is the initial electron distribution:

$$\int p(\vec{k})d\vec{k}=1\ . \tag{7}$$

The probability $P_{b\vec{k}}(t)$ will be calculated in the following by a nonperturbative approach. For weak intensity of the inducing field, however, one can anticipate that

$$P_{b\vec{k}}\propto I\propto\frac{n_{\rm ph}}{V}\ .$$

Then Eq. (5) gives, in the weak-field limit, what is expected for a three-body reaction (electron-ion-photon):

$$\frac{N_{\rm rec}(t)}{V}\propto\frac{n_i}{V}\frac{n_e}{V}\frac{n_{\rm ph}}{V}\ . \tag{8}$$

Equation (5) can be generalized to include spontaneous emission from the bound state $|b\rangle$ (if it is not the ground state). First the probability $P_{b\vec{k}}(t)$ is computed by considering that spontaneous emission contributes $\gamma_{\rm sp}$ to the width of $|b\rangle$ and then adding a further term to Eq. (5). This should take into account that all the population, which decays from state $|b\rangle$ by spontaneous emission in the time interval 0–t, can be considered recombined irreversibly (since it cannot undergo further reionization). The required more general expression is

$$N_{\rm rec}(t)=\frac{n_i n_e}{V}\left[\int P_{b\vec{k}}(t)p(\vec{k})d\vec{k}+\gamma_{\rm sp}\int_0^t dt'\left[\int P_{b\vec{k}}(t')p(\vec{k})d\vec{k}\right]\right]\ . \tag{9}$$

This is the basic equation. One has now to compute $P_{b\vec{k}}(t)$ and to specify $p(\vec{k})$. For our purpose it is now useful to decompose $P_{b\vec{k}}(t)$ in spherical waves. One has

$$|\vec{k}\rangle\equiv|\vec{k}_+\rangle=\sum_{l,m}Y_{lm}(\hat{k})|k,l,m\rangle\ , \tag{10}$$

where $|k,l,m\rangle$ are simultaneous eigenstates of $H_{\rm at}$, the angular momentum, and its projection along the z axis. They are δ normalized, i.e.,

$$\langle k,l,m|k',l',m'\rangle=\delta(k-k')\delta_{ll'}\delta_{mm'}\ .$$

The electron distribution is also expanded in spherical waves:

$$p(\vec{k})=\sum_{l,m}h_{lm}(k)Y_{lm}(\hat{k})\ . \tag{11}$$

From Eqs. (6) and (10) one has

$$P_{b\vec{k}}(t)=\sum_{\substack{l,m,\\ l',m'}}Y^*_{lm}(\hat{k})Y_{l'm'}(\hat{k})\times\langle b,(n+1)\omega|U(t)|k,l',m';n\omega\rangle\times\langle k,l,m;n\omega|U(t)|b,(n+1)\omega\rangle\ . \tag{12}$$

From now on we will stop indicating the photon states with the bras and kets for the sake of simplicity. This should cause no ambiguity in what follows. We insert the above result in Eq. (9) and have

$$N_{\rm rec}(t)=\frac{n_i n_e}{V}\sum_{l,m}\sum_{l',m'}\sum_{l'',m''}\left[F(t,l,m,l',m',l'',m'')+\gamma_{\rm sp}\int_0^t dt'F(t',l,m,l',m',l'',m'')\right]\ , \tag{13a}$$

where

$$F(t,l,m,l',m',l'',m'')=\int \langle b \mid U(t) \mid k,l',m' \rangle \langle k,l,m \mid U(t) \mid b \rangle h_{l''m''}(k) Y^{*}_{lm}(\hat{k}) Y^{(\hat{k})}_{l'm'} Y_{l''m''}(\hat{k}) d\vec{k} \ . \tag{13b}$$

The above expression looks quite complicated but, as we will see, it simplifies considerably for the kind of experiment we discuss. Here we imagine a scenario in which electrons and ions are produced *in situ* by multiphoton ionization of a neutral atom. This can be achieved by a strong laser pulse shining a cell. Immediately after this ionization the other laser source is switched on. The frequency is appropriately chosen to stimulate recombination to a specific bound state. In this situation, which allows one to have a large concentration of electrons and ions in contrast to a beam experiment, it is appropriate to take $p(\vec{k})$ as spherically symmetric and Eq. (13a) becomes much simpler, due to the orthogonality of spherical harmonics:

$$N_{\rm rec}(t)=\frac{n_i n_e}{V}\sum_{lm}\left[\int h(k) \mid \langle b \mid U(t) \mid k,l,m \rangle \mid^2 dk+\gamma_{\rm sp}\int_0^t dt' \left[\int h(k) \mid \langle b \mid U(t') \mid k,l,m \rangle \mid^2 dk\right]\right] . \tag{14}$$

The distribution $h(k)$ which is to be identified with the $l=0$, $m=0$ component in the expansion (11) is normalized, i.e.,

$$\int h(k)k^2 dk=1 \ . \tag{15}$$

In choosing $h(k)$ one should take into account the various mechanisms of broadening for the initial energy of the electrons. Equation (14) gives us the total number of atoms formed by the stimulated recombination for an initial electron-energy distribution which is spherically symmetric. Due to the angular momentum selection rules, the sum in Eq. (14) reduces to just one or two terms. In the following, for simplicity, we consider recombination to a bound state of S type. In this case Eq. (14) becomes

$$N_{\rm rec}(t)=\frac{n_i n_e}{V}\left[\int h(k) \mid \langle b \mid U(t) \mid k,l=1,m=0 \rangle \mid^2 dk+\gamma_{\rm sp}\int_0^t dt' \left[\int h(k) \mid \langle b \mid U(t) \mid k,l=1,m=0 \rangle \mid^2 dk\right]\right] . \tag{16}$$

The next step concerns the evaluation of the transition amplitude, i.e., $\langle b \mid U(t) \mid k,l,m \rangle$. This amounts to solving the Schrödinger equation. An approach based on the resolvent-projection operator has been found to be particularly convenient for problems involving the continuum.[4] The resonance is handled by considering that it originates from a Fano diagonalization of a state embedded in the continuum.[5] We decide to work in the situation before the diagonalization. In this way one has two bound states coupled to the continuum by the laser field V_L and the Coulombic perturbation V_C, giving rise to the autoionization. This is schematized in Fig. 1(c). The continuum is now flat and it can be easily projected out. Finally one has to handle a 2×2 effective Hamiltonian. The details of the derivation are given in Appendix B. The final result is

$$\mid \langle b \mid U(t) \mid k,l,m \rangle \mid^2 = \left| \frac{\epsilon_1+i\gamma_a}{(\epsilon_1-\epsilon_2)(\epsilon_1-\epsilon_k)} e^{-i\epsilon_1 t} - \frac{\epsilon_2+i\gamma_a}{(\epsilon_1-\epsilon_2)(\epsilon_2-\epsilon_k)} e^{-i\epsilon_2 t} + \frac{\epsilon_k+i\gamma_a}{(\epsilon_k-\epsilon_1)(\epsilon_k-\epsilon_2)} e^{-i\epsilon_k t} \right|^2 \left[C+\frac{A-B\epsilon_k}{\epsilon_k^2+\gamma_a^2} \right] , \tag{17}$$

where

$$A=\frac{1}{\pi}\gamma_a(q^2-1)\gamma_{ab}^2 \ ,$$

$$B=\frac{2}{\pi}\gamma_{ab}^2 q \ , \tag{18}$$

$$C=\frac{1}{\pi}\gamma_{ab} \ ,$$

and q is the Fano parameter. ϵ_1 and ϵ_2 are the complex eigenvalues of the effective Hamiltonian

$$H^{\rm eff}=\begin{bmatrix} E_b+\omega-i\gamma_b+\delta_b & -\gamma_{ab}(q+i) \\ -\gamma_{ab}(q+i) & -i\gamma_a+\delta_a \end{bmatrix} . \tag{19}$$

Here γ_b and δ_b are the level broadening and the shift of the recombined state due to the laser-induced coupling to the continuum and γ_{ab} is the effective coupling between the state $\mid a \rangle$ giving rise to the resonance and the bound state $\mid b \rangle$ (see the Appendix).

Equation (17) describes the stimulated recombination taking into account that both the bound state $\mid b \rangle$ and the continuum near the resonance may be strongly distorted by the e.m. field. The mechanism for this distortion involves all-order coupling of the resonance to the bound state by the e.m. field neglecting free-free transitions.

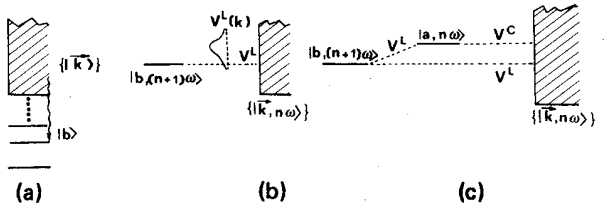

FIG. 1. (a) shows the schematic levels of the atom and the bound-continuum transition giving rise to the stimulated recombination. (b) shows the level and the coupling scheme (in the resonant approximation) in the second-quantization formalism. The laser-induced bound-continuum coupling is also depicted. The bump indicates the presence of the autoionizing resonance. In (c) the bumps have been eliminated by going back to the states before the Fano diagonalization. One has now two bound states coupled (the coupling function is now flat) to the continuum, due both to the laser and to the Coulombic interaction.

From the expression of the effective Hamiltonian, Eq. (19), one concludes that the distortion is negligible (and we call this the weak-field limit) if

$$\frac{|H_{12}^{\text{eff}}|^2}{|H_{11}^{\text{eff}}-H_{22}^{\text{eff}}|}=\frac{\gamma_{ab}^2(q^2+1)}{[\Delta^2+(\gamma_b-\gamma_a)^2]^{1/2}}\ll 1\ , \tag{20}$$

where

$$\Delta=E_1+\omega+\delta_b-\delta_a\ . \tag{21}$$

Equations (9) and (17) are the main results of this paper. To get some insight into Eq. (17) let us consider the small detuning case, i.e., $\Delta\sim 0$. For the recombination to an S state one has (see Appendix) $\gamma_{ab}^2=\gamma_b\gamma_a$. Hence the relation (20) becomes

$$\frac{\gamma_b\gamma_a(q^2+1)}{|\gamma_b-\gamma_a|}\ll 1\ . \tag{22}$$

This means that a significant distortion is expected only when γ_b becomes close to γ_a, i.e., to the width of the unperturbed resonance. γ_b can be written as a sum of two terms,

$$\gamma_b=\gamma_b^{\text{sp}}+\gamma_b^{\text{ion}}\ . \tag{23}$$

The first one comes from the spontaneous emission and is field independent. The second is due to the field-induced ionization and therefore increases linearly with the intensity (for one-photon recombination). The range of validity of the weak-field limit depends on the particular system one is studying. Much of the well-known autoionizing resonances are in the range $10^{-12}\ \text{sec}^{-1}\lesssim\gamma_a\lesssim 10^{14}\ \text{sec}^{-1}$. The rate constant for spontaneous emission is usually several orders of magnitude less, i.e., $\gamma^{\text{sp}}\sim 10^9\ \text{sec}^{-1}$. Since for the one-photon ionization one has roughly

$$\gamma_b^{\text{ion}}(\text{sec}^{-1})\sim I(\text{W cm}^{-2}) \tag{24}$$

one can conclude that in many cases the weak-field limit continues to be valid for intensities up to $10^{11}\ \text{W cm}^{-2}$. It is to be noted that the new high-resolution devices[6] permit us to distinguish resonances as sharp as $10^6\ \text{sec}^{-1}$. For such resonances a significant distortion takes place at much lower field intensity (in the megawatt region). The weak-field limit is easily obtained from Eq. (17). By setting

$$\epsilon_1=E_b+\omega-i\gamma_b\ ,\qquad \epsilon_2=-i\gamma_a \tag{25}$$

(i.e., the unperturbed energies) one has for the probability

$$|\langle b\,|\,U(t)\,|\,k,l,m\rangle|^2 = \frac{1+e^{-2\gamma_b t}-2e^{-\gamma_b t}\cos(E_b+\omega-\epsilon_k)t}{(E_b+\omega-E_k)^2+\gamma_b^2}\times\left[C+\frac{A-B\epsilon_k}{\epsilon_k^2+\gamma_a^2}\right]\ . \tag{26}$$

This coincides with the expression used previously[3] apart from the second factor on the right-hand side (rhs), which accounts for the resonance. For short times this gives a t^2 dependence. If we first integrate over a broad electron distribution and then develop in powers of t, we obtain a linear dependence for short times. The situation is analogous to what one has for the transition between two bound states due to polychromatic light. In both cases one has a continuum to bound transition. In the bound two-level system the continuum is due to the photon modes, whereas in the present case the continuum is that of the electron (we have only one photon mode).

III. NUMERICAL EXAMPLES

Using Eqs. (9) and (17) (the main results of this paper) one can compute the number of recombined pairs produced by a given rectangular pulse of duration τ. Equation (14) is a special case of Eq. (9) assuming a spherical electron distribution. Equation (17), which will be used for the numerical examples, is a particular case of Eq. (14), corresponding to the recombination to an S state.

Equation (17) is perfectly general and one need only specifically consider the relation connecting the widths γ_b, γ_a and the parameter γ_{ab} appearing in the extradiagonal matrix element, which depends on the symmetry of the bound state. For the recombination to an S state one has (see Appendix B)

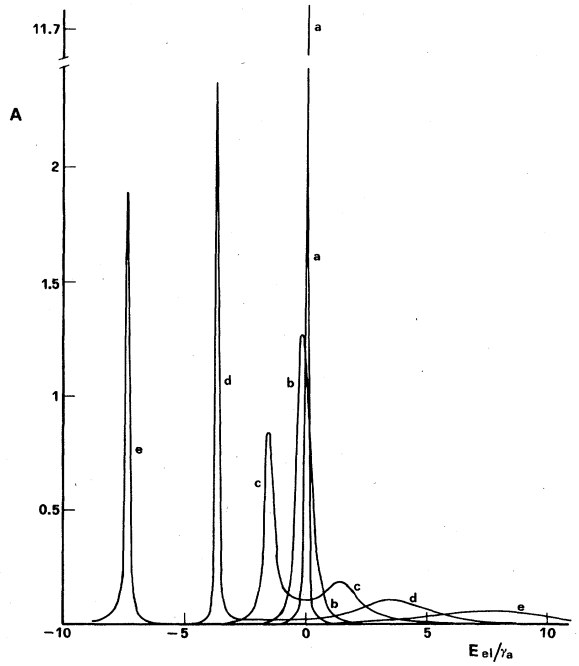

FIG. 2. The quantity $A=N_{\text{rec}}(\tau)V/(n_i n_e)$ (proportional to the number of recombined pairs produced by a pulse whose duration is $\tau=10^4/\gamma_a$) is plotted against the energy of the distribution for electrons (see the text). We treat the case of a resonance in the Sr spectrum for which $q=-5.2$. The various curves refer to different values of the ratio $\gamma_b^{\text{ion}}/\gamma_a$, which is proportional to the intensity (for further details see the text). Curve a, $\gamma_b^{\text{ion}}/\gamma_a=10^{-3}$; curve b, $\gamma_b^{\text{ion}}/\gamma_a=10^{-2}$; curve c, $\gamma_b^{\text{ion}}/\gamma_a=10^{-1}$; curve d, $\gamma_b^{\text{ion}}/\gamma_a=2$.

$\gamma_{ab}^2=\gamma_a\gamma_b$.

In order to illustrate the main features of the present theory we give now some examples, assuming that the laser is tuned at resonance, i.e., $\Delta=0$, Eq. (21). First we consider the recombination to the ground state, so that the spontaneous emission is absent. We give the results for the Sr atom, assuming that the electron energy is close to the $^1P_1^o$ resonance (resonance no. 3 in Ref. 7). For that case $q=-5.2$, $\gamma_a=78\times10^{12}$ sec^{-1}, and the laser wavelength must be 1970 Å. Figure 2 gives the quantity $A=N_{\rm rec}(\tau)V/(n_in_e)$ as a function of the electron energy assuming that the spherical electron distribution is δ-like in energy and $\tau=100/\gamma_a$. Different curves refer to different intensities. The latter is not given directly but through the widths ratio $\gamma_b^{\rm ion}/\gamma_a$ (which is proportional to the intensity). Furthermore, γ_a (i.e., the width of the unperturbed resonance) is taken as the energy unit. In Fig. 3 the spherical electron-energy distribution is broad, i.e.,

$$h(k)k^2=\begin{cases}\dfrac{1}{2s}, & E_a-s<\epsilon_k<E_a+s\\ 0, & \text{otherwise}\end{cases}$$

and $s\gg\gamma_a$. In this case

$$P=\frac{N_{\rm rec}(\tau)V}{n_in_e}(2s)$$

is plotted in Fig. 2, as a function of $\gamma_b^{\rm ion}/\gamma_a$ in a log-log scale.

Looking at Fig. 2 one sees that at the weak intensity the recombination takes place only when the total energy is conserved, i.e., one has essentially a δ-like peak at the electron energy for which there is resonance with the energy of the bound state plus the photon (curve *a*). By increasing the intensity one observes first a power broadening (curve *b*) and then also the dynamical Stark splitting (curves *c*—*e*). It is worthwhile to notice that for weak intensity (curve *a*) or for sufficiently high intensity (curve *d*) one has very sharp peaks in the number of recombined pairs for a suitably chosen electron energy (at the center of the resonance for curve *a* and near the left peak in curve *d*). As already pointed out, the above curves are calculated for a δ distribution of the electron energy, which is rather unrealistic. Even if one has nearly monochromatic electrons, in practice one has to multiply by a distribution with a small but finite width and integrate. If

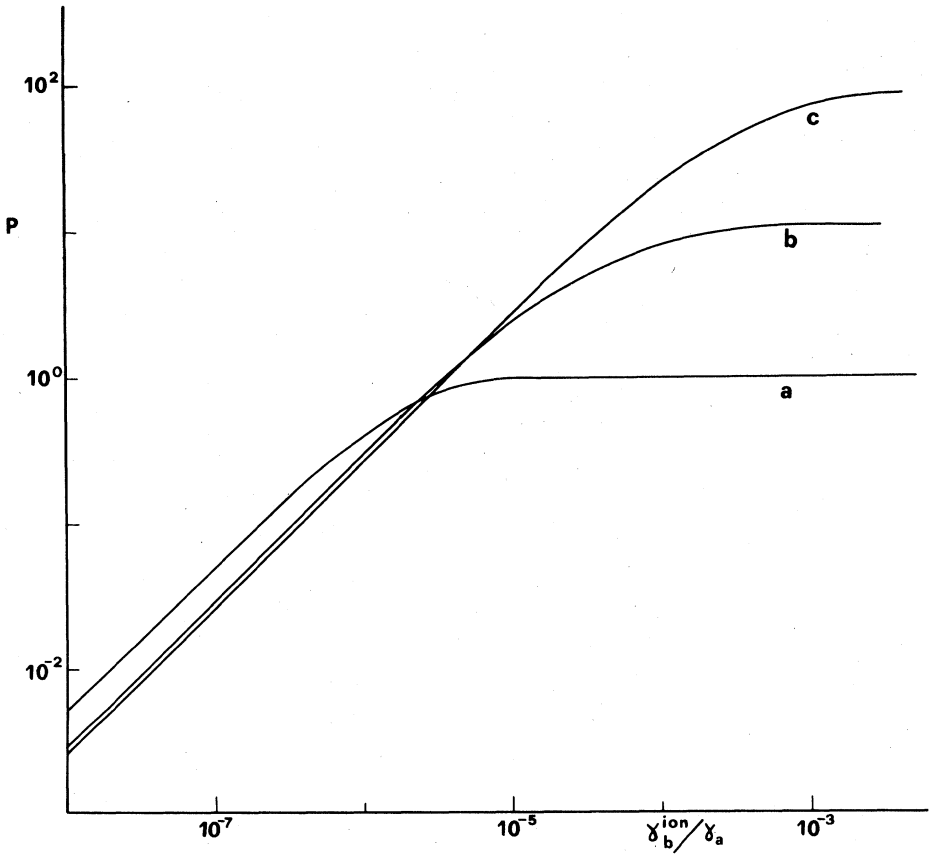

FIG. 3. The quantity $P=N_{\rm rec}(\tau)V/(n_in_e)$ (proportional to the number of recombined pairs produced by a pulse whose duration is $\tau=10^4/\gamma_a$) is plotted against the ratio $\gamma_b^{\rm ion}/\gamma_a$, in a log-log scale. The different curves refer to different values of the width of state $|b\rangle$ due to spontaneous emission, i.e., $\gamma^{\rm sp}$. The other parameters are the same as for Fig. 2. Curve *a*, $\gamma^{\rm sp}=0$; curve *b*, $\gamma^{\rm sp}=10^{-3}\gamma_a$; curve *c*, $\gamma^{\rm sp}=10^{-2}\gamma_a$.

this is done the peaks are smoothed out more or less depending on the relative width of the peak with respect to the electron distribution. The very sharp peak for the weak field (e.g., curve *a*), for example, tends to disappear more easily if the effect of a realistic electron distribution is taken into account. Another interesting point to notice is the nonmonotonic behavior of the left peak heights as a function of intensity.

In Fig. 3 the electron distribution is broad. The various parameters are the same as in Fig. 2 but we study here also the effect of the spontaneous emission, i.e., of the second term in the rhs of Eq. (9). Curve *a* refers to the case $\gamma^{sp}=0$. Each point in this curve corresponds to the area under a curve like those in Fig. 2. This is the only curve in the figure which refers to a specific atomic case, i.e., the case of the recombination from the previously mentioned autoionization resonance in the Sr atom, to the ground state. Here the complicated features of Fig. 2 are completely lost and the log-log plot exhibits the expected behavior. In fact, the number of recombined pairs increases first linearly with the intensity and then is saturated. The other curves *b*—*d* are built assuming an increasing value of γ^{sp} to make evident the important role of spontaneous emission in augmenting the recombination yield.

IV. CONCLUSION

We have treated the problem of stimulated electron-ion (-atom) recombination near an autoionizing resonance by considering that the interaction of the laser light with the *e*-ion system takes place coherently and for a finite time. Since the light matter interaction is handled in a nonperturbative way, we were able to include in our treatment the field-induced distortion of the continuum near the resonance.[8,4] We also investigated the role of the spontaneous emission (or, by analogy, other relaxation processes) from the recombined state in increasing the recombination yield. The influence of the width of the electron-energy distribution has been also stressed.

As a concluding remark, we note that the number of recombined pairs which has been the subject of our calculations can obviously be identified with the number of photons produced. Our results can then be utilized to investigate the possibility of obtaining photon gain from such recombination processes along the lines suggested in a previous paper.[3]

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APPENDIX A

Let us derive an expression for the number of recombined pairs at time t. We consider that our system consists of a certain number of electron-ion pairs and each pair does not interact with the others. The initial state for a given pair is written as a diagonal density matrix in the basis set of the recombined system, i.e., of the neutral atom (in a box):

$$\rho_i^{at}=\sum_{\vec{k}} P_{\vec{k}} \,|\, \vec{k}\rangle\langle \vec{k} \,|\ , \tag{A1}$$

where $P_{\vec{k}}$ is the normalized distribution.

We write (A1) as a sum since the process takes place in a finite volume, say v. The volume v cannot be identified with the interaction volume V. In fact, we are interested in a situation where many electrons and ions are simultaneously present in V and one cannot assign reasonably one electron to one ion (or vice versa) in V. We suppose that when the laser is switched on, there is a certain number of electron-ion pairs sufficiently close together, both being contained in the arbitrarily small volume v, as we assume in writing Eq. (A1). The latter is taken much smaller than the interaction volume V, so that the probability that it contains other *e*-ions pairs is essentially zero.

We now compute the probability of recombination for an *e*-ion pair in the volume v and then multiply by the number of pairs N_p which are simultaneously in a similar situation. One has

$$N_p=\left[n_i\frac{v}{V}\right]\left[n_e\frac{v}{V}\right]\left[\frac{V}{v}\right]=n_i n_e\frac{v}{V}\ , \tag{A2}$$

where n_i and n_e are the number of ions and electrons, respectively, in the volume V. The first two factors in (A2) give, respectively, the probability that an ion or an electron is in a volume v. The third factor is the number of ways the volume v can be chosen. The point is that since, as we will see, the probability of recombination is proportional to $1/v$, the arbitrary volume v disappears in the expression for the actual number of recombined pairs.

In order to derive an expression for the recombination probability, we take as the initial density matrix the following tensorial product of the atomic density matrix and the photon density matrix (in pure number state):

$$\rho(0)=\rho_i^{at}\otimes \,|\, n\omega\rangle\langle n\omega \,|\ \tag{A3}$$

and ρ_i^{at} is given in Eq. (A1).

Then the recombination probability is

$$P_{rec}(t)=\langle b,(n+1)\omega \,|\, \rho(t) \,|\, b,(n+1)\omega\rangle\ . \tag{A4}$$

The density matrix at a time t is given by

$$\rho(t)=U(t)\rho(0)U^{\dagger}(t)\ , \tag{A5}$$

where

$$U(t)\equiv e^{-iHt}\ .$$

Utilizing the Hamiltonian given in the expression (4), Eq. (A4) becomes

$$P_{rec}(t)=\sum_{\vec{k}} |\, \langle b,(n+1)\omega \,|\, U(t) \,|\, \vec{k},n\omega\rangle \,|^2 P_{\vec{k}}\ . \tag{A6}$$

Let us remember now that the states $|\,\vec{k}\rangle$ are normalized in the volume v. It is useful for our purpose to make this dependence explicit:

$$|\,\vec{k}\rangle\rightarrow\frac{1}{v^{1/2}}\,|\,\vec{k}\rangle\ . \tag{A7}$$

In the limit $v\rightarrow\infty$ the state $|\,\vec{k}\rangle$ becomes now the δ-

normalized [i.e., $\langle \vec{k} \mid \vec{k}' \rangle = \delta(\vec{k}-\vec{k}')$] continuum states (this is true for plane waves and consequently for all continuum functions since the former form a complete set). From Eq. (A6) one has

$$P_{\rm rec}(t)=\frac{1}{v}\sum_{\vec{k}} \mid \langle b,(n+1)\omega \mid U(t) \mid \vec{k},n\omega \rangle \mid^2 P_{\vec{k}} . \quad \text{(A8)}$$

The continuum limit is now obtained in the usual way $[\sum_{\vec{k}} \to v/(2\pi)^3 \int d\vec{k}]$:

$$P_{\rm rec}(t)=\frac{1}{(2\pi)^3}\int \mid \langle b,(n+1)\omega \mid U(t) \mid \vec{k},n\omega \rangle \mid^2 P(\vec{k}) d\vec{k} . \quad \text{(A9)}$$

Attention has to be paid to the correct normalization of $P(\vec{k})$, in Eq. (A9). One has

$$\sum_{\vec{k}} P_{\vec{k}}=1 \quad \text{(A10)}$$

and in the continuum limit this becomes

$$\frac{v}{(2\pi)^3}\int P(\vec{k}) d\vec{k}=1 . \quad \text{(A11)}$$

Hence

$$P(\vec{k})=p(\vec{k})\frac{(2\pi)^3}{v} \quad \text{(A12)}$$

and $p(\vec{k})$ is normalized, i.e.,

$$\int p(\vec{k}) d\vec{k}=1 . \quad \text{(A13)}$$

Equation (A9) can then be rewritten as

$$P_{\rm rec}(t)=\frac{1}{v}\int \mid \langle b,(n+1)\omega \mid U(t) \mid \vec{k},n\omega \rangle \mid^2 p(\vec{k}) d\vec{k} . \quad \text{(A14)}$$

The number of recombined pairs is obtained by multiplying Eq. (A14) by N_p which is given in Eq. (A2):

$$N_{\rm rec}(t)=\frac{n_i n_e}{V}\int \mid \langle b,(n+1)\omega \mid U(t) \mid \vec{k},n\omega \rangle \mid^2 p(\vec{k}) d\vec{k} . \quad \text{(A15)}$$

APPENDIX B

We compute here the probability amplitude

$$\langle b,(n+1)\omega \mid U(t) \mid k,l,m;n\omega \rangle \equiv U_{bk}^{lm}(t) , \quad \text{(B1)}$$

where

$$U=e^{-iHt} \quad \text{(B2)}$$

and H is the Hamiltonian in the resonant approximation, Eq. (4) [see also Fig. 1(b)]. We use a resolvent-projection operator approach to solve the Schrödinger equation.[9,4] After defining

$$H=H_0+V , \quad \text{(B3)}$$

where

$$H_0=\text{diag}H , \quad \text{(B4)}$$

and

$$G(z)=(z-H)^{-1} , \quad \text{(B5)}$$

$$g(z)=(z-H_0)^{-1} , \quad \text{(B6)}$$

we can write

$$U_{bk}^{lm}(t)=-\frac{1}{2\pi i}\int_{-\infty}^{+\infty} \langle b,(n+1)\omega \mid G(E+i\eta) \times \mid k,l,m;n\omega \rangle e^{-iEt} dE . \quad \text{(B7)}$$

From the identity

$$G=g+GVg \quad \text{(B8)}$$

we immediately obtain

$$G_{bk}^{lm}=G_{bb}\frac{1}{E-E_k}V_{bk}^{lm} , \quad \text{(B9)}$$

where

$$G_{bk}^{lm} \equiv \langle b,(n+1)\omega \mid G \mid k,l,m;n\omega \rangle ,$$
$$G_{bb} \equiv \langle b,(n+1)\omega \mid G \mid b,(n+1)\omega \rangle , \quad \text{(B10)}$$

and

$$V_{bk}^{lm}=\langle b,(n+1)\omega \mid H \mid k,l,m;n\omega \rangle . \quad \text{(B11)}$$

Let us first derive an expression for G_{bb} and then for V_{bk}^{lm}. For this purpose we find it convenient to go back to the states before the Fano diagonalization [Ref. 5; see also Fig. 1(c)]. Now there are two bound states coupled to the continuum by two distinct perturbations, the interaction with the laser V_L and an intra-atomic (for example, Coulombic) interaction V_C.

Let us introduce two projection operators

$$P=\mid b,(n+1)\omega \rangle\langle b,(n+1)\omega \mid + \mid a,n\omega \rangle\langle a,n\omega \mid , \quad \text{(B12)}$$

$$Q=1-P=\sum_{l,m} Q_{lm} , \quad \text{(B13)}$$

$$Q_{lm} \equiv \sum_k \mid k,l,m;n\omega \rangle\langle k,l,m;n\omega \mid . \quad \text{(B14)}$$

We have the following expression for the P-projected resolvent:

$$PGP=(z-H^{\rm eff})^{-1} , \quad \text{(B15)}$$

where

$$H^{\rm eff}=PHP+PRP \quad \text{(B16)}$$

and the level shift operator is

$$R=HQ\frac{1}{z-QHQ}QH . \quad \text{(B17)}$$

The required matrix element G_{bb}, Eq. (B9), is now calculated by first constructing $H^{\rm eff}$ and then inverting the matrix $(zI-H^{\rm eff})$. The effective Hamiltonian is (choosing $E_a+n\omega+\delta_a$ as zero of the energy)

$$H^{\rm eff} \equiv \begin{bmatrix} \Delta-i\dot{\gamma}_b & -\gamma_{ab}(q+i) \\ -\gamma_{ab}(q+i) & -i\gamma_a \end{bmatrix} , \quad \text{(B18)}$$

where (for simplicity we do not indicate the photon indices in the bras and kets)

$$-i\gamma_b^{\text{ion}}+\delta_b=\sum_{l,m}(-i\gamma_b^{lm}+\delta_b^{lm})$$

$$=\sum_{l,m}\int\frac{|\langle b|V_L|klm\rangle|^2}{E-\epsilon_k}dk\ , \tag{B19}$$

$$-i\gamma_a+\delta_a=\sum_{l,m}(-i\gamma_a^{lm}+\delta_b^{lm})$$

$$=\sum_{l,m}\int\frac{|\langle a|V_C|k,l,m\rangle|^2}{(E-\epsilon_k)}dk\ , \tag{B20}$$

$$-i\gamma_{ab}+\delta_{ab}=\sum_{l,m}(-i\gamma_{ab}^{lm}+\delta_{ab}^{lm})$$

$$=\sum_{l,m}\int\frac{\langle a|V_c|k,l,m\rangle\langle k,l,m|V_L|b\rangle}{(E-\epsilon_k)}dk\ , \tag{B21}$$

$$q=-\frac{\delta_{ab}+\langle a|V_L|b\rangle}{\gamma_{ab}} \tag{B22}$$

It is to be noted that the various shifts and widths depend now only weakly on the energy E and this dependence is disregarded in the following [we take $E=E_b+(n+1)\omega$].

From Eqs. (B19)–(B21) one obtains a relation among γ_{ab}^{lm} and $\gamma_a^{lm},\gamma_b^{lm}$:

$$(\gamma_{ab}^{lm})^2=\gamma_a^{lm}\gamma_b^{lm}\ . \tag{B23}$$

If we consider a linearly polarized radiation and assume that V_C is spherically symmetric, then m remains that of the initial state and therefore the sum over m in Eqs. (B19)–(B21) disappears. If the initial state is of the S type the resonance must be of the P type and only the $l=1$ continuum contributes. In this case Eq. (B23) becomes

$$\gamma_{ab}^2=\gamma_a\gamma_b\ . \tag{B24}$$

From Eqs. (B15) and (B18) one has now

$$G_{bb}(E)=\frac{E-H_{22}^{\text{eff}}}{(E-H_{11}^{\text{eff}})(E-H_{22}^{\text{eff}})-(H_{12}^{\text{eff}})^2}\ . \tag{B25}$$

The integral (B7) is easily evaluated by the residue theorem. The poles of $G_{bb}(E)$ are the complex eigenvalues of H^{eff}, i.e., the roots ϵ_1 and ϵ_2 of the secular equation. One gets

$$(E-H_{11}^{\text{eff}})(E-H_{22}^{\text{eff}})-(H_{12}^{\text{eff}})^2=0\ . \tag{B26}$$

Equation (B25) is then rewritten as

$$G_{bb}(E)=\frac{E-H_{22}^{\text{eff}}}{(E-\epsilon_1)(E-\epsilon_2)}\ . \tag{B27}$$

From Eqs. (B7), (B9), and (B18), performing the Fourier transform, we obtain

$$U_{bk}(t)=\left[\frac{\epsilon_1+i\gamma_a}{(\epsilon_1-\epsilon_2)(\epsilon_1-\epsilon_k)}e^{-i\epsilon_1 t}-\frac{\epsilon_2+i\gamma_a}{(\epsilon_1-\epsilon_2)(\epsilon_2-\epsilon_k)}e^{-i\epsilon_2 t}+\frac{\epsilon_k+i\gamma_a}{(\epsilon_k-\epsilon_1)(\epsilon_k-\epsilon_2)}e^{-i\epsilon_k t}\right]V_{bk}\ . \tag{B28}$$

The remaining problem is to give the explicit dependence of V_{bk} on k. This problem has been solved by Fano:[5]

$$V_{bk}=e^{i\phi}\left[C+\frac{A-B\epsilon_k}{\epsilon_k^2+\gamma_d^2}\right]^{1/2}\ ,$$

where

$$A=\frac{1}{\pi}\gamma a(q^2-1)\gamma_{ab}^2\ ,$$

$$B=\frac{2}{\pi}\gamma_{ab}^2 q\ ,$$

$$C=\frac{\gamma_b^{\text{ion}}}{\pi}\ ,$$

and ϕ is an arbitrary phase factor which does not enter in the calculations, since only $|V_{bk}|^2$ appears in the relevant formulas.

[1]See, e.g., D. R. Bates and A. Dalgarno, *Atomic and Molecular Processes*, edited by D. R. Bates (Academic, New York, 1962), p. 245; M. P. S. Nightingale and D. D. Burgess, J. Phys. B **16**, 4101 (1983).

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