Radiative binding of slowly colliding atoms into a molecule in a laser field

M. Ya. Agre and L. P. Rapoport

Voronezh State University
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We consider radiative binding of colliding atoms into a molecule, accompanied by absorption of a nonresonant laser photon: $A_1+A_2+\omega\to(A_1A_2)+\Omega$. An expression is obtained for the binding cross sections and the resonant singularities due to the existence of bound or quasibound levels of two nuclei, moving in the effective field, are separated with account taken of the centrifugal repulsion. The dependence of the cross section on the intensity of the laser radiation is investigated and it is shown that the barrier resonances can lead to nonlinear effects when the nonadiabaticity parameter remains much less than unity.

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1. INTRODUCTION

The investigation of the effect of intense electromagnetic radiation on atom collisions has recently attracted the attention of experimenters and theoreticians. Excitation and ionization of colliding atoms in a laser field have already been discussed in the literature both in the case of long-range collisions (see the review of Yakovlenko[1]) and in the case of short-range collisions.[2] It is also of interest to investigate the simplest chemical reaction–radiative binding of atoms, when the excess energy is carried away spontaneously by an emitted photon:

$$A_1+A_2+\omega\to(A_1A_2)+\Omega.$$

In a sufficiently rarefied gas, the radiative binding is the principal mechanism of molecule formation. Laser radiation, as the catalyst of the reaction, can actively influence the binding process.

We are interested in the case when the absorption of a quantum of a strong electromagnetic field takes place in the course of the collision. For this purpose it is necessary that the laser radiatiation not be resonant to an isolated atomic transition.

Chemical reactions in a laser field were experimentally investigated in a number of studies (see Ref. 1). We know, however, of only one experiment[3] in which nonlinear effects were observed in radiative binding of alkali-metal vapor atoms in a laser field. The molecule formation was detected in Ref. 3 by registering the molecular fluorescence. Nonlinear effects were observed at relatively low intensity of the laser radiation, $\sim10^8$ W/cm^2, when the probabilities of the non-adiabatic transitions remained much less than unity.

Binding calls for the atoms to approach each other to a distance on the order of the dimensions of the molecule. The time of motion of the atoms in a region of the order of molecular dimensions ($\sim10^{-12}$ – 10^{-13} sec) is short compared with the lifetime of the excited state of the quasimolecule ($\sim10^{-8}$ sec). Therefore in the usual case the cross section of the radiative binding also turns out to be small. We do not refer here to the radiative binding that takes place within the limits of one electronic term of the quasimolecule. The probability of this process is low by virtue of the exponential smallness of the matrix elements of the free-bound transitions, and in the homonuclear case (collision of like atoms) the dipole transitions in a single electron term are entirely forbidden. A delayed stay of the atoms in a region of the order of the molecule dimensions should obviously lead to an increase in the binding cross section. In the quantum-mechanical analsis, the delay manifests itself as a cross-section resonance due to the existence of a bound or quasibound energy level of the system of two nuclei moving in the effective field of the quasimolecule, with account taken of the centrifugal collision.

We note that resonant singularities should be observed in this case also in the elastic and inelastic collision cross sections. Thus, for example, when the lower quasimolecule term over which the atoms approach each other is purely repelling, the resonance in the cross section for excitation of an atom with absorption of a photon is governed by the transition of the colliding particles into a quasibound-motion state in the upper term. Such an excitation of an atom with absorption of a photon in collisions was considered quantum-mechanically in Ref. 4, and in the quasiclassical approximation with allowance for the strong coupling of the two channels in Ref. 5.

In theoretical investigations of the radiative binding of the atoms without laser action, use is made of the semiclassical impact-parameter method. In this case the resonant singularities of the cross sections are lost. To take into account the resonances, and the effects nonlinear in the laser-infield intensity which they produce, we describe in the present article the radiative binding in a consistent quantum-mechanical manner. In Sec. 2 we consider the problem of collision of atoms in a laser field in the two-channel WKB approximation. In Sec. 3 the spontaneous radiation that leads to binding is taken into account by perturbation theory, and an expression is obtained for the cross section, and the resonant singularities are separated. The possibilities of observing resonances and associated nonlinear effects is discussed in Sec. 4.

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2. WAVE FUNCTIONS OF TWO-CHANNEL SCATTERING PROBLEM IN THE QUASICLASSICAL APPROXIMATION

Neglecting the spontaneous radiation, we consider the problem of slow atomic collisions in a laser field. We assume that the relative velocity of the nuclei is much less than the characteristic velocity of the electrons in the quasimolecule, $v_{\rm nuc} \ll v_e$. We write the Schrödinger equation for two atoms colliding in the field of an electromagnetic wave in the form[1)]

$$i\partial\Psi(\mathbf{r},\mathbf{R},t)/\partial t=\{\hat{H}(\mathbf{r},R)+\hat{T}+\hat{V}(t)\}\Psi(\mathbf{r},\mathbf{R},t), \quad (1)$$

where $\mathbf{r}$ is the aggregate of the coordinate of the electrons, $\mathbf{R}$ are the coordinates of the relative motion of the nuclei, $\hat{H}$ is the Hamiltonian of the internal motion and determines the set of eigenfunctions $\Phi_n(\mathbf{r},R)$ and terms $U_n(R)$ of the quasimolecule, $\hat{T}=(2\mu)^{-1}\nabla_{\mathbf{R}}^2$ is the operator of the kinetic energy of the relative motion of the nuclei, μ is the reduced mass, $\hat{V}(t)=-\mathbf{F}_0\mathbf{d}e^{i\omega t}/2+\text{h.c.}$ is the operator of the interaction of the atoms with the electromagnetic wave in the dipole approximation, and $\mathbf{F}_0$ and ω are the amplitudes of the electric field intensity and the frequency of the wave.

We assume that prior to the collision the atoms were in states unperturbed by the laser field. The internal motion of the system was consequently described by one of the eigenfunctions of the operator $\hat{H}(\mathbf{r},R\to\infty)$, e.g., by the function $\Phi_1(\mathbf{r},R\to\infty)$. The scattering problem admits of a stationary formulation in the language of quasienergy states (QES). It is known that in the case of a Hamiltonian that depends periodically on the time, the QES play a role analogous to the stationary state for a time-independent Hamiltonian.[6] It is thus necessary to find a solution of Eq. (1) in the form which satisfies the boundary condition of the scattering. Here ε is the quasienergy of the QES.

$$\Psi(t)=e^{-i\varepsilon t}U(t),\quad U(t+2\pi/\omega)=U(t),$$

By virtue of the assumption that the nuclei move slowly, we seek the function $\Psi(\mathbf{r},\mathbf{R},t)$ in the form of an expansion in the complete set of states of the quasimolecule, forming an adiabatic base:

$$\Psi(\mathbf{r},\mathbf{R},t)=e^{-i\varepsilon t}\sum_{nk}\Phi_n(\mathbf{r},R)\chi_{nk}(\mathbf{R})e^{ik\omega t}. \quad (2)$$

Substitution of the expansion (2) in (1) leads to a system of equation for the functions χ_{nk}:

$$\{\hat{T}+U_n(R)+k\omega-\varepsilon\}\chi_{nk}(\mathbf{R})=-\sum_m\{V_{nm}\chi_{mk-1}(\mathbf{R})+(V^+)_{nm}\chi_{mk+1}(\mathbf{R})\}, \quad (3)$$

where $V_{nm}(R)=-\langle\Phi_n|\mathbf{d}|\Phi_m\rangle\mathbf{F}_0/2$. Small non-adiabatic terms of the type $\chi_{mk}\hat{T}_{nm}\sim\mu^{-1}\chi_{mk}$ and $\mu^{-1}(\nabla_{\mathbf{R}})_{nm}\nabla_{\mathbf{R}}\chi_{mk}\sim v_{\rm nuc}\chi_{mk}$ were omitted.

We assume that the terms $U_1(R)$ and $U_2(R)$ of the quasimolecule are arranged in the manner shown in cases A and B of the figure. The operator V in (3) can be regarded as a perturbation, in the absence of which the nuclear wave function coincides with the function $\chi_{10}^{(0)}(\mathbf{R})$. Therefore in the quasiclassical approximation the system (3) becomes simpler and reduces to two equations, strongly coupled in the nonadiabaticity region $U_1(R_\omega)=U_2(R_\omega)-\omega$, for the nuclear wave functions $\chi_1(\mathbf{R})=\chi_{10}(\mathbf{R})$ and $\chi_2(\mathbf{R})=\chi_{2-1}(\mathbf{R})$:

$$\begin{aligned}&[-(2\mu)^{-1}\nabla_{\mathbf{R}}^2+U_1(R)-\varepsilon]\chi_1(\mathbf{R})=-V_{12}\chi_2(\mathbf{R}),\\&[-(2\mu)^{-1}\nabla_{\mathbf{R}}^2+U_2(R)-\omega-\varepsilon]\chi_2(\mathbf{R})=-V_{12}^*\chi_1(\mathbf{R}).\end{aligned} \quad (4)$$

Thus, in our approximation the total wave function of the system takes the form

$$\Psi(\mathbf{r},\mathbf{R},t)=e^{-i\varepsilon t}[\chi_1(\mathbf{R})\Phi_1(\mathbf{r},R)+\chi_2(\mathbf{R})\Phi_2(\mathbf{r},R)e^{-i\omega t}],$$

where $\varepsilon=U_1(\infty)+E$, $E=(2\mu)^{n-1}k^2$ is the initial energy of the relative motion of the nuclei. As $R\to\infty$ the function χ_1 should take the asymptotic form of a decreasing and outgoing wave, and χ_2 of an outgoing wave.

To separate the angular parts in (4), we expand the nuclear wave functions in spherical harmonics:

$$\chi_{2(1)}(\mathbf{R})=2\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}i^{l+1}\exp(\mp i\eta_1^l)\chi_{2(1)}^{lm}(R)(kR)^{-1}Y_{lm}^{(*)}(\mathbf{k}/k)Y_{lm}(\mathbf{R}/R), \quad (5)$$

where η_1^l is the quasiclassical phase shift of the partial wave in elastic scattering by the potential $U_1(R)$. We assume that the electromagnetic wave is linearly polarized, and write down the coupling matrix element V_{12} in the form

$$V_{12}=V_{12}^*=-F_0d_{12}(R)\cos\theta/2,$$

where $d_{12}(R)$ is the matrix element of the dipole moment between the states 1 and 2 of the quasimolecule, and the field $\mathbf{F}_0$. We shall show below that to find the cross sections of the transitions of interest to us we can put $\chi_{1,2}\approx\chi_{1,2}^{l\pm1\,m}$. Assuming also $l\gg1$ in accordance with the quasiclassical-treatment condition and substituting expansion (5) in (4), we arrive at a two-channel system of equations in the angular-momentum representation

$$\alpha^2d^2\chi^{lm}(R)/dR^2+P^{lm}(R)\chi^{lm}(R)=0, \quad (6)$$

where

$$\chi^{lm}(R)=\begin{pmatrix}\chi_1^{lm}(R)\\ \chi_2^{lm}(R)\end{pmatrix},$$

$$P^{lm}(R)=\begin{pmatrix}1-[U_{1l}(R)-U_{1l}(\infty)]E^{-1} & V^{lm}(R)E^{-1}\\ V^{lm*}(R)E^{-1} & 1-[U_{2l}(R)-U_{1l}(\infty)-\omega]E^{-1}\end{pmatrix},$$

$$U_{jl}(R)=U_j(R)+E\alpha^2(l+{}^1/_2)^2R^{-2},\quad j=1,2;$$

$$V^{lm}(R)=-F_0d_{12}(R)(l^2-m^2)^{1/2}[Y_{l+1m}(\mathbf{k}/k)\exp(-i\eta_1^{l+1})+Y_{l-1m}(\mathbf{k}/k)\exp(-i\eta_1^{l-1})][4lY_{lm}^*(\mathbf{k}/k)\exp(i\eta_1^l)]^{-1},$$

$\alpha=\lambda$ is a quasiclassical parameter ($\alpha\ll1$), $\lambda=(2\mu E)^{-1/2}$ is the de Broglie wavelength. The coupling matrix element $|V^{lm}|$ depends on the angle between the direction of the initial motion of the nuclei $\mathbf{k}/k$ and the field $\mathbf{F}_0$, and does not depend on the azimuthal angle φ'. This is due to the axial symmetry of the problem: in the case of linear polarization of the electromagnetic field, the total scattering cross section should be independent of the azimuthal angle.

It was shown earlier[7] that in the quasiclassical approximation, far from the turning points and from the non-adiabaticity region, the solution of the system of equations (6) can be represented in the form[2)]

$$\chi_j(R)=\lambda_j^{-1/4}\{a_{j-}\exp[-i(L_j(R_j,R)+\pi/4)]-a_{j+}\exp[i(L_j(R_j,R)+\pi/4)]\}, \quad (7)$$

where R_j is the turning point closest to zero for motion in the adiabatic well U_j

$$L_j(R,R')=\alpha^{-1}\int_R^{R'}\lambda_j^{1/2}(x)\,dx,$$

$$\lambda_{1,2}=(P_{11}+P_{22})/2\pm|P_{12}|(1+q^2)^{1/2},\quad q=(P_{11}-P_{22})(2|P_{12}|)^{-1}.$$

A connection was also found[7] between the amplitudes a_{j+} and a_{j-} in the region $R_\omega < R < R'$, where R' is the turning point closest to R_ω in one of the terms, under the condition that the nuclear functions are regular at zero:

$$a_{j+}=T_{j1}a_{1-}+T_{j2}a_{2-}. \tag{8}$$

Here

$$T_{12}=T_{21}=2i\cos(\sigma-\Phi)e^{-\delta}(1-e^{-2\delta})^{1/2}, \tag{9a}$$

$$T_{11}=T_{22}^*=e^{-2\delta}-e^{-2i(\sigma-\Phi)}(1-e^{-2\delta}), \tag{9b}$$

$$\delta=\frac{i}{2\alpha}\oint|P_{12}(x)|\left[(\lambda_1^{1/2}(x)+\lambda_2^{1/2}(x))\frac{dq}{dx}\right]^{-1}(1+q^2)^{1/2}dq \tag{10}$$

is the integral along a contour around the branch point of the function $(1+q^2)^{1/2}$ in the complex R plane,

$$\sigma=L_1(R_1,R_\omega)-L_2(R_2,R_\omega), \tag{11}$$

$$\Phi=\pi/4-\delta/\pi+\ln(\delta/\pi)\delta/\pi-\arg\Gamma(1+i\delta/\pi). \tag{12}$$

The elements of the matrix T_{ij} were written out for the case $P_{11}(\infty)>P_{22}(\infty)$, and in the transition to the complex R plane the function $P_{11}(R)$, $P_{22}(R)$ and $|P_{12}(R)|$ are analytically continued. The sign of the real function $(1+q^2)^{1/2}$ is chosen such that $\lambda_1=P_{11}$, $\lambda_2=P_{22}$ far from R_ω.

The incident partial wave in the second channel must be sought in the form

$$\chi_1^{(-)lm}(R)=\lambda_1^{-1/4}\exp[-i(L_1'(x_1,R)+\pi/4)]$$
$$=\lambda_1^{-1/4}\exp[-i(kR-l\pi/2+\eta_l')],\quad R\to\infty, \tag{13}$$

where x_1 is the largest turning point,

$$\eta_l'=\lim_{R\to\infty}[L_1^l(x_1,R)-L_1^{0l}(x_1^0,R)],$$

$L_1^{0l}(x_1^0,R)$ is the quasiclassical phase of the wave function of the free motion $[U_1(R)=0]$. In fact, substitution of the function (13) in the expansion (5) shows that the terms of the obtained series coincide with the incident partial waves in the expansion of the plane wave

$$\exp(i\mathbf{kR})=4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l}i^l\sin\left(kR-\frac{l\pi}{2}\right)\frac{1}{kR}Y_{lm}^*\left(\frac{\mathbf{k}}{k}\right)Y_{lm}\left(\frac{\mathbf{R}}{R}\right).$$

This ensures satisfaction of the scattering boundary condition.

We now obtain the explicit form of the functions χ_j (7) for various arrangements of the terms of the quasimolecule, and correspondingly for various positions of the potential barriers in the effective fields $U_{jl}(R)$.

A. Inelastic channel closed

We consider the situation when the upper term has a deeper potential well, i.e., the term difference $\Delta U(R)\equiv|U_2(R)-U_1(R)|$ increases monotonically. The inelastic channel may then turn out to be closed if $\varepsilon+\omega<U_2(\infty)$ (see case A in the figure).

To determine the form of the nuclear functions it is necessary to postulate as $R\to\infty$ a boundary condition that corresponds to exponential damping of the function $\chi_2(R)$ inside the classically forbidden region. The first term of the incident wave is determined by the Eq. (13). Thus, the nuclear wave functions should take the following form:

$$\chi_1(R)=\lambda_1^{-1/4}\exp[-i(L_1(R_1'',R)+\pi/4)]+A_{1+}\lambda_1^{-1/4}\exp[i(L_1(R_1'',R)+\pi/4)],$$

$$\chi_2(R)=A_2|\lambda_2|^{-1/4}\exp[-|L_2(R_2',R)|],\ R\to\infty.$$

We denote the amplitudes that determine the nuclear functions χ_1 and χ_2 (7) in the classically allowed regions $R_\omega<R<R_1'$ and $R_\omega<R<R_2'$ by $a_{1\pm}$ and $a_{2\pm}$, respectively, and in the classically allowed regions $R<R_\omega$ by $b_{1\pm}$ and $b_{2\pm}$. With the aid of the methods of single-channel quasiclassical approximation[8] we can obtain the following conjugation formulas:

$$-a_{2+}\exp[iL_2(R_2,R_2')]=a_{2-}\exp[-iL_2(R_2,R_2')]=A_2,$$
$$a_{1-}\exp[-iL_1(R_1,R_1')]=A_{1+}(\tilde R/T)^{1/2}+T^{-1/2}\exp[i(\pi/2-\varphi)],$$
$$-a_{1+}\exp[iL_1(R_1,R_1')]=(\tilde R/T)^{1/2}+A_{1+}T^{-1/2}\exp[-i(\pi/2-\varphi)], \tag{14}$$

where the reflection coefficients $\tilde R$ and the coefficients of transmission through the barrier T are defined in the first term by the relations

$$\tilde R=(1+e^{-2K})^{-1},\quad T=(1+e^{2K})^{-1},$$

$$K=\alpha^{-1}\int_{R_1'}^{R_1''}|\lambda_1^{1/2}(x)|dx>0 \tag{15}$$

in the case of an impenetrable barrier and

$$K=\mathrm{Re}\left(2i\alpha^{-1}\int_{R'}^{R'+iR''}\lambda_1^{1/2}(x)dx\right)<0,\quad \lambda_1(R'+iR'')=0$$

in the case of a penetrable barrier.

The phase φ can be determined by joining together the quasiclassical solution with the exact solution in the case of a parabolic barrier:

$$\varphi=\pi/2-K/\pi+\ln|K/\pi|K/\pi+\arg\Gamma(1/2-iK/\pi).$$

The system of equations (8) and (14) determines all the unknown amplitudes. We write down the amplitudes needed for the determination of the function $\chi_2(R)$[3)]:

$$A_2=-T_{21}T^{1/2}\exp[i(L_1+L_2+\pi/2-\varphi)]\{[1+T_{22}\exp(2iL_2)]$$
$$\cdot[1+\tilde R^{1/2}T_{11}\exp[i(2L_1+\pi/2-\varphi)]]-T_{12}T_{21}\tilde R^{1/2}\exp[i(2L_1+2L_2+\pi/2-\varphi)]\}^{-1},$$

$$a_{1-}=-A_2T_{21}^{-1}[1+T_{22}\exp(2iL_2)]\exp(-iL_2). \tag{16}$$

The amplitudes $a_{2\pm}$ are determined from the first pair of equations in (14), while $b_{j\pm}$ are connected with $a_{j\pm}$ (Ref. 7):

$$b_{1\pm}=a_{1-}e^{-\delta}+ie^{i(\sigma-\Phi)}(1-e^{-2\delta})^{1/2}a_{2-},$$
$$b_{2\pm}=-a_{2-}e^{-\delta}-ie^{-i(\sigma-\Phi)}(1-e^{-2\delta})^{1/2}a_{1-}. \tag{17}$$

B. Deeper upper potential well. Open inelastic channel.

In this case, if a barrier exists in the upper term, the motion in the lower term, depending on the orbital angular momentum of the relative motion of the nuclei, can be either below or above the barrier.

To find the nuclear functions we formulate a boundary condition corresponding to a single incident wave in the input channel (13) and to the absence of an incident wave in the inelastic channel. Just as in the preceding case, we write down the conjugation formulas

$$a_{1-}\exp(-iL_1)=A_{1+}(\tilde{R}_1/T_1)^{1/2}+T_1^{-1/2}\exp[i(\pi/2-\varphi_1)],$$
$$-a_{1+}\exp(iL_1)=(\tilde{R}_1/T_1)^{1/2}+A_{1+}T_1^{-1/2}\exp[-i(\pi/2-\varphi_1)], \qquad (18)$$
$$a_{2-}\exp(-iL_2)=A_{2+}(\tilde{R}_2/T_2)^{1/2},$$
$$-a_{2+}\exp(iL_2)=A_{2+}T_2^{-1/2}\exp[-i(\pi/2-\varphi_2)],$$

where the reflection and the transmission coefficients R_j and T_j for the barrier in the j-th term are defined in analogy with (15).

The solutions of the system (8), (18) of interest to us are of the form

$$A_{2+}=-T_{21}(T_1T_2)^{1/2}\exp[i(L_1+L_2+\pi-\varphi_1-\varphi_2)]\{[1+\tilde{R}_2^{1/2}T_{22}\exp[i(2L_2+\pi/2-\varphi_2)]][1+\tilde{R}_1^{1/2}T_{11}\exp[i(2L_1+\pi/2-\varphi_1)]]-T_{12}T_{21}(\tilde{R}_1\tilde{R}_2)^{1/2}\exp[i(2L_1+2L_2+\pi-\varphi_1-\varphi_2)]\}^{-1}, \qquad (19)$$
$$a_{1-}=-A_{2+}T_2^{-1/2}T_{21}^{-1}[1+\tilde{R}_2T_{22}\exp[i(2L_2+\pi/2-\varphi_2)]]\exp[-i(L_2+\pi/2-\varphi_2)].$$

The amplitudes $b_{j\pm}$, which determine the form of the nuclear functions in the classically allowed regions $R<R_\omega$, are determined as before by the formulas (17).

The square of the modulus of the amplitude A_{2+}, at the chosen normalization, determines the probability of excitation of the atoms upon collision. In the absence of barriers ($T_j\to 1, \tilde{R}_j\to 0, \varphi_j\to\pi/2$) we obtain from (19) and (9) the following relation:

$$|A_{2+}|^2=|T_{21}|^2=4\cos^2(\sigma-\Phi)e^{-2\delta}(1-e^{-2\delta}),$$

which coincides, in the linear-term approximation, with the Landau-Zener formula with quantum-oscillations included. Consequently, expression (19) actually generalizes the formula for the probability of the nonadiabatic transitions, taking the resonant barrier effects into account. The generalization of the Landau-Zener formula to the case of a barrier in an inelastic channel, when the lower term is pure repelling, was obtained in Ref. 5.

C. Deeper lower potential well.

This is the most common case for quasimolecules. The difference between the terms $\Delta U(R)$ decreases monotonically, so that the inelastic channel is always open.

We introduce first some changes in notation. We take $U_2(R)$ to be the lower term of the molecule, at which the approach of the atoms takes place. The diagonal elements of the matrix P in the system of equations (6) then take the form

$$P_{11}(R)=1-[U_{1l}(R)-U_{2l}(\infty)-\omega]E^{-1},$$
$$P_{22}(R)=1-[U_{2l}(R)-U_{2l}(\infty)]E^{-1},$$

and the total energy of the system is given by $\varepsilon=E+U_2(\infty)$. In the new notation, the condition $P_{11}(\infty)>P_{22}(\infty)$ is satisfied, so that we can use the coupling matrix T_{ij} (9) between the amplitudes a_j.

We impose a boundary condition that corresponds to a single incident wave in the input channel 2 and the absence of an incident wave in channel 1. The system of equations for the amplitudes that determine the form of the nuclear functions differs from Eqs. (8) and (18) of the preceding case in that the indices 1 and 2 are interchanged. The nuclear wave function in the inelastic channel χ_1 turns out to be proportional to $T_2^{1/2}$. This is physically due to the fact that to land in the non-adiabaticity region the nuclei must tunnel through the potential barrier in term 2, and the probability of tunneling is determined by the transmission coefficient T_2. In the considered case, when the orbital angular momentum of the relative motion of the nuclei increases, the barrier arises initially in the term 2. At larger angular momentum when the barrier appears in term 1, the transmission coefficient T_2 becomes a sufficiently small exponential quantity. We can confine ourselves therefore to finding the amplitudes that determine the form of the nuclear function $\chi_1(R)$ in the case when the barrier exists only in the lower term (see case C in the figure).

Rearranging the indices in the corresponding formulas of the preceding section and putting $T_1=1, \tilde{R}_1=0, \varphi_1=\pi/2$, we obtain the following formulas for the sought amplitudes:

$$a_{2-}=\frac{T_2^{1/2}\exp[i(L_2+\pi/2-\varphi_2)]}{1+\tilde{R}_2^{1/2}T_{22}\exp[i(2L_2+\pi/2-\varphi_2)]}$$
$$a_{1-}=0, \quad a_{1+}=T_{12}a_{2-}. \qquad (20)$$

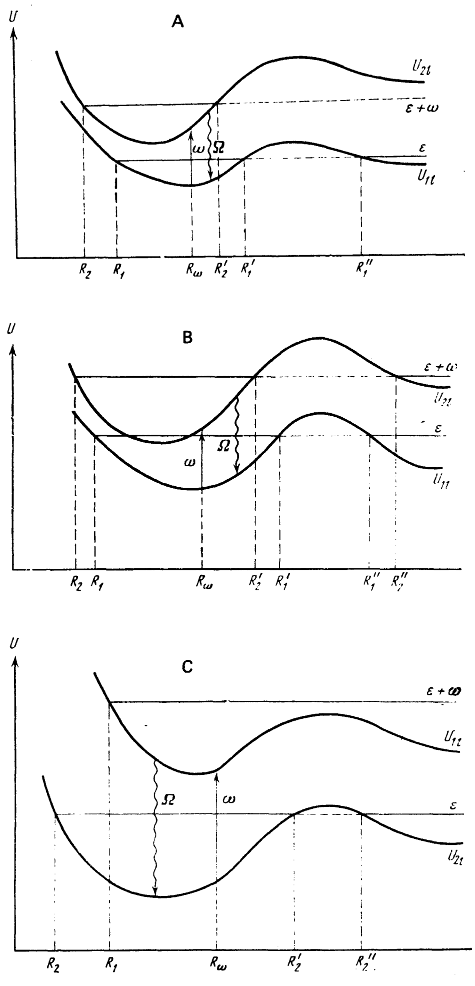

FIG. 1. Possible postions of the barriers in the effective fields $U_{jl}(R)$ as functions of the relative arrangement of the terms of the quasimolecule, the values of the total initial energy ε, of the colliding atoms and the orbital momentum of the relative motion of the nuclei, corresponding to the cases A, B, and C in the text.

The probability of excitation of the atoms upon collision is determined by the square of the modulus a_{1+}. The amplitudes $b_{1\pm}$ can be obtained from Eqs. (17).

In concluding this section let us estimate the accuracy with which the angular parts are separated in the system of equations (4). We shall be interested below in the cases of weak ($\delta \ll 1$) and strong ($\delta \gg 1$) coupling, in which, as follows from the explicit form of the amplitude, resonant effects are observed. In these cases one of the functions χ_j turns out to be small, $\sim\delta^{1/2}$ or $\sim e^{-\delta}$, relative to the other. Of the same order of smallness are the corrections to the other function when l is replaced by ± 1 on account of the change of δ. Therefore to separate the angles it is necessary that the phases of the functions χ_j^l and $\chi_j^{l\pm 1}$ be close in the non-adiabaticity region:

$$|L_j^l(R,R')-L_j^{l\pm1}(R,R')|\ll 1, \qquad (21)$$

where $R'-R\sim 1$. Recognizing that $l\gg 1$, we can write the condition (21) in the form

$$l\ll[2\mu(\varepsilon-U_{jl}(R_\omega))]^{1/2}R_\omega^2.$$

Putting by way of estimate $\varepsilon-U_{jl}(R_\omega)\sim 0.1$, $R_\omega\sim 2$, we obtain in the most unfavorable case of hydrogen atoms $l\ll 100$.

3. RADIATIVE-BINDING CROSS SECTION

We proceed not to calculate the cross section for radiative binding of the atoms. We assume that the binding is due to direct spontaneous transition of the system to the electronic ground state, with respect to the term of which the approach of the atoms took place. The amplitude of the transition (the corresponding element of the S matrix) is represented in the form

$$S_{f0}=-i\int_{-\infty}^{\infty}\langle\Psi_f(t)|\hat V(t)+\hat W|\Psi_0^{(+)}(t)\rangle dt. \qquad (22)$$

Here $\Psi_0^{(+)}$ is the solution of the Schrödinger equation for atoms colliding in the presence of a strong and quantized weak electromagnetic field, which satisfy the scattering condition, the function Ψ_f describes the final state of the system, and $\hat W=-\hat{\mathbf{E}}\mathbf{d}$ is the operator of the interaction of the atoms with the quantized electromagnetic field in the dipole approximation

$$\hat{\mathbf{E}}=(2\pi)^{-1}\sum_{\alpha=1,2}\int d\mathbf{q}(i\Omega^{1/2}\mathbf{e}_\mathbf{q}^{(\alpha)}\hat c_{\mathbf{q}\alpha}+\text{H.c.}),$$

where $\hat c^+_{\mathbf{q}\alpha}$ is the operator of production of a photon with momentum $\mathbf{q}$ and polarization α, $\Omega=q$ is the frequency of the photon, and $\mathbf{e}_\mathbf{q}^{(\alpha)}$ is the polarization unit vector.

We take the perturbation $\hat W$ into account in first order, and therefore the function $\Psi_0^{(+)}$ must be represented in the form of the product of a vector vacuum state of the field and a function describing the collision of the atoms in the presence of a strong field:

$$\Psi_0^{(+)}=\Psi|0\rangle. \qquad (23)$$

In the two-channel approximation considered in Sec. 2, the function Ψ takes the form

$$\Psi(\mathbf{r},\mathbf{R},t)=e^{-i\varepsilon t}[\chi_i(\mathbf{R})\Phi_i(\mathbf{r},R)+\chi_j(\mathbf{R})\Phi_j(\mathbf{r},R)e^{-i\omega t}], \qquad (24)$$

where $\varepsilon=U_i(\infty)+E$ is the total energy of the colliding atoms, $i=1$ and $j=2$ in the case of a deeper upper well, and $i=2$ and $j=1$ in the opposite case. The function Ψ_f is expressed in terms of the product of the state vector of the field with a photon having a momentum $\mathbf{q}$ and a polarization α, $|\mathbf{q},\alpha\rangle e^{-i\Omega t}$, by the wave function of a molecule, which is factorized in the adiabatic approximation:

$$\Psi_f=\Phi_i(\mathbf{r},R)\chi_f(\mathbf{R})|\mathbf{q},\alpha\rangle\exp[-i(\varepsilon_f+\Omega)t], \qquad (25)$$

where ε_f is the energy of the corresponding bound state of the molecule, and

$$\chi_f(\mathbf{R})=\chi_v^l(R)R^{-1}Y_{lm}(\mathbf{R}/R) \qquad (26)$$

is the nuclear wave function.

Substituting the functions (23)–(25) in the general formula (22) for the transition amplitude, and performing standard transformations, we obtain an expression for the number of transitions per unit time. The ratio of the number of transitions per unit time to the flux density of the incident atoms, which is numerically equal to their relative velocity $v=k\mu^{-1}$ if the initial velocity is suitably normalized, yields the differential cross section of the process. Summing the differential cross section over the directions of the emission and polarization of the photon, just as in the usual case of spontaneous emission,[9] and also over all the values of the projection m of the orbital angular momentum of the nuclei in the final state, we obtain the cross section for binding with emission of a photon of frequency $\Omega(\Omega')$:

$$\sigma_{vl}=4(3v)^{-1}\Omega^3\sum_m|\langle\Phi_i\chi_f|\mathbf{d}|\Phi_j\chi_j\rangle|^2,\quad \Omega=\varepsilon-\varepsilon_f+\omega;$$
$$\sigma_{vl}'=4(3v)^{-1}\Omega'^3\sum_m|\langle\Phi_i\chi_f|\mathbf{d}|\Phi_i\chi_i\rangle|^2,\quad \Omega'=\varepsilon-\varepsilon_f. \qquad (27)$$

It was already noted in the introduction that the cross sections of the transitions are exponentially small within the limits of a single electronic term, and in the case of the collision of identical atoms the dipole transitions are at all forbidden. We shall therefore investigate in greater detail the cross section for binding with emission of a photon at a frequency $\Omega=\varepsilon-\varepsilon_f+\omega$ of Raman scattering of laser radiation, accompanied by a free-bound transition. We calculate the matrix element of the dipole moment from the nuclear functions (5) and (26):

$$\langle\Phi_i\chi_f|\mathbf{d}|\Phi_j\chi_j\rangle=\langle\chi_f|d_{ij}\mathbf{n}|\chi_j\rangle$$
$$=2\pi\sum_{\substack{l'=l\pm1\\ m'=m,m\pm1}}i^{l'+1}\exp(-i\eta_i^{l'})M_{ij}^{vll'm'}k^{-1}Y_{l'm'}(\mathbf{k}/k)\langle lm|\mathbf{n}|l'm'\rangle. \qquad (28)$$

We have taken into account explicitly here the selection rules for the matrix elements of the unit vector $\mathbf{n}=\mathbf{R}/R$, and introduced the notation

$$M_{ij}^{vll'm'}=\int\chi_v^{l*}(R)d_{ij}(R)\chi_j^{l'm'}(R)dR. \qquad (29)$$

Far from the point R_ω, which determines the non-adiabaticity region, the function χ_j^{lm} is represented in the form [see (7)]

$$\chi_j^{lm}(R)=\frac{1}{(\alpha p_j^l)^{1/2}}\left\{a_-^{lm}\exp\left[-i\left(\int_{R_j}^{R}p_j^l dR+\frac{\pi}{4}\right)\right]\right.$$
$$\left.-a_+^{lm}\exp\left[i\left(\int_{R_j}^{R}p_j^l dR+\frac{\pi}{4}\right)\right]\right\},$$

where

$$p_j^l(R)=[2\mu(\varepsilon+\omega-U_{jl}(R))]^{1/2}.$$

The function χ_ν^l will also be regarded as quasiclassical:

$$\chi_\nu^l(R)=A(p_f^l)^{-1/2}\cos\left(\int_{R_f}^{R} p_f^l dR-\pi/4\right);$$

here

$$p_f^l(R)=[2\mu(\varepsilon_f-U_{il}(R))]^{1/2},\quad A=\left[\int_{R_f}^{R_f'}(2p_f^l)^{-1}dR\right]^{-1/2};$$

R_f and R_f' are classical turning points.

We calculate the integral $M_{ij}^{\nu ll'm'}$, which contains two rapidly oscillating functions, by the stationary-phase method:

$$M_{ij}^{\nu ll'm'}=A\frac{d_{ij}\pi^{1/2}}{p_f^l}\left|2\alpha\frac{d(p_f^l-p_j^{l'})}{dR}\right|_{R=R_\Omega}^{-1/2}(a_-^{l'm'}e^{-i\varphi}-a_+^{l'm'}e^{i\varphi}),$$

$$\varphi=\frac{\pi}{2}+\int_{R_f}^{R_\Omega}p_j^{l'}dR-\int_{R_f}^{R_\Omega}p_f^l dR+\frac{\pi}{4}\operatorname{sign}\frac{d[p_j^{l'}(R_\Omega)-p_f^l(R_\Omega)]}{dR}. \quad (30)$$

The stationary point R_Ω, which we assume not to coincide with the classical turning points, is determined by the condition

$$p_j^{l'}(R_\Omega)=p_f^l(R_\Omega). \quad (31)$$

If it is recognized that in our case $l'=l\pm1$ [see (28)], $l\gg1$, and

$$(l+1/2)^2(2\mu R^2)^{-1}\leqslant U_{i,j}(R),$$

then we can approximately put $U_{jl'}(R)-U_{il}(R)\approx U_j(R)-U_i(R)$ and represent the condition (31) in the form

$$\Omega=U_j(R_\Omega)-U_i(R_\Omega).$$

Summing $\sigma_{\nu l}$ (27) over the final state of the nuclei, we obtain the total binding cross section

$$\sigma=\sum_{\nu l}\sigma_{\nu l}. \quad (32)$$

The binding cross section depends on the parameters of the intense electromagnetic radiation in terms of the amplitudes $a_{j\pm}^{l'm'}$, which determine the form of the nuclear wave function in the inelastic channel [see (30)]. As follows from the results of the preceding section [formulas (16), (19), and (20)], these amplitudes have resonant singularities. Obviously, barrier effects can lead to resonance in the cross section only in the case of a low tunneling probability ($T_j=e^{-2K}\ll1, \tilde{R}_j\to1, \varphi_j\to\pi/2, j=1,2$). Let us analyze in greater detail the cases of weak ($\delta\ll1$) and strong ($\delta\gg1$) coupling of the channels.

In the case of weak coupling, the elements of the matrix (9) satisfy the relations $T_{ii}\to1, T_{ij}\to0$, and the resonances are determined by the condition

$$L_i^{l_0}(R_i,R_i')=\pi(n+1/2), \quad (33)$$

where $n\gg1$ is a positive integer and $i=1$ or 2. The condition (33) coincides with the quasiclassical quantization rule for a particle moving in a field $U_{il_0}(R)$ or $U_{jl_0}(R)-\omega$, so that we can state that the resonances are determined by the positions of the quasibound levels in the diabatic wells.

In the case of strong coupling we can obtain for the matrix elements T_{ij} (9) the following estimates:

$$T_{11}=T_{22}^*\to-\exp[-2i(\sigma-\Phi)],\quad T_{12}=T_{21}\to0,$$

with $\Phi\to0$, as follows from (12). The resonances are determined by the condition

$$L_1^{l_0}(R_1,R_1')-\sigma^{l_0}=\pi n$$

or

$$L_2^{l_0}(R_2,R_2')+\sigma^{l_0}=\pi n.$$

From the last relations and from the explicit form of the phase σ(11) it follows that in the case of strong channel coupling the resonances are determined in fact by the position of the quasibound levels in the adiabatic wells.

To find the resonant value of the total binding cross section it suffices to retain in (32) the terms with $l=l_0\pm1$.

4. DISCUSSION OF RESULTS

Let us examine the effects that can be made observable by resonances produced in the binding cross section by the existence of quasistationary levels of nuclei moving in a potential field with an effective barrier.

The frequency Ω of the photon emitted in the course of the binding of the atoms should be higher than the frequency ω of the laser radiation. Therefore, according to (30) and (31), the dependence of the cross section on the parameters of the intense electromagnetic radiation is determined in cases A and B considered in Sec. 2, by the amplitudes $a_{2\pm}$, and in case C by the amplitudes $b_{1\pm}$.

We analyze now in greater detail the cases of a barrier in the lower term (cases A and C, Sec. 2). Under resonance conditions the cross section is proportional in case A, when the upper channel is closed, to $|a_{2\pm}|^2=|A_2|^2$, and in case C to $|b_{1\pm}|^2$. In the linear-term approximation, the parameter δ (10), which characterizes the coupling of the channels, is of the form

$$\delta=\pi|V^{lm}(R_\omega)|^2\left[\left|\frac{d(U_1(R_\omega)-U_2(R_\omega))}{dR}\right|v(R_\omega)\right]^{-1},$$

where $v(R_\omega)$ is the radial velocity of the relative motion of the nuclei at the point R_ω, and depends linearly on the intensity of the laser field. If we put $v(R_\omega)\sim10^{-2}-10^{-3}, d_{12}\sim1, |d\Delta U/dR|\sim10^{-1}$, then we obtain the estimate $\delta\sim(10^3-10^4)F_0^2$. The coefficient T of transmission through the barrier (15) varies in a wide range, depending on the shape of the barrier and on the energy of the relative motion of the colliding atoms. To estimate the cross section and its dependence on the laser intensity, we use the explicit forms of the amplitudes (16), (17), and (20) and analyze the various cases.

In the case of weak coupling ($\delta\ll1$) we obtain under resonance conditions ($T=e^{-2K}\ll1$) the following estimates:

$$|A_2|^2\sim\delta e^{2K},\quad \delta\leqslant e^{-2K};\quad |A_2|^2\sim(\delta e^{2K})^{-1},\quad \delta\gg e^{-2K}.$$

Outside the resonance region we have $|A_2|^2\sim\delta T$. Similar estimates are obtained for $|b_{1\pm}|^2$.

Thus, the dependence of the binding cross section on the laser-field intensity becomes nonlinear on account of the resonances, when the non-adiabaticity parameter reaches a value of the order of $e^{-2K} \ll 1$, i.e., the width of the quasi-bound level, due to the transition to the other electronic state, becomes comparable in order of magnitude with the tunnel width. The probability of non-adiabatic transition remains in this case much less than unity. The nonlinear effects observed in the experiment of Bonch-Bruevich *et al.*[3] in the case of a closed upper channel are, in our opinion, of the same character. They cannot be attributed to competition between spontaneous transitions that lead to binding, or spontaneous transitions in the free-motion state, as is done in Ref. 3, since the corresponding widths, which are governed by the action of the laser radiation, greatly exceed the spontaneous widths.

In the case of strong coupling of the channels ($\delta \gg 1$) it is possible to obtain the following estimates in the resonant case:

If $e^{-\delta} \lesssim e^{-K}$, and
$$|A_2|^2 \sim e^{2(K-\delta)}, \quad |b_{1\pm}|^2 \sim e^{2K},$$
$$|A_2|^2 \sim e^{2(\delta-K)}, \quad |b_{1\pm}|^2 \sim e^{2(2\delta-K)},$$
if $e^{-\delta} \gg e^{-K}$. In the nonresonant case
$$|A_2|^2 \sim e^{-2\delta}T, \quad |b_{1\pm}|^2 \sim T.$$

As follows from the presented estimates, in the resonant case the binding cross section can increase strongly, and this corresponds to the concept of prolonged motion of the nuclei in the non-adiabaticity region. The widths Δ of these resonances are quite small, and are determined in the considered cases of weak and strong coupling of the channels by the relation
$$\Delta \sim \nu \max\left[e^{-2K}, e^{-2\delta}(1-e^{-2\delta})\right],$$
where ν is the characteristic distance between the quasiclassical energy levels in the effective potential field $U_{j1}(R)$. Therefore averaging over the energy interval $\tau \gtrsim \nu \gg \Delta$ smoothes out the sharp energy dependence of the cross section. In the regime linear in the laser intensity, the resonant part of the cross section σ_r exceeds the nonresonant σ_{nr} by a factor e^{2K}, as follows from our estimates.

If we assume that τ/ν resonances are spanned by the interval τ, then the averaging can be estimated in the following manner:
$$\bar{\sigma} \sim \tau^{-1}[\sigma_{nr}\tau + \sigma_r \Delta\tau/\nu] = \sigma_{nr} + \sigma_r e^{-2K} \approx 2\sigma_{nr}.$$

Thus, in the linear regime, after averaging, the resonances increase the cross section by a factor of 2. Consequently, the effect nonlinear in the laser-radiation intensity, which we analyzed above, should take place even when account is taken of a Maxwellian energy distribution in a real gas.

1) The atomic system of units is used in this paper.

2) In the analysis of the system of Eqs. (6) we shall not write out the indices lm of the matrix elements or of the functions if no misunderstanding results.

3) Here and below we do not write out, for the sake of brevity, the arguments of the functions $L_1(R_1, R_1')$ and $L_2(R_2, R_2')$.

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