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TRANSITION PROBABILITY OF THE SYSTEM OF TWO COLLIDING ATOMS WITHIN A LASER BEAM*

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The free-quasibound transitions of an alkali–noble gas system within a laser beam are analysed in the density matrix formulation. New formulae for one- and two-photon transition probabilities are derived without the use of the perturbation theory. Numerical calculations are carried out for one-photon electric dipole transitions of the Na + Kr system in the limit of weak radiation fields.

1. *Introduction*

There have been many papers on the interaction of atomic and molecular systems with an intense laser field. It is well-known that in such cases the usual perturbative method fails. Therefore, to obtain probabilities of radiative transitions in atomic and molecular systems being in contact with an intense radiation field, many authors propose the use of some nonperturbative methods. Lately Kroll and Watson [1] gave a non-perturbative analysis of the problem. Their idea has been further developed by Lau [2, 3]. The authors dealt with two atom scattering in an intense laser-field mode. Treating the scattering as near-adiabatic they obtained a formula for the many-photon transition probability. Two atoms colliding in an intense laser field were handled by them as a "quasimolecule" with a finite number of discrete energy levels. In the adiabatic collision approximation there are no radiation transitions among the energy levels of the quasi-molecule, but the energy levels are strongly disturbed in the intense laser field. Therefore, energy gaps between some levels may become so small that transitions between them can occur either with the participation of a number of field photons, as requred by the resonance condition, or simply due to collisions themselves. When the interatomic distance is such that the energy gap reaches a minimum, the transition probability becomes

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maximal and it can be calculated by means of a Landau-Zener-like formula. However, Kroll, Watson and Lau demonstrate through numerical results that it seems that their approach to this problem is not satisfactory. It is so because the authors do not treat the quasimolecule consequently as a two-atom molecule with its vibrational-rotational structure. In the present work we shall restrict ourselves to the study of radiative transitions between two discrete states of a quasimolecule formed during a collision of two atoms in an intense electromagnetic field. We shall derive a formula for the probability of such transitions in the density operator formulation. Although our considerations will be limited mainly to the study of the two-state system it will be shown that the proper equations for a system of many discrete states reduce to the equations obtained for the first one. It the next Section we give a short analysis of the equilibrium state of gas composed of two sorts of atoms being in contact with an intense radiation field. The third Section is devoted to obtaining a system of differential equations for the matrix elements of the density operator between the different molecular states. In Section 4 we give an analysis of the interaction operator between the quasimolecule and the free radiation field. The numerical calculations and the discussion of the obtained results are in Section 7. The work ends with a general discussion of the obtained equations.

2. *Equilibrium state*

Consider a gas composed of two sorts of atoms contained in a volume $\mathscr{V}$ and being in contact with a one mode intense radiation field. In general, if a gas is composed of some atoms or molecules then in order to describe the state of the gas it is enough to know the probabilities of respective states of a single gas atom (or molecule) and the total number of the gas atoms. Thus we can express the state of the gas in terms of the so-called population numbers of the states of a single gas particle. Let the radiation field be not in resonance with the particles of the gas. Thus there occur no radiative transitions in the gas. But when two different atoms collide then during the collision the energy levels of such a diatomic modify considerably due to presence of the radiation field and some radiative transitions can appear. Because the effective interaction between the diatomic and the radiation field takes place only if the resonance condition is satisfied, we can say that the interaction responsible for the transition is "turned on" short before a collision occurs and "turned off" after the collision. When the resonance condition is not satisfied the quasimolecule remains still in the ground state as long as collisions are adiabatic. Therefore, the diagonal matrix element of the diatomic density operator in the ground state is equal to unity and the others are equal to zero. After the collision the quasimolecule can be found with some probability in one of the upper states. This means that now also the other diagonal matrix elements of the density operator are different from zero. How to calculate them is the aim of the present work. Now we are going to write a rate equation for gas interacting with a radiation field. Let the gas under consideration be composed of N_s alkali atoms and N_p rare gas atoms so that $n_p = N_p/\mathscr{V}$ is the density of the noble gas atoms. Let a denote the ground state of the quasimolecule and b stands for an upper state. If N_m is the number of the quasimolecules in the upper state then we have the rate equation

$$\frac{dN_m}{dt} = N_s n_p v \sigma_{ba} - N_m \tau^{-1} - N_m w_c - N_m n_p v \sigma_{ba}. \tag{1}$$

Here σ_{ba} denotes the cross section for a transition from the lower to the upper state during a single collision, v is the relative velocity of the atoms before the collision, τ^{-1} is the probability per unit time for spontaneous emission of the quasimolecule from the upper to the lower state and w_c stands for the probability per unit time of the decay of the quasimolecule in the $|b\rangle$-state due to collisions. Solving equation (1) we get

$$N_m(t) = \frac{N_s n_p v \sigma_{ba}}{\tau^{-1} + w_c + n_p v \sigma_{ba}} \left(1 - e^{-(\tau^{-1} + w_c + n_p v \sigma_{ba})t}\right). \tag{2}$$

In the equilibrium state one obtains that

$$N_m(t \to \infty) = \frac{N_s n_p v \sigma_{ba}}{\tau^{-1} + w_c + n_p v \sigma_{ba}} \tag{3}$$

and the ratio $N_m(t \to \infty)/N_s$ determines the probability that the quasimolecule will be found in the $|b\rangle$-state. The value of this ratio is different from ϱ_{bb} (ϱ being the density operator) but there is close relation between ϱ_{bb} and σ_{ba}.

3. *Transition probability in the density operator formulation*

Now we want to formulate a general theory of radiative transitions between two discrete states of two atoms colliding within a laser beam. Such a situation can be realized, for example, by performing an atomic-beam scattering experiment with a laser focused in the region of collision. We assume further the collisions to be adiabatic. Treating the colliding atoms as one quasimolecule which interacts with an intense radiation field we can write the Hamiltonian of the whole of the system as

$$H = H_{\mathrm{M}} + H_{\mathrm{R}} + V \equiv H_0 + V, \tag{4}$$

where H_{M} denotes the Hamiltonian of the quasimolecule, H_{R} is the Hamiltonian of the free radiation field and V stands for the interaction between both subsystems. Denoting by ϱ the density operator of the system we have Liouville equation

$$i\hbar \frac{\partial \varrho(t)}{\partial t} = [H, \varrho(t)]. \tag{5}$$

The last equation is the starting point for our analysis. The molecular states $|\psi_a\rangle$ are solutions to the eigenvalue equation

$$H_{\mathrm{M}} |\psi_a\rangle = \mathscr{E}_a |\psi_a\rangle. \tag{6}$$

Similarly, the field states $|\varphi_n\rangle$ satisfy the equation

$$H_{\mathrm{R}} |\varphi_n\rangle = E_n |\varphi_n\rangle. \tag{7}$$

In general, for a many mode field, $n = \{n_1, n_2, \ldots, n_l, \ldots\}$, where n_l is the photon number of l^{th} mode. Each of the molecular states depends on time through the internuclear distance $\boldsymbol{R}$. The vector $\boldsymbol{R}$ is assumed to be a known function of time and can be obtained as the solution of classical motion on the appropriate molecular potential surfaces. In the remote past the interaction V has not been "turned on" and the quasimolecule is in the ground state, say $|\psi_a\rangle$. Let the relative velocity of the two atoms v be directed parallel to the z-axis and the impact parameter be b, then, in the straightline trajectory approximation, we have $z = vt$ and $R^2 = b^2+z^2$. The laser-beam interaction is slowly "turned on" and the two atoms collide. After the collision the beam interaction is slowly "turned off" and the final quasimolecular state is observed. Let us now define Liouville space $\mathscr{L}$ as the direct product of the Hilbert space $\mathscr{H}$ generated by the Hamiltonian H_0 and of the dual space as $\mathscr{H}$, $\mathscr{H}^\dagger$ i. e. $\mathscr{L} = \mathscr{H} \otimes \mathscr{H}^\dagger$. If A is any element of $\mathscr{L}$ then the Hamiltonian $\hat{H}$ acts according to the following rule $\hat{H}A = AH-HA$. Thus we can rewrite Eq. (5) as

$$\frac{\partial \varrho(t)}{\partial t} = \frac{i}{\hbar} \hat{H}\varrho(t). \tag{8}$$

Taking now the functions

$$|an; t\rangle = \exp\left\{-\frac{i}{\hbar}\int^{t} (\mathscr{E}_a+E_n+\langle an|V(t')\,|an\rangle)dt'\right\} |\psi_a\rangle\,|\varphi_n\rangle, \tag{9}$$

we can expand ϱ in states $|an; t\rangle\,\langle bm; t|$ as

$$\varrho(t) = \sum_{an,bm} \varrho_{an,bm}(t)\,|an; t\rangle\,\langle bm; t|, \tag{10}$$

where

$$\varrho_{an,bm}(t) = \langle an; t|\varrho|bm; t\rangle.$$

By the sign $\sum$ we understand here the sum over all the discrete states and the integral over all the continuous states of the quasimolecule. Now inserting (10) into (8) we get the following equations

$$\dot{\varrho}_{an,bm}(t) = \frac{i}{\hbar}\left[\sum_{b'm' \neq bm} \varrho_{an,b'm'}(t)\,\langle b'm'; t|V(t)\,|bm; t\rangle \right.$$
$$\left. - \sum_{a'n' \neq an} \varrho_{a'n',bm}(t)\,\langle an; t|V(t)\,|a'n'; t\rangle\right] \tag{11}$$

and

$$\dot{\varrho}_{an,an}(t) = -\frac{2}{\hbar}\,\mathrm{Im}\left(\sum_{bm} \varrho_{an,bm}(t)\,\langle bm; t|V(t)\,|an; t\rangle\right). \tag{12}$$

Here a dot over a symbol means $\partial/\partial t$ and Im (z) denotes the imaginary part of z. In deriving the last equations we neglected all the terms with matrix elements of the type $\langle \psi_a | d\psi_b/dt \rangle$ (see, e. g. Schiff [8], Section 8).

4. *Interaction operator*

We shall restrict the quasimolecule radiation field interaction to that in the dipole approximation. The alkali-rare gas quasimolecule has a permanent dipole moment $\boldsymbol{d}_M$ directed along the internuclear axis. Besides, in an external electromagnetic field, there appears an induced dipole moment that depends on the polarizability of the quasimolecule. It is also worth noting that in an intense external radiation field the interaction energy of the atoms changes during the collision compared with that without the field. This is due to appearance of the additional interaction term connected with the induced dipole moments of the atoms. Therefore, the interaction operator can be put in the following form

$$V(\boldsymbol{R}) = -\boldsymbol{d}_M \cdot \boldsymbol{E}(0) - \tfrac{1}{2}\, \alpha_M(R) \boldsymbol{E}(0) \cdot \boldsymbol{E}(0) + \tfrac{1}{2}\, R^{-3} \left(\boldsymbol{d}_s \cdot \boldsymbol{d}_p - \frac{3(\boldsymbol{d}_s \cdot \boldsymbol{R})\,(\boldsymbol{d}_p \cdot \boldsymbol{R})}{R^2} \right). \quad (13)$$

Here $\boldsymbol{d}_M$ denotes the permanent dipole moment of the quasimolecule, $\alpha_M(R)$ is its polarizability and $\boldsymbol{d}_s$ and $\boldsymbol{d}_p$ are the induced dipole moments of the alkali and rare gas atoms respectively. The vector $\boldsymbol{E}(0)$ stands for the external electric field at the centre of the quasimolecule. According to Silberstein [7], the mean polarizability of a two-atom molecule can be expressed in terms of the atomic polarizabilities of the individual atoms as

$$\alpha_M(R) \simeq (\alpha_s + \alpha_p)\,(1 + 2\alpha_s \alpha_p R^{-6}), \quad (14)$$

where α_s and α_p are the polarizabilities of alkali and rare gas atoms respectively. Similarly we have

$$\boldsymbol{d}_s = \alpha_s(R) \boldsymbol{E}(0), \qquad \boldsymbol{d}_p = \alpha_p(R) \boldsymbol{E}(0), \quad (15)$$

where

$$\alpha_s(R) \simeq \alpha_s(1 + 2\alpha_s \alpha_p R^{-6}), \qquad \alpha_p(R) \simeq \alpha_p(1 + 2\alpha_s \alpha_p R^{-6}). \quad (16)$$

Since equation (5) is given in the Schrödinger picture we take $\boldsymbol{E}$ as independent of time i. e. we put

$$\boldsymbol{E}(\boldsymbol{R}) = i \sum_{l\lambda} \left(\frac{\hbar \omega_l}{2\varepsilon_0 \mathcal{V}} \right)^{1/2} \boldsymbol{e}_{l\lambda} (a_{l\lambda} e^{i\boldsymbol{k}_l \boldsymbol{R}} - a^\dagger_{l\lambda} e^{-i\boldsymbol{k}_l \boldsymbol{R}}), \quad (17)$$

where a and $a^\dagger$ are photon annihilation and creation operators. Keeping in mind that

$$a|n\rangle = \sqrt{n}\,|n-1\rangle, \qquad a^\dagger |n\rangle = \sqrt{n+1}\; |n+1\rangle$$

and restricting our further considerations to one mode electromagnetic field (l, λ) we obtain

$$\langle a n_l | V(\boldsymbol{R}) \, | a n_l \rangle = -\frac{n_l \hbar \omega_l}{2\varepsilon_0 \mathcal{V}} \left[\langle a | \alpha_M(R) \, | a \rangle - \langle a | \alpha_s(R) \alpha_p(R) \, | a \rangle \, (1 - 3 \cos^2 \vartheta) R^{-3} \right], \quad (18)$$

where $n_l\hbar\omega_l/\mathscr{V}$ is the density of the field energy and ϑ is the angle between the axis of the molecule and the polarization vector $\boldsymbol{e}_{l\lambda}$. In similar way we get the nondiagonal matrix elements of V. For one photon absorption i. e. for the $|bn_l-1\rangle \leftarrow |an_l\rangle$ transition we have

$$\langle nb_l-1|V(\boldsymbol{R})\,|an_l\rangle = i\left(\frac{n_l\hbar\omega_l}{2\varepsilon_0\mathscr{V}}\right)^{1/2} \langle b|\,(\boldsymbol{e}_{l\lambda}\cdot\boldsymbol{d}_{\mathrm{M}})\,|a\rangle \tag{19}$$

and for two photon absorption

$$\langle bn_l-2|V(\boldsymbol{R})\,|an_l\rangle = \sqrt{n_l(n_l-1)}\,\frac{\hbar\omega_l}{4\varepsilon_0\mathscr{V}}\,[\langle b|\alpha_{\mathrm{M}}(R)\,|a\rangle$$

$$+\langle b|\alpha_s(R)\alpha_p(R)\,|a\rangle\,(1-3\cos^2\vartheta)R^{-3}]. \tag{20}$$

Putting now $\mathscr{E}_{an_l}(R) = \mathscr{E}_a+\langle an_l|V(\boldsymbol{R})|an_l\rangle$ and $\mathscr{E}_{bm}(R) = \mathscr{E}_b+\langle bm|V(R)|bm\rangle$ we get

$$\langle bm;t|V(\boldsymbol{R})\,|an_l;t\rangle \equiv \exp\left\{\frac{i}{\hbar}\int^{t}[\mathscr{E}_{bm}(R)-\mathscr{E}_{an_l}(R)+E_m-E_{n_l}]dt'\right\}\langle bm|V(\boldsymbol{R})\,|an_l\rangle$$

$$= [\cos\gamma_{ba}(t)+i\sin\gamma_{ba}(t)]\,\langle bm|V(\boldsymbol{R})\,|an_l\rangle, \tag{21}$$

with

$$\gamma_{ba}(t) = \hbar^{-1}\int^{t}[\mathscr{E}_{bm}(R)-\mathscr{E}_{an_l}(R)+E_m-E_n]dt' \tag{22}$$

and m equal $n-1$ or $n-2$, n_l being the initial number of photons in the (l, λ)-mode. The eigenvalues E_m and E_n are, of course, equal to $m\hbar\omega_l$ and $n_l\hbar\omega_l$ respectively.

5. Two-state approximation

In the remaining part of this paper we shall restrict ourselves to the two-state approximation for the quasimolecule. Such an idealisation of a diatomic system seems to be far from reality but thanks to that our expressions for the matrix elements of ϱ simplify it appreciably. Besides, it will be pointed out that in a general case, when treating the quasimolecule as a system of many discrete states, the corresponding expressions reduce to those obtained in the two-state approximation. Let us consider then the one photon absorption from the lower state $|an\rangle$ to the upper state $|bn-1\rangle$. Putting $\varrho_{an,an}(t)-\varrho_{bn-1,bn-1}(t) = F(t)$ Eqs. (11) and (12) reduce in the two-state approximation to the following equations

$$\dot{F}(t) = -\frac{4}{\hbar}\left(\frac{n_l\hbar\omega_l}{2\varepsilon_0\mathscr{V}}\right)^{1/2}\langle b|\,(\boldsymbol{e}_{l\lambda}\cdot\boldsymbol{d}_{\mathrm{M}})\,|a\rangle\,(\mathrm{Re}\,\varrho_{an,bn-1}(t)\cos\gamma_{ba}(t)-\mathrm{Im}\,\varrho_{an,bn-1}(t)\sin\gamma_{ba}(t)).$$

$$\mathrm{Re}\,\dot{\varrho}_{an,bn-1}(t) = \hbar^{-1}\left(\frac{n_l\hbar\omega_l}{2\varepsilon_0\mathscr{V}}\right)^{1/2}\langle b|\,(\boldsymbol{e}_{l\lambda}\cdot\boldsymbol{d}_{\mathrm{M}})\,|a\rangle\cos\gamma_{ba}(t)F(t),$$

$$\mathrm{Im}\,\dot{\varrho}_{an,bn-1}(t) = -\hbar^{-1}\left(\frac{n_l\hbar\omega_l}{2\varepsilon_0\mathscr{V}}\right)^{1/2}\langle b|\,(\boldsymbol{e}_{l\lambda}\cdot\boldsymbol{d}_{\mathrm{M}})\,|a\rangle\sin\gamma_{ba}(t)F(t). \tag{23}$$

Making use of the relation

$$\varrho_{an,an}(t)+\varrho_{bn-1,bn-1}(t) = 1 \tag{24}$$

we obtain finally

$$\varrho_{an,an}(t) = \tfrac{1}{2}(1+F(t)), \qquad \varrho_{bn-1,bn-1}(t) = \tfrac{1}{2}(1-F(t)). \tag{25}$$

For the two-photon absorption we get equations identical in form to Eqs. (23) but with other matrix elements of the interaction operator. The set of equations (23) is to be solved with the boundary conditions such that in the remote past $\varrho_{aa} = 1$, $\varrho_{bb} = 0$ and $\varrho_{ab} = 0$.

6. *Semi-classical treatment*

It is well-known that the ground state of the quasimolecule composed of alkali-rare gas atoms is repulsive or has a very shallow minimum at some internuclear distance. But, as it was calculated by Baylis [4] and Pascale et al. [5] some excited states are pronounced attractive. In our considerations we treat the quasimolecule itself quantum mechanically whereas the relative motion of both atoms in the ground state is described classically. In the straight line trajectory approximation $z = vt$ and we can easily express $\partial\varrho/\partial t$ by $\partial\varrho/\partial z$. In the integration of Eqs. (23) the behaviour of the function $\gamma_{ba}(t)$ plays a great role. Since the functions $\sin\gamma_{ba}(t)$ and $\cos\gamma_{ba}(t)$ oscillate very quickly in time, we conclude that the main contribution to the integral results from the surroundings of the extremum of the function $\gamma_{ba}(t)$. As one can easily convince himself, the function $\gamma_{ba}(t)$ has the extremum if the resonance condition is satisfied. Therefore, expanding the function $\gamma_{ba}(t)$ in a series around the point where the resonance occurs, we have

$$\gamma_{ba}(t) \equiv \gamma_{ba}(z) = (\hbar v)^{-1}\int^{z_0}[\mathscr{E}_b(z')-\mathscr{E}_a(z')-\hbar\omega_l]dz' + \frac{z_0}{2\hbar v R_0}\left[\left(\frac{\partial\mathscr{E}_b(R)}{\partial R}\right)_0 - \left(\frac{\partial\mathscr{E}_a(R)}{\partial R}\right)_0\right]z^2, \tag{26}$$

where $z_0 = vt_0$ and $R_0 = (b^2+z_0^2)^{1/2}$. In deriving the last expression we made use of the fact that the first derivative of $\gamma_{ba}(t)$ vanishes at the resonance point. As one can see from (23) to obtain the required matrix elements of the interaction operator we need first to know the corresponding molecular wave-functions of the quasimolecule. Concerning the electronic wave-functions we guessed that they can be calculated via the method proposed by Baylis. The others can be taken as those for a two-atom molecule. If it happens that the matrix elements of the dipole moment of the quasimolecule are slowly varying functions of R then it will be a good approximation to take for the calculation their values at the resonance point.

7. *Calculations and results*

In order to illustrate our method we have solved the set of Eqs. (23) for the Na + Kr system in the limit of a weak laser field when the absorption (emission) coefficients for electric dipole transitions are proportional to the radiation intensity. The set of Eqs. (23)

has been solved for one-photon transitions only. It is due to the fact that we do not know as yet the electronic wave functions of the quasimolecule. If they were known one could solve Eqs. (23) for the two-photon transitions as well. The calculations concern the two electronic transitions ${}^2\Sigma^+_{1/2} \to {}^2\Pi_{1/2}$ and ${}^2\Sigma^+_{1/2} \to {}^2\Pi_{3/2}$ with the vibrational quantum numbers of the upper state $v = 0$ and $v = 5$. The corresponding potential surfaces have been taken from York et al. [9] (see Fig. 1). Besides, the calculations are limited to the case when the lower state of atoms is the s-colliding state ($l = 0$). Thus, according to the required selection rule, the quantum number J of the quasimolecule does not change for the ${}^2\Sigma^+_{1/2} \to {}^2\Pi_{1/2}$ transition and changes by one for the ${}^2\Sigma^+_{1/2} \to {}^2\Pi_{3/2}$ transition. It was assumed the total wave function of the quasimolecule to be a product of the electronic wave function, of the rotational wave function and the vibrational wave function. The vibrational wave functions $\psi_{EJ}(r)$ put in the form $\psi_{EJ}(r) = R(r)/r$ satisfy for both the lower state and the upper state of the quasimolecule the wave equation

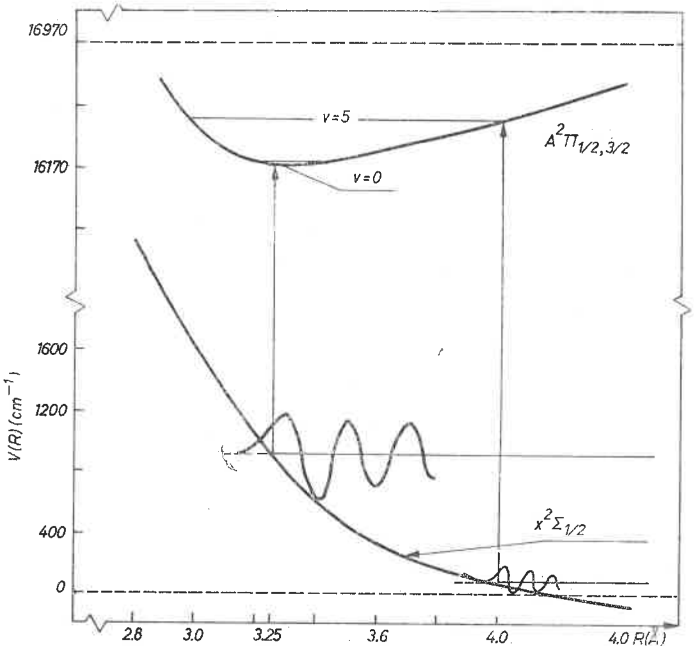

Fig. 1. Potential curves for the ground and the first excited state of the Na + Kr system

$$-\frac{\hbar^2}{2\mu}\frac{d^2R(r)}{dr^2}+V_J(r)R(r) = E_JR(r), \tag{27}$$

with

$$V_J(r) = U(r)+\frac{\hbar^2 J(J+1)}{2\mu r^2}.$$

To solve the set of Eqs. (23) we need the vibrational functions from the small range around the resonance point r_0 only. Therefore, for the lower state they can be well approximated by the corresponding Airy functions. Thus we put $R(r) = A\Phi(-\xi)$, where $\xi = (2\mu F_J/\hbar^2)^{1/2}(r-r_0)$ with $F_J = |(dV_J(r)/dr)_0|$ and $\Phi(x)$ is the Airy integral. The normalizing constant A has been taken so that the function $R(r)$ can be normalized asymptotically to the particle flux density in the ingoing (or outgoing) wave equal $1/2\pi\hbar$ (see Landau et al. [10]). The interaction potential $U(r)$ for the upper electronic state of the Na+Kr system was approximated by means of the Morse potential

$$U(r) = D_e\{[e^{-B(r-r_e)}-1]^2-1\}$$

with the parameters $D_e = 730\ \text{cm}^{-1}$, $r_e = 3.25$ Å and $B = 1.45\ \text{Å}^{-1}$ (see [9]). As was shown by Pekeris [11] the solutions of the wave equation (27) can be well approximated in terms of the generalized Laguerre polynomials. Particularly, when neglecting the rotational term the solution of Eq. (27) can be expressed as $R_v(r) = N_v e^{-y/2}y^{s/2}L_{sv}(y)$, where $y = \exp\{-B(r-r_e)\}$, $s = k-2v-1$ and $k = \omega_e x_e/\omega_e$ is a characteristic parameter of a two-atom molecule. Generalized Laguerre polynomials are given by

$$L_{sv}(x) = x^v - \frac{v}{1!}(s+v)x^{v-1} + \frac{v(v-1)}{2!}(s+v)(s+v-1)x^{v-2} + \dots$$
$$+(-1)^v(s+v)(s+v-1)\dots(s+1),$$

and the normalizing factor N_v is

$$N_v = \left[\frac{B(k-2v-1)}{v!(k-v-1)\Gamma(k-v-1)}\right]^{1/2}.$$

On the other hand the rotational wave functions of the quasimolecule are taken to be those for a symmetric top given by so-called Jacoby (hypergeometric) polynomials

$$\Phi^J_{MK}(\theta_i) = \sqrt{\frac{2J+1}{8\pi^2}}\,D^J_{MK}(\theta_i)$$

(see, e.g. Herzberg [12], p. 118). Since we do not know the electronic functions of the quasimolecule, therefore, to have the corresponding matrix element of the dipole moment (see Eqs. (23)) we have replaced it by its asymptotic value taken at the interatomic distance, where the electronic wave functions of the system go over into the corresponding atomic wave functions. Thus for the matrix element $\langle R_{31}|r|R_{30}\rangle$ of the atom of sodium we took from Bates et al. [13] the value to be 4.41588 a_0, where a_0 is the Bohr radius. For the transitions under consideration we have obtained

$$\langle {}^2\Pi_{1/2}|(\boldsymbol{e}_{l\lambda}\cdot\boldsymbol{d}_{\mathrm{M}})|{}^2\Sigma^+_{1/2}\rangle = 0.346944ea_0$$

and

$$\langle {}^2\Pi_{3/2}|(\boldsymbol{e}_{l\lambda}\cdot\boldsymbol{d}_{\mathrm{M}})|{}^2\Sigma^+_{1/2}\rangle = -0.520416ea_0,$$

where e is the electronic charge. Since we consider the interaction of a two-atom system with the laser beam of definite polarization therefore to perform the calculations, one can take an arbitrary geometry of the system. Our calculations were carried out for the case

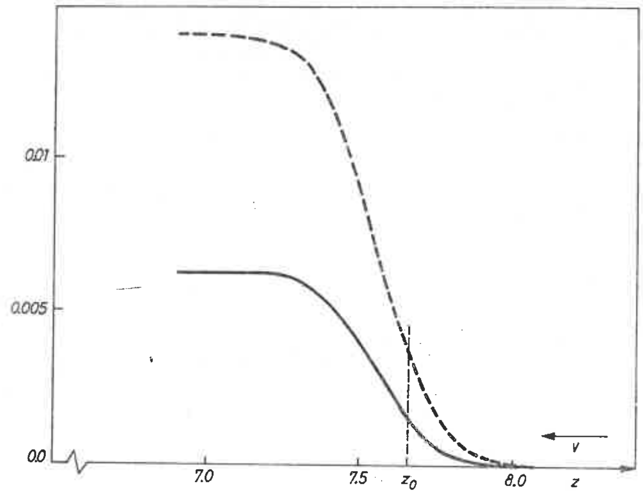

Fig. 2. Diagonal matrix element ϱ_{bb} versus the parameter $z = vt(a_0)$. The solid line corresponds to the $^2\Sigma^+_{1/2} \rightarrow {}^2\Pi_{1/2}$ transition and the dashed line corresponds to the $^2\Sigma^+_{1/2} \rightarrow {}^2\Pi_{3/2}$ transition (both for $v = 5$). The arrow shows the direction of the relative velocity of atoms

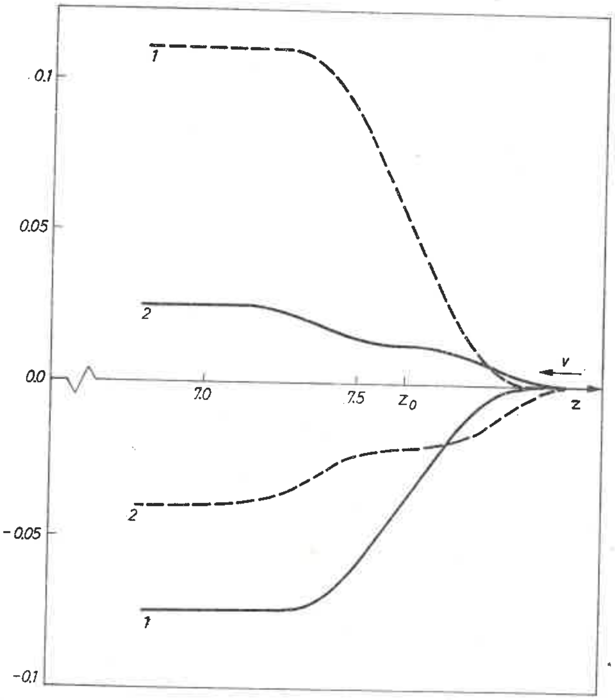

Fig. 3. Same as Fig. 2 for an off-diagonal matrix element ϱ_{ba}. Re ϱ_{ba} and Im ϱ_{ba} are denoted, respectively, by *1* and *2*

when the polarization vector $e_{i\lambda}$ of the laser light has the same direction as the relative velocity of the colliding atoms. Finally, the set of Eqs. (23) has been solved numerically with the help of the sixth-order Runge–Kutta routine. Figs 2 and 3 present the solutions for the two electronic transitions ${}^2\Sigma^+_{1/2} \to {}^2\Pi_{1/2}$ and ${}^2\Sigma^+_{1/2} \to {}^2\Pi_{3/2}$ with $v = 5$ (the transition energies equal 16518 cm^{-1} and 16535 cm^{-1} respectively) for the radiation intensity 118 W/sec. In order for these transitions to take place the relative energy of the colliding atoms has to be equal to 82 K. This means that the atoms can collide in the s-colliding state if the impact parameter b is smaller than its boundary value $b_m = 0.18$ Å. Fig. 2 presents the diagonal matrix element ϱ_{bb} versus the parameter $z = vt(a_0)$ (with $r = (b^2+z^2)^{1/2}$) for an arbitrary value of $b < b_m$. The solutions of Eqs (23) do not depend practically on b for $0 < b < b_m$. We see that two atoms colliding within a laser beam can go over into a quasibound state provided the resonance condition is satisfied. The probability of being the atoms in the quasibound state increases gradually when the perturbing particle (Krypton) approaches the resonance position r_0 and reaches a constant value at some interatomic distance a little smaller than r_0. We note also that the probability of finding the two atoms in the quasibound state after the collision is for the (1/2 → 3/2) transition nearly about a factor of two larger than for the (1/2 → 1/2) transition. On the other hand both transitions with $v = 0$ (the transition energies equal 15354 cm^{-1} and 15371 cm^{-1} respectively) can take place with the relative energy of the colliding atoms at 1306 K. This corresponds to $b_m = 0.05$ Å. For these transitions we have obtained the asymptotic values of ϱ_{bb} to be 0.0036 and 0.008, respectively. Since the cross section for the transition from the lower state $|a\rangle$ to the upper state $|b\rangle$ of the quasimolecule can be defined as

$$\sigma_{ab} = 2\pi \int_0^{b_m} \varrho_{bb}(b) b db,$$

we can calculate it for all the transitions considered to get

$$\sigma_{ab}(1/2 \to (v = 0)1/2) = 1.6 \cdot 10^{-4} a_0^2, \quad \sigma_{ab}(1/2 \to (v = 0)3/2) = 3.29 \cdot 10^{-4} a_0^2,$$

$$\sigma_{ab}(1/2 \to (v = 5)1/2) = 1.31 \cdot 10^{-3} a_0^2, \quad \sigma_{ab}(1/2 \to (v = 5)3/2) = 2.92 \cdot 10^{-3} a_0^2.$$

From the obtained results we conclude that the free-quasibound transition of a two-atom system during the collision within a laser beam is more probable for the (1/2 → 3/2) transition than that for the (1/2 → 1/2) transition. Besides the transitions with $v = 5$ occur about ten times more frequently than those for $v = 0$. The latter result means that the free-quasibound transitions of the atoms induced by collisions are more probable at smaller relative energies of colliding atoms.

8. *Discussion and conclusion*

We have obtained the set of differential equations for the matrix elements of the density operator of a quasimolecule in the two-state approximation. But describing the real quasimolecule with more than two levels is more useful, since the role of near-resonant intermediate states in determining the one- and two-photon transition probabilities is important. We want now to point out that in the density operator formulation, as it has been done in the present work, the appropriate set of differential equations for the quasimolecule of a finite number of well-separated levels reduces to that obtained in the two-level approximation. Consider for example a three-level quasimolecule and let the resonance condition be satisfied for two pairs of levels. Of course, the resonance condition is not satisfied for both pairs simultaneously. If it is satisfied primarily for one pair of the levels during the collision it is not satisfied for the other one. Therefore, in the integration of the equations the nonresonance terms can be dropped and we obtain again the set of three equations to solve. Afterwards, the second pair of the levels is in resonance with the electromagnetic field whereas the first one is not. Now in integrating the equations in the other integration range we can drop again nonresonance terms. Thus, we get another set of three equations to be solved with the corresponding boundary conditions. We note only that now any matrix element of the density operator depends on the remaining ones. The considerations carried out in the present work show also that one can obtain the probability of one- and two-photon transitions in two-atom systems within a laser beam without use of the perturbation theory. Therefore, it seems that the procedure outlined in this paper can be applied to some classes of atomic systems being in contact with an intense radiation field with success.

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