Influence of atomic coherence induced by laser-assisted near-resonant collisions on the far-wing absorption profile

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An analysis of near-resonant collisions between dissimilar atoms in the presence of a radiation field reveals their effect on the far wings of the absorption profile. Extending a model due to Cavalieri, Arimondo, and Matera, we take into account the collisional shifts of atomic levels, as well as the collisional coupling between atoms and the coupling with the radiation field. A general formula for the absorption profile is derived and expressed in terms of the universal line-shape function of the unified Franck-Condon treatment of pressure broadening. We show that in some cases collision-induced coherence can give rise to a strongly depressed red wing that exhibits transparency for some values of the laser detuning.

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I. INTRODUCTION

Atomic coherences that are created when an atom is driven by a radiation field to a coherent superposition of states are the subject of an extensive series of experimental studies performed by laser-spectroscopy methods. Although in many cases the coherences are damped by collisions, there are processes such as pressure-induced extra resonances occurring in four-wave mixing [1] and in fluorescence emission [2,3] in which the collisional interaction plays a critical role in the creation of the atomic coherences.

Cavalieri *et al.* [4] have recently performed a theoretical study of near-resonant collisions of two dissimilar atoms A and B in the presence of a laser field and have shown that the absorption profile in the line wings can be significantly affected by the collision-induced coherence between excited levels of these atoms. In their approach, the colliding atoms A and B are coupled to a radiation field with n photons of frequency ω_L. The absorption process in this system can follow either of two paths:

$$A^* + B + (n-1)\hbar\omega_L, \qquad (1)$$
$$A + B + n\hbar\omega_L \nearrow \qquad \uparrow$$
$$\searrow A + B^* + (n-1)\hbar\omega_L.$$
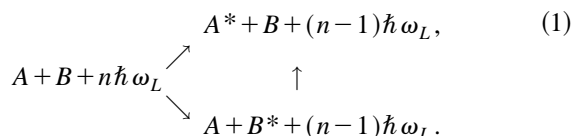
The excitation of atom A can take place either directly by the absorption of a photon or indirectly by a collisional-energy transfer following photon absorption by atom B. As shown by Cavalieri *et al.* [4], quantum interference between the transition amplitudes for these two paths can produce a substantial modification of the far-wing absorption profile.

To calculate these amplitudes, Cavalieri *et al.* follow a methodology developed by Berman and coworkers [5] and apply the dressed-state technique, which has been used much in the literature to describe laser-assisted collisions [6,7]. However, the only collisional interaction included in their derivation of the absorption cross section is the dipole-dipole

interaction, and indeed only its off-diagonal elements, responsible for the collisional coupling between the excited atoms A^* and B^*. No effort was made in their paper to consider the effects of *diagonal elements* of the interatomic potential, which represent the potential curves of the adiabatic molecular states of the $A + B$ system. This means that the collisional shifts (in particular, those due to the van der Waals interaction) of the atomic levels are *not* included in their treatment. However, it is precisely these collisional shifts of atomic levels that are the most important cause of the pressure broadening in spectral lines. Because the authors of Ref. [4] have ignored such shifts, we find, in contrast to a statement made by them, that their derivation of an absorption profile with a double slope similar to that experimentally observed by Niemax for the Eu-Sr system [8], *cannot* be regarded as evidence for the transition from a van der Waals to resonant interaction. Such an interpretation was originally proposed by Niemax on the basis of the quasistatic theory.

In the present paper, we extend the model of Cavalieri *et al.* [4] to derive a general formula for the absorption profile in the case of near-resonant collisions between dissimilar atoms. The main modifications made to their model comprise the inclusion of collisional shifts of the atomic levels due to adiabatic potentials and the application of cubic expansions of the corresponding phase functions in place of the quadratic ones used in Ref. [4]. One goal of this paper is to show that the Niemax interpretation, which relates the double-slope behavior of the absorption profile of the line wings to the transition from a van der Waals to resonant interaction, can, in fact, be corroborated in the framework of the model proposed by Cavalieri *et al.* [4] provided the collisional shifts of atomic levels are taken into account.

II. PHYSICAL MODEL

The starting point in our derivation is the same as in the approach of Cavalieri *et al.* [4]. We consider a near-resonant collision of two dissimilar atoms A and B in the presence of a laser radiation field

$$\mathscr{E} = \mathscr{E}_0 \cos\omega_L t, \qquad (2)$$

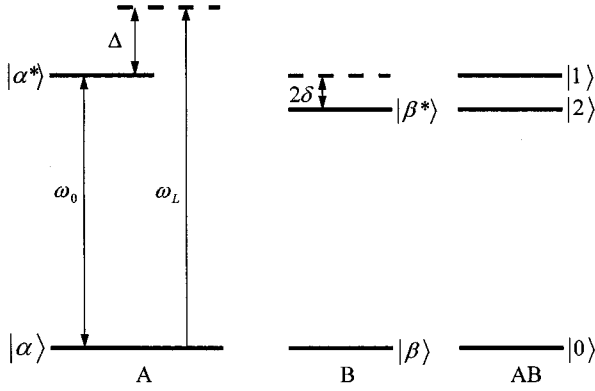*Permanent address: Institute of Physics, Nicholas Copernicus University, Torun, Poland.

FIG. 1. Schematic energy-level diagram for the near-resonant collisions of two dissimilar atoms A and B, showing the basis states and frequencies for the model of Cavalieri *et al.* [4].

where the amplitude $\mathscr{E}_0$ is assumed to be constant during collision. The atoms are taken to be two-level systems, as shown in Fig. 1, where the same notation is used as in Ref. [4]. We let $|\alpha\rangle$ and $|\beta\rangle$ be the ground states and $|\alpha^*\rangle$ and $|\beta^*\rangle$ the excited states of atoms A and B, respectively. As shown in Fig. 1, $\Delta=\omega_L-\omega_0$ denotes the detuning of the laser frequency ω_L from the unperturbed frequency $\omega_0=[E(\alpha^*)-E(\alpha)]/\hbar$ of the $|\alpha\rangle\rightarrow|\alpha^*\rangle$ transition in atom A. The energy defect between the excited levels $|\alpha^*\rangle$ and $|\beta^*\rangle$ is characterized by the parameter

$$2\delta=\frac{E(\alpha^*)-E(\beta^*)}{\hbar}, \tag{3}$$

where $E(\alpha^*)$ and $E(\beta^*)$ are the energies of the corresponding levels of A and B, respectively.

In the absence of the radiation field, the compound system $A+B$ is described in the basis of the relevant product states:

$$|0\rangle=|\alpha,\beta\rangle\equiv|\alpha\rangle|\beta\rangle,$$

$$|1\rangle=|\alpha^*,\beta\rangle\equiv|\alpha^*\rangle|\beta\rangle, \tag{4}$$

$$|2\rangle=|\alpha,\beta^*\rangle\equiv|\alpha\rangle|\beta^*\rangle,$$

with energies $E_0=0$, $E_1=\hbar\omega_0$, and $E_2=\hbar(\omega_0-2\delta)$, respectively. The collisional interaction between atoms A and B is described by an operator $V(R)$, where R denotes the interatomic distance. The strength of the atom-radiation-field interaction is given by

$$\Omega_A=-\frac{\mu_A\mathscr{E}_0}{2\hbar}, \quad \Omega_B=-\frac{\mu_B\mathscr{E}_0}{2\hbar}, \tag{5}$$

where μ_A and μ_B are the dipole transition moments of atoms A and B, respectively.

To describe the evolution of the quasimolecular states modified by coupling to the radiation field, we follow Ref. [4] and apply a standard dressed-state picture. Using the same notation as in Ref. [4], we introduce the field-dressed atomic states $|0,n\rangle$, $|1,n-1\rangle$, and $|2,n-1\rangle$. The energies of these states are $E_{0,n}=\hbar\Delta$, $E_{1,n-1}=0$, and $E_{2,n-1}=-2\hbar\delta$, respectively.

The wave function $|\Psi(t)\rangle$ of the dressed $(A+B)$ quasi-molecule can be expanded,

$$|\Psi(t)\rangle=a_0|0,n\rangle+a_1|1,n-1\rangle+a_2|2,n-1\rangle. \tag{6}$$

The Schrödinger equation then gives the coupled differential equations

$$i\dot{\mathbf{a}}=\hbar^{-1}H\mathbf{a} \tag{7}$$

for the time derivatives, where

$$\mathbf{a}=\begin{pmatrix} a_0 \\ a_1 \\ a_2 \end{pmatrix}, \tag{8}$$

and the Hamiltonian H (in the rotating-wave approximation) is

$$\hbar^{-1}H=\begin{pmatrix} \Delta+V_{00} & \Omega_A & \Omega_B \\ \Omega_A & V_{11} & V_{12} \\ \Omega_B & V_{12}^* & -2\delta+V_{22} \end{pmatrix}. \tag{9}$$

Here

$$V_{00}=\hbar^{-1}\langle\alpha,\beta|V|\alpha,\beta\rangle\equiv\hbar^{-1}\langle0|V|0\rangle \tag{10}$$

represents the adiabatic potential describing the interaction between A and B when both atoms are in their ground states α and β ,

$$V_{11}=\hbar^{-1}\langle\alpha^*,\beta|V|\alpha^*,\beta\rangle\equiv\hbar^{-1}\langle1|V|1\rangle \tag{11}$$

is the adiabatic potential describing the interaction of atom A excited to state α^* with the ground-state atom B, and

$$V_{22}=\hbar^{-1}\langle\alpha,\beta^*|V|\alpha,\beta^*\rangle\equiv\hbar^{-1}\langle2|V|2\rangle \tag{12}$$

describes the interaction of atom B excited to state β^* with the ground-state atom A. In Ref. [4], these adiabatic potentials were neglected and set to zero: $V_{00}=V_{11}=V_{22}=0$. The collisional coupling between the excited states is described by the off-diagonal element

$$V_{12}=\hbar^{-1}\langle\alpha^*,\beta|V|\alpha,\beta^*\rangle\equiv\hbar^{-1}\langle1|V|2\rangle, \tag{13}$$

which in Ref. [4] was assumed to be in the form of the resonance interaction

$$V_{12}=\frac{C_3}{R^3}, \tag{14}$$

with C_3 a real constant. As in Ref. [4], we assume the collisional interaction between the ground state $|0\rangle$ and either of the excited states is negligible: $V_{01}\approx V_{02}\approx0$.

As the next step, a unitary transformation

$$\mathbf{b}=\mathbf{T}\mathbf{a} \tag{15}$$

is performed, with

$$\mathbf{T} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{pmatrix}. \tag{16}$$

The coupled equations (7) are then transformed into

$$i\dot{\mathbf{b}} = \hbar^{-1}(H' + \dot{\mathbf{T}}\mathbf{T}^{-1})\mathbf{b}, \tag{17}$$

where

$$\mathbf{b} = \begin{pmatrix} b_0 \\ b_1 \\ b_2 \end{pmatrix}, \tag{18}$$

and

$$H' = \mathbf{T}H\mathbf{T}^{-1}. \tag{19}$$

Let

$$D = \delta + \frac{1}{2}(V_{11} - V_{22}). \tag{20}$$

If the condition

$$\tan 2\theta = \frac{V_{12}}{D} \tag{21}$$

is fulfilled, then the transformed Hamiltonian H' has the form

$$\hbar^{-1}H' = \begin{pmatrix} \Delta + V_{00} & \Omega_1 & \Omega_2 \\ \Omega_1 & \lambda_+ & 0 \\ \Omega_2 & 0 & \lambda_- \end{pmatrix}, \tag{22}$$

where

$$\Omega_1 = \Omega_A\cos\theta + \Omega_B\sin\theta, \quad \Omega_2 = \Omega_B\cos\theta - \Omega_A\sin\theta \tag{23}$$

and

$$\lambda_\pm = -\delta + \frac{1}{2}(V_{11} + V_{22}) \pm (D^2 + V_{12}^2)^{1/2}. \tag{24}$$

As in Ref. [4], the parameters λ_+ and λ_- can be interpreted as eigenvalues corresponding to the adiabatic collisional dress states $|+,n-1\rangle$ and $|-,n-1\rangle$ defined by

$$|+,n-1\rangle = \cos\theta|1,n-1\rangle + \sin\theta|2,n-1\rangle, \tag{25}$$

$$|-,n-1\rangle = -\sin\theta|1,n-1\rangle + \cos\theta|2,n-1\rangle.$$

In the limit $V_{00} = V_{11} = V_{22} = 0$, we obtain $D = \delta$ and Eqs. (21)–(24) become identical to Eqs. (13)–(15) of Ref. [4].

We assume that the energy defect 2δ between the excited levels is large enough to make the collision adiabatic in the absence of the laser field. This assumption is justified if $2\delta \gg 1/\tau_c$, where τ_c is the duration time of the collision. Using arguments given in Ref. [4], one can show that when the collisional interaction can be taken to be adiabatic, the matrix $\dot{\mathbf{T}}\mathbf{T}^{-1}$ in Eq. (17) can be neglected, leaving

$$i\dot{\mathbf{b}} = \hbar^{-1}H'\mathbf{b}. \tag{26}$$

Our aim is to calculate the absorption profile assuming that both atoms are initially in their ground states. The initial conditions needed for Eq. (26) are therefore

$$b_0(-\infty) = a_0(-\infty) = 1, \tag{27}$$

$$b_1(-\infty) = a_1(-\infty) = 0,$$

$$b_2(-\infty) = a_2(-\infty) = 0.$$

Assuming that the atoms move along classical straight-line trajectories, the interatomic distance at time t is $R(t) = (\rho^2 + v^2 t^2)^{1/2}$, where ρ is the impact parameter and v the relative velocity.

We now consider two cases of absorption in the $(A+B)$ quasimolecule. In the first case we consider positive laser detunings $\Delta > 0$, which correspond to frequencies in the blue wing of the $\alpha \to \alpha^*$ transition in atom A. The absorption cross section $\sigma_1(\Delta)$ there can be generally written as

$$\sigma_n(\Delta) = 2\pi \int_0^\infty |b_n(\infty)|^2 \rho \, d\rho \tag{28}$$

with $n = 1$. The second case corresponds to negative laser detunings $\Delta < -2\delta$, i.e., to the red wing of the $\beta \to \beta^*$ transition in atom B, where the absorption cross section has the same form (28) but with $n = 2$. Equation (28) permits calculations of the cross sections for a fixed relative velocity v. To compare with data from cell experiments, the equations should be averaged over a Maxwellian distribution of velocities. The thermally averaged cross sections, which we denote $Q_1(\Delta)$ and $Q_2(\Delta)$, are defined by

$$Q_n(\Delta) = \frac{1}{\bar{v}}\langle v\sigma_n(\Delta)\rangle, \quad n = 1,2, \tag{29}$$

where $\bar{v}$ is the mean relative velocity for a given temperature T, and the symbol $\langle \ \rangle$ denotes an average over relative velocities v.

III. PERTURBATION TREATMENT

To calculate the absorption cross sections $\sigma_n(\Delta)$, Eqs. (26) must first be solved with the initial conditions (27). If we assume the laser field to be weak, the equations can be solved by perturbation theory. (See the end of Sec. IV for a fuller discussion of the condition on the laser field.) The first-order solutions for the dressed-state amplitudes $b_1(\infty)$ and $b_2(\infty)$ following the collision can be written in the form

$$|b_n(\infty)| = \left| \int_{-\infty}^\infty dt \, \Omega_n(t) \exp[-i\phi_n(t)] \right|, \tag{30}$$

where Ω_1 and Ω_2 are given in Eqs. (23), and θ fulfills condition (21). The phase functions $\phi_1(t)$ and $\phi_2(t)$ are given by

$$\phi_1(t) = \int_{-\infty}^t [\Delta + V_{00}(t') - \lambda_+(t')]dt' \tag{31}$$

and

$$\phi_2(t) = \int_{-\infty}^{t} [\Delta + V_{00}(t') - \lambda_-(t')] dt'. \tag{32}$$

Here we concentrate our attention on the behavior of $|b_1(\infty)|$ and $|b_2(\infty)|$ at large laser detunings $|\Delta|$, i.e., for frequencies in the far wings of either the $\alpha \rightarrow \alpha^*$ or the $\beta \rightarrow \beta^*$ transition in atom A or B, respectively. At large $|\Delta|$, the integrand in Eq. (30) contributes significantly to $|b_1(\infty)|$ and $|b_2(\infty)|$ only in regions of stationary phase, i.e., near points t_S where

$$\dot{\phi}_n(t_S) = 0. \tag{33}$$

According to Eqs. (31) and (32), these stationary-phase points are solutions of

$$\Delta = \lambda_\pm(t_S) - V_{00}(t_S). \tag{34}$$

In the case of straight-line trajectories, there are generally two stationary phase points for each given impact parameter ρ:

$$t_S^{(1)} = \frac{1}{v}(R_S^2 - \rho^2)^{1/2} \tag{35}$$

and

$$t_S^{(2)} = -t_S^{(1)}, \tag{36}$$

corresponding to the same interatomic separation R_S. To evaluate the integral (30), we use an *extended* stationary phase method, in which the phase functions ϕ_1 and ϕ_2 are approximated by cubic expansions around t_S:

$$\phi_n(t) \approx \phi_n(t_S) + \frac{1}{2}\ddot{\phi}_n(t_S)(t - t_S)^2 + \frac{1}{6}\dddot{\phi}_n(t_S)(t - t_S)^3. \tag{37}$$

The integrand in Eq. (30) then yields approximately

$$|b_n(\infty)|^2 = 8\pi^2 \frac{|\Omega_n(t_S)|^2}{|\dddot{\phi}_n(t_S)|} y_n^{1/2} \mathrm{Ai}^2(-y_n), \tag{38}$$

where $\mathrm{Ai}(-y)$ is the regular homogeneous Airy function

$$\mathrm{Ai}(-y) = \frac{1}{2\pi}\int_{-\infty}^{\infty} ds \, \exp\left[i\left(-ys + \frac{1}{3}s^3\right)\right], \tag{39}$$

with

$$y_n = 2^{-2/3}[\ddot{\phi}_n(t_S)]^2 |\dddot{\phi}_n(t_S)|^{-4/3}. \tag{40}$$

According to Eqs. (31), (32), and (24),

$$\ddot{\phi}_n(t_S) = -\frac{1}{2}F_n'(R_S)v_\rho(R_S) \tag{41}$$

and

$$\dddot{\phi}_n(t_S) = -\frac{1}{2}F_n''(R_S)v_\rho^2(R_S), \tag{42}$$

where $R_S = R(t_S)$ and

$$F_n'(R_S) \equiv \left(\frac{dF_n(R)}{dR}\right)_{R_S}, \quad F_n''(R_S) \equiv \left(\frac{d^2F_n(R)}{dR^2}\right)_{R_S}. \tag{43}$$

Here

$$F_1(R) = V_{11} + V_{22} - 2V_{00} + 2(D^2 + V_{12}^2)^{1/2} \tag{44}$$

and

$$F_2(R) = V_{11} + V_{22} - 2V_{00} - 2(D^2 + V_{12}^2)^{1/2}. \tag{45}$$

In Eqs. (41) and (42),

$$v_\rho(R_S) \equiv \left(\frac{dR}{dt}\right)_{t_S} = \frac{\hbar}{\mu}k_\rho(R_S), \tag{46}$$

with

$$k_\rho(R_S) = \hbar^{-1}\left\{2\mu[E_i - V_{00}(R_S)] - \left(\frac{\mu v \rho}{R_S}\right)^2\right\}^{1/2}, \tag{47}$$

where E_i is the initial energy of the relative motion of the colliding atoms, and μ is their reduced mass.

Using the above expressions, we can write the parameter y_n in Eq. (40) as

$$y_n = p_n(R_S)[k_\rho(R_S)]^{-2/3}, \tag{48}$$

where

$$p_n(R_S) = \left(\frac{\mu}{4\hbar}\right)^{2/3}[F_n'(R_S)]^2 |F_n''(R_S)|^{-4/3}. \tag{49}$$

Inserting Eq. (48) into (28) and replacing the integration over impact parameters ρ by an integration over the variable y_1 or y_2, one obtains, for the detuning dependence of the absorption cross sections $\sigma_1(\Delta)$ and $\sigma_2(\Delta)$ at fixed relative velocity v, the result

$$\sigma_n(\Delta) = 3\pi \left|\frac{2\pi\Omega_n(R_S)R_S F_n'(R_S)}{vF''(R_S)}\right|^2 W_S^{(n)}, \tag{50}$$

where

$$W_S^{(n)} = \int_{y_{\min}^{(n)}}^{\infty} y^{-2}\mathrm{Ai}^2(-y)dy \tag{51}$$

with

$$y_{\min}^{(n)} = p_n(R_S)\left(\frac{\hbar^2}{2\mu}\right)^{1/3}[E_i - V_{00}(R_S)]^{-1/3}. \tag{52}$$

The factors Ω_n are given by (23)

$$\Omega_1(R_S) = \Omega_A\cos\theta_S + \Omega_B\sin\theta_S,$$
$$\Omega_2(R_S) = \Omega_B\cos\theta_S - \Omega_A\sin\theta_S, \tag{53}$$

with $\theta_S = \theta(R_S)$ is the value of θ corresponding to the stationary phase-point R_S. Combining Eqs. (21) and (34), one can show that

$$\sin\theta_S = \frac{1}{\sqrt{2}}\left(\frac{M_S - D_S}{M_S}\right)^{1/2}, \tag{54}$$

and

$$\cos\theta_S = \frac{1}{\sqrt{2}}\left(\frac{M_S + D_S}{M_S}\right)^{1/2}, \tag{55}$$

where $D_S = D(R_S)$ and hence, according to Eq. (20),

$$D_S = \delta + \frac{1}{2}[V_{11}(R_S) - V_{22}(R_S)] \tag{56}$$

and

$$M_S = \{D_S^2 + [V_{12}(R_S)]^2\}^{1/2}. \tag{57}$$

To derive the thermally averaged cross sections Q_n, we insert (50) into Eq. (29) and assuming a Maxwellian distribution of initial energies E_i of relative motion, we make use of a method due to Sando and Wormhoudt [9]. Introducing the new variable ξ defined by

$$y_{\min}^{(n)} = z_S^{(n)}\xi, \tag{58}$$

where

$$z_S^{(n)} = p_n(R_S)\left(\frac{\hbar^2}{2\mu kT}\right)^{1/3}, \tag{59}$$

we can replace the integration over E_i by an integration over ξ. In this way, we obtain

$$Q_n(\Delta) = a_n\frac{L(z_S^{(n)})}{z_S^{(n)}}\exp\left[-\frac{V_{00}(R_S)}{kT}\right], \tag{60}$$

where k is the Boltzmann constant, where

$$a_n = \frac{6\pi}{\bar{v}}\left(\frac{\mu}{2\pi kT}\right)^{1/2}\left|\frac{2\pi\Omega_n(R_S)R_S F_n'(R_S)}{F_n''(R_S)}\right|^2, \tag{61}$$

and

$$L(z_S^{(n)}) = \int_0^\infty d\xi\,\xi^{-2}\text{Ai}^2(-z_S^{(n)}\xi)\exp(-\xi^{-3}) \tag{62}$$

is the universal line-shape function of the unified Franck-Condon (UFC) theory of pressure broadening [10].

Note the different behavior of the absorption profile given by Eq. (60) in the blue ($n=1$) and red ($n=2$) wings. According to Eq. (53), it is possible that at some value of the

laser detuning Δ, absorption in the red wing can be reduced to zero so that the system becomes transparent. This occurs for detunings Δ for which $\Omega_2 = 0$, since then by Eqs. (61) and (60) $a_2 = 0$ and $Q_2(R_S) = 0$. The condition is thus

$$\frac{\Omega_A}{\Omega_B} = \frac{\cos\theta_S}{\sin\theta_S} = \left(\frac{M_S + D_S}{M_S - D_S}\right)^{1/2}. \tag{63}$$

If the adiabatic potentials are neglected ($V_{00} = V_{11} = V_{22} = 0$), then $D_S = \delta$ and Eq. (63) becomes identical to the condition for a transparency point as given by Cavalieri $et\ al.$ [4]:

$$\frac{\Omega_A}{\Omega_B} = \left(\frac{\Delta}{\Delta + 2\delta}\right)^{1/2} = \left(\frac{\Delta_B + 2\delta}{\Delta_B}\right)^{1/2}. \tag{64}$$

Here, $\Delta_B = -\Delta - 2\delta$ denotes the laser detuning with respect to the unperturbed frequency of the $\beta \to \beta^*$ transition in atom B ($\Delta_B > 0$ for $\Delta < -2\delta$).

IV. QUASISTATIC LIMIT

The general formula (60) for the absorption profile can be substantially simplified in the quasistatic limit, which corresponds to collisions of "slow" atoms whose collisional duration time τ_c is large compared to the frequency resolution $\Delta\omega$: $\Delta\omega\tau_c \gg 1$. The "collisional duration time" τ_c should be viewed as the time during which the frequency shift of the adiabatic transition lies within $\Delta\omega$ of the line position. In practice, "slow" collisions tend to be those for which the stationary-phase points are located within the vicinity of the turning points, where $E_i \approx V_{00}(R_S)$. In such cases—as seen from Eq. (52)—$y_{\min}^{(n)} \equiv z_S^{(n)}\zeta \gg 1$ and the dominant contribution to the integral in Eq. (62) comes from large values of $z_S^{(n)}\zeta$. As shown in Ref. [10], the universal line-shape function $L(z_S^{(n)})$ then has the asymptotic form

$$L(z_S^{(n)}) \sim (36\pi z_S^{(n)})^{-1/2}, \quad |z_S^{(n)}\zeta| \gg 1. \tag{65}$$

After substitution in Eq. (60) this yields

$$Q_n \approx \frac{|4\pi R_S\Omega_n(R_S)|^2}{\bar{v}|F_n'(R_S)|}\exp\left[-\frac{V_{00}(R_S)}{kT}\right]. \tag{66}$$

The stationary-phase points $R_S = R(t_S)$ are the solutions of Eq. (34). In this paper, we consider only those cases in which the solutions R_S of Eq. (34) are real.

A. Blue wing: $\Delta > 0$

According to Eq. (34), for laser detunings $\Delta > 0$, corresponding to the blue wing of the $\alpha \to \alpha^*$ transition in atom A, the equation for R_S can be written in the form

$$\Delta + \delta = \frac{1}{2}F_1(R_S) = M_S + U_S, \tag{67}$$

where $U_S = U(R_S)$ with

$$U(R) = \frac{1}{2}[V_{11}(R) + V_{22}(R)] - V_{00}(R). \qquad (68)$$

Using Eqs. (53) and (67), we write the absorption cross-section formula (66) for the blue wing ($n=1$) as

$$Q_1(\Delta) = \frac{4\pi^2 R_S^2}{\bar{v}} \frac{[\Omega_A\sqrt{M_S+D_S} + \Omega_B\sqrt{M_S-D_S}]^2}{|U_S'M_S + D_S'D_S + V_{12}'(R_S)V_{12}(R_S)|}$$

$$\times \exp\left[-\frac{V_{00}(R_S)}{kT}\right]. \qquad (69)$$

As previously, the primes denote derivatives with respect to R. Equation (69) can be further simplified in two limiting cases: (1) when there are no resonance interactions between atoms, and (2) when the adiabatic potentials are negligible.

1. No resonance interactions: $V_{12}=0$

In this case $M_S = D_S$ and Eq. (67) for stationary-phase points R_S becomes

$$V_{11}(R_S) - V_{00}(R_S) = \Delta. \qquad (70)$$

This equation is identical to the equation for Condon points in the ordinary adiabatic theory of the absorption line shape of the $\alpha \to \alpha^*$ transition in atom A perturbed by atom B in its ground state β [10,11]. Equation (69) can then be transformed into the form

$$Q_1(\Delta) = \frac{8\pi^2\Omega_A^2}{\bar{v}} \frac{R_S^2\exp[-V_{00}(R_S)/kT]}{|V_{11}'(R_S) - V_{00}'(R_S)|}. \qquad (71)$$

This is the usual one-perturber quasistatic distribution.

Assuming a difference potential of the van der Waals form

$$V_{11}(R) - V_{00}(R) = C_6^{(\alpha)}R^{-6} \qquad (72)$$

with $C_6^{(\alpha)} > 0$, the absorption cross section (71) for $V_{00}(R_S) \ll kT$ takes the form of a power-law dependence

$$Q_1(\Delta) = \frac{4\pi^2\Omega_A^2|C_6^{(\alpha)}|^{1/2}}{3\bar{v}}|\Delta|^{-3/2}. \qquad (73)$$

In this case, a double logarithmic plot of the absorption cross section against laser detuning Δ is given by a straight line with slope $-3/2$.

2. Negligible adiabatic potentials: $V_{11}=V_{22}=V_{00}=0$

In this case, $U_S=0$, $D_S=\delta$, and the condition (67) for stationary-phase points takes the form

$$\Delta + \delta = \{\delta^2 + [V_{12}(R_S)]^2\}^{1/2}. \qquad (74)$$

The absorption cross section (69) can then be written

$$Q_1(\Delta) = \frac{4\pi^2 R_S^2}{\bar{v}} \frac{(\Omega_A\sqrt{\Delta+2\delta} + \Omega_B\sqrt{\Delta})^2}{|V_{12}'(R_S)V_{12}(R_S)|}. \qquad (75)$$

Assuming the resonance form (14) for $V_{12}(R)$, we obtain

$$Q_1(\Delta) = \frac{4\pi^2 C_3}{3\bar{v}} \frac{(\Omega_A\sqrt{\Delta+2\delta} + \Omega_B\sqrt{\Delta})^2}{\Delta^{3/2}(\Delta+2\delta)^{3/2}}. \qquad (76)$$

This formula shows exactly the same detuning dependence as that derived by Cavalieri et al. [4]. The only difference is the multiplicative factor: in place of the factor 16π in Ref. [4], we have the factor $4\pi^2$.

If we neglect the coupling of atom B with the radiation field ($\Omega_B=0$), then Eq. (76) becomes

$$Q_1(\Delta) = \frac{4\pi^2 C_3}{3\bar{v}} \frac{\Omega_A^2}{\Delta^{3/2}(\Delta+2\delta)^{1/2}}. \qquad (77)$$

Obviously, for $\Delta \gg 2\delta$, this formula approaches a $|\Delta|^{-2}$ behavior that is the result of the assumed form ($\sim R^{-3}$) of the resonance interaction. However, for $\Delta \ll 2\delta$, it reduces to

$$Q_1(\Delta) = \frac{4\pi^2 C_3}{3\bar{v}} \frac{\Omega_A^2}{\Delta^{3/2}(2\delta)^{1/2}}, \qquad (78)$$

which has the same $|\Delta|^{-3/2}$ power-law dependence (73) as that derived from the quasistatic distribution in the case of the van der Waals interaction. However, note that the origin of this dependence is quite different in the two cases, as indicated by the very different multiplicative coefficients in the two formulas.

It is true that a double-logarithm plot of the absorption cross section (77) can be represented by two straight lines of slopes $-3/2$ for smaller Δ and to -2 for large Δ. However, contrary to the opinion expressed in Ref. [4], this can hardly serve as evidence of the transition from van der Waals to resonant interaction since Eq. (77) was derived assuming that the van der Waals interactions are negligible.

An interpretation relating the change of slope from $-3/2$ to -2 with the transition from van der Waals to resonant interaction was originally proposed by Niemax [8], who studied the absorption of the 459.53 nm line of Eu perturbed by Sr. The correctness of his interpretation can be justified on the basis of Eq. (69) as follows: As shown by Niemax, the interaction Eu($^8P_{9/2}$)+Sr at large interatomic separations R can be well described by a repulsive van der Waals potential $C_6^{(\alpha)}R^{-6}$ with $C_6>0$. Thus, neglecting V_{12} in Eq. (69), we obtain the quasistatic dependence $|\Delta|^{-3/2}$ given in Eq. (73) at small detunings and hence at large R_S. At small R_S, the collisional coupling V_{12} may predominate; Eq. (69) then yields the $|\Delta|^{-2}$ dependence at large detunings if the adiabatic potentials are neglected.

B. Red wing: $\Delta < -2\delta$

Now we consider laser detunings $\Delta < -2\delta$, corresponding to the red wing of the $\beta \to \beta^*$ transition in atom B. According to Eq. (34), the stationary phase points R_S are in this case solutions of

$$\Delta + \delta = U_S - M_S. \qquad (79)$$

Using Eqs. (58)–(60), the absorption cross section (66) for the red wing ($n=2$) can be expressed as

$$Q_2(\Delta) = \frac{4\pi^2 R_S^2}{\bar{v}} \frac{[\Omega_A \sqrt{M_S - D_S} - \Omega_B \sqrt{M_S + D_S}]^2}{|U_S' M_S - D_S' D_S - V_{12}'(R_S) V_{12}(R_S)|} \exp\left[-\frac{V_{00}(R_S)}{kT} \right]. \tag{80}$$

By comparing this equation with Eq. (69), we note that the absorption profile in the red wing differs significantly from that in the blue wing. In particular, the red wing may be strongly depressed for detunings in the vicinity of transparency point defined by Eq. (63). As for the blue wing, we now discuss two limiting cases in which Eq. (80) can be significantly simplified.

1. No resonance interactions: $V_{12} = 0$

In this case, $M_S = D_S$ and Eq. (79) for stationary-phase points at R_S becomes

$$V_{22}(R_S) - V_{00}(R_S) = -\Delta_B, \tag{81}$$

which is identical to the equation for Condon points in the ordinary theory of pressure broadening of an absorption line $\beta \rightarrow \beta^*$ in atom B perturbed by atom A in its ground state α. Note that $\Delta_B > 0$ for $\Delta < -2\delta$. Equation (80) can then be transformed to the form

$$Q_2(\Delta) = \frac{8\pi^2 \Omega_B^2}{\bar{v}} \frac{R_S^2 \exp[-V_{00}(R_S)/kT]}{|V_{22}'(R_S) - V_{00}'(R_S)|}, \tag{82}$$

which is identical to that from the quasistatic theory.
In the case of a van der Waals interaction

$$V_{22}(R_S) - V_{00}(R_S) = C_6^{(\beta)} R^{-6} \tag{83}$$

with $C_6^{(\beta)} < 0$, Eq. (82) for $V_{00}(R_S) \ll kT$ takes the power-law dependence

$$Q_2(\Delta_B) = \frac{4\pi^2 \Omega_B^2 |C_6^{(\beta)}|^{1/2}}{3\bar{v}} |\Delta_B|^{-3/2}, \tag{84}$$

which is a typical behavior of red wings for van der Waals potentials. Note that a $|\Delta|^{-3/2}$ dependence in the blue wing can occur if and only if $C_6^{(\alpha)} > 0$, i.e., if and only if the van der Waals interaction is more repulsive (or less attractive) in the excited state $|1\rangle$ than in the ground state $|0\rangle$.

2. Negligible adiabatic potentials: $V_{11} = V_{22} = V_{00} = 0$

The stationary-phase points R_S are now solutions of the equation

$$\Delta + \delta = -\{\delta^2 + [V_{12}(R_S)]^2\}^{1/2}. \tag{85}$$

The absorption cross section (80) then takes the form

$$Q_2(\Delta) = \frac{4\pi^2 R_S^2}{\bar{v}} \frac{(\Omega_A \sqrt{\Delta + 2\delta} - \Omega_B \sqrt{\Delta})^2}{|V_{12}'(R_S) V_{12}(R_S)|}, \tag{86}$$

which, if the resonance form (14) for $V_{12}(R)$ is assumed, can be transformed to

$$Q_2(\Delta_B) = \frac{4\pi^2 C_3}{3\bar{v}} \frac{(\Omega_A \sqrt{\Delta_B} - \Omega_B \sqrt{\Delta_B + 2\delta})^2}{\Delta_B^{3/2}(\Delta_B + 2\delta)^{3/2}}. \tag{87}$$

This is exactly the formula derived by Cavalieri et al. [4], except that we have the factor $4\pi^2$ in place of the factor 16π in Ref. [4].

When the coupling of atom A with the radiation field is ignored ($\Omega_A = 0$), then Eq. (87) becomes

$$Q_2(\Delta_B) = \frac{4\pi^2 C_3}{3\bar{v}} \frac{\Omega_B^2}{\Delta_B^{3/2}(\Delta_B + 2\delta)^{1/2}}. \tag{88}$$

Thus, in full analogy to the blue wing, for $\Delta_B \gg 2\delta$, a power law $|\Delta_B|^{-2}$ holds for the red wing, provided the adiabatic potentials can be neglected. Similarly, for $\Delta_B \ll 2\delta$, a $|\Delta_B|^{-3/2}$ behavior, analogous to that given in Eq. (78) for the blue wing, results from Eq. (88). We should emphasize once more that, as in the blue wing in this detuning range, a $|\Delta_B|^{-3/2}$ dependence, if it occurs in the experimental profile, should rather be related to the van der Waals interaction, as in Eq. (84).

C. Validity of model

The range of validity of the line-shape formulas derived in our treatment is restricted by our use of perturbation theory and by the stationary-phase approximation employed to evaluate the integral in Eq. (30).

The perturbation solution of Eq. (26) is valid provided the collisional interaction $V(R)$ is much greater than the atom-field interaction:

$$|V(R)| \gg |\Omega_A + \Omega_B| = \frac{\mu_A + \mu_B}{2\hbar} \mathscr{E}_0. \tag{89}$$

If we neglect the adiabatic potentials and take into account only the resonance interaction $V(R) \sim V_{12} = C_3 R^{-3}$, then the above condition yields

$$\mathscr{E}_0 \ll \mathscr{E}_{\text{cr}} = \frac{2\hbar}{\mu_A + \mu_B} C_3 R^{-3}. \tag{90}$$

To estimate $\mathscr{E}_{\text{cr}}$ we take the value $C_3 = 1.3 \times 10^{-14}$ s m^3 of the effective resonance interaction Eu($J = 9/2$)–Sr as given by Niemax [8] and assume that $\mu_A \simeq \mu_B = 1.6$ a.u., which is the value of μ_B for Sr. For interatomic distances $R = 1.5$ nm where the resonance interaction between Eu and Sr dominates, one obtains from Eq. (90) $\mathscr{E}_{\text{cr}} = 3 \times 10^7$ V/m. This value corresponds to a laser light intensity $I_{\text{cr}} = \epsilon_0 \mathscr{E}_{\text{cr}}^2 = 2.5 \times 10^8$ W/cm^2. Thus condition (90) is well fulfilled for most experiments on laser-assisted collisions performed in the weak-field regime corresponding to laser fields of the order of a few MW/cm^2 or less. At these intensities, multiphoton effects are expected to be negligible, especially in the far wings of the line.

The second limitation of our final line-shape formulas is caused by the stationary-phase approximation used to evaluate the integrals (30) for $b_n(\infty)$. This implies that the final expressions for the line shape can be applied to the detunings Δ corresponding to far wings such that $|\Delta|\tau_c \gg 1$, where τ_c is the collisional duration. Note, however, that in Sec. II we assumed that the adiabaticity condition $2\delta \gg \tau_c^{-1}$ is fulfilled. One can thus conclude that our line-shape formulas are valid for detunings such that $|\Delta| \gtrsim 2\delta$.

V. SUMMARY

Starting with the model proposed by Cavalieri *et al.* [4], we have derived a more general formula for the absorption profile in the line wings for the case of near-resonant collisions of two dissimilar atoms in the presence of laser light. We have shown that the absorption profile that takes into account both the adiabatic potentials and the collisional coupling between atoms as well as the coupling with the radiation field can be expressed by means of the universal line-shape function of the UFC treatment of pressure broadening [10]. Our intention was to provide a firmer justification of the model proposed in Ref. [4], which predicts the possible occurrence of a strongly depressed red wing. We included collisional shifts of the atomic levels into the model and used an extended stationary-phase method that enables one to express the transition probabilities in terms of the Airy function.

In the limit that the adiabatic potentials can be neglected and the only collisional interaction retained is the resonant collisional coupling ($\sim R^{-3}$) between atoms, our model agrees exactly with Ref. [4] except for a factor $\pi/4$. In the same limit and for $|\Delta| \gg 2\delta$, our conditions (34) for stationary phase yield $\theta_S \to \pi/4$ with the consequence that $\cos\theta_S \approx \sin\theta_S \approx 1/\sqrt{2}$. In this case, our results agree with the conclusion of Ref. [4] that the adiabatic collisional dressed states $|+,n-1\rangle$ and $|-,n-1\rangle$, Eq. (25), at the stationary-phase points, behave as super-radiant and subradiant Dicke states, respectively.

We should emphasize that our Eqs. (69) and (80) permit evaluation of the absorption cross sections $Q_1(\Delta)$ and $Q_2(\Delta)$ for any form of the potentials. Their range of validity is restricted primarily by the quasistatic approximation, which corresponds to collisions of "slow" atoms, when the universal line-shape function can be approximated by its asymptotic form (65). We should also emphasize that the Boltzmann factor $\exp[-V_{00}(R_S)/kT]$ in Eqs. (69) and (80) may in some cases have a strong influence on the far-wing profile, as observed in the well-known experiments by Gallagher and coworkers [12] for the resonance lines of alkali-metal atoms. The Boltzmann factor does not appear in expression derived in Ref. [4], but it may also play a crucial role in studies of the temperature dependence of the absorption cross section in the far wings in the case of near-resonant collisions.

[1] Y. Prior, A. R. Bogdan, M. Dagenais, and N. Bloembergen, Phys. Rev. Lett. **46**, 111 (1981).

[2] E. Giacobino and P. R. Berman, Phys. Rev. Lett. **58**, 21 (1987).

[3] G. Grynberg and P. R. Berman, Phys. Rev. A **41**, 2677 (1990); **43**, 3994 (1991).

[4] S. Cavalieri, E. Arimondo, and M. Matera, Phys. Rev. A **45**, 8005 (1992).

[5] A. Bambini and P. R. Berman, Phys. Rev. A **35**, 3753 (1987); A. Agresti, P. R. Berman, A. Bambini, and A. Stefanel, *ibid.* **38**, 2259 (1988).

[6] E. Courtens and A. Szöke, Phys. Rev. A **15**, 1588 (1977).

[7] K. Burnett, Phys. Rep. **118**, 340 (1985).

[8] K. Niemax, Phys Rev. Lett. **55**, 56 (1985).

[9] K. M. Sando and J. C. Wormhoudt, Phys. Rev. A **7**, 1889 (1973).

[10] J. Szudy and W. E. Baylis, J. Quantum Spectrosc. Radiat. Transfer **15**, 641 (1975); **17**, 269 (1977).

[11] N. F. Allard and J. Kielkopf, Rev. Mod. Phys. **54**, 1103 (1982).

[12] R. E. M. Hedges, D. L. Drummond, and A. Gallagher, Phys. Rev. A **6**, 1519 (1972); C. G. Carrington, D. Drummond, A. V. Phelps, and A. Gallagher, Chem. Phys. Lett. **22**, 511 (1973); C. G. Carrington and A. Gallagher, Phys. Rev. A **10**, 1464 (1974).