PHYSICAL REVIEW A VOLUME 25, NUMBER 3 MARCH 1982

Collisional redistribution of radiation in strong fields: Modification of the collision dynamics

K. Burnett, J. Cooper, and P. D. Kleiber
Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards and Department of Physics, University of Colorado, Boulder, Colorado 80309

A. Ben-Reuven*
Department of Chemistry, Tel-Aviv University, 69978 Tel-Aviv, Israel
(Received 8 September 1981)

We extend the theory of light scattering from an atom undergoing collisions to the case of strong laser fields, where the expansion in powers of $\Omega\tau_c$ that was used formerly in a series of papers by Burnett *et al.* breaks down. In particular we consider in detail the conditions necessary to relate the observable quantities to intense-field collisional rate constants in a dressed-state basis (such as those calculated by Light and Szöke). We also show (following Rabin and Ben-Reuven) that by studying the spectrum emitted by the atoms in the presence of a strong field one may measure the collisional rates for transfer between the dressed states of atom plus radiation field.

I. INTRODUCTION

The study of how collision dynamics is modified by the presence of a strong radiation field[1] not only offers exciting possibilities for laser modified energy transfer[2] and chemical reactions[3] but also presents a considerable challenge to practitioners of molecular collision theory.[4–6] One method of studying such phenomena is via the spectrum of light emitted by colliding atoms in a strong field. In this paper we shall consider in detail the conditions necessary to relate the observed spectrum to collision rates in the presence of a strong field. In particular, the main purpose of this paper is to relate the S-matrix calculations that are being performed[5–7] for such collisions to the observable emission spectra, and indicate what aspects of the strong field plus collision problem can be observed via the spectrum of the scattered light.

We shall consider throughout that the collisions couple a set of excited states of an atom or molecule—some of which are coupled to a lower-lying state by a dipole-allowed transition that is driven by the strong laser field. This problem is, of course, closely related to the collisional broadening of spectral lines and more particularly, to the theory of collisional redistribution.[8–10]

The weak-field case has been studied in detail in several papers.[8–11] One of the important features of this work is, for scattering in the line wings, the inclusion of radiative transitions *coincident* with a collisional event. Hence we have here an example of the modification of collision dynamics by the radiation even at weak fields (provided one is outside the "impact" region in the atomic basis).

The extension to strong fields has been discussed by Rabin and Ben-Reuven[12] using a steady-state Liouville-space formalism.[13] These authors make a clear distinction between what is called the *medium-coupling* case and the *strong-coupling* case. In the first case, the secular motion of the free atoms (between collisions) is strongly modified by the applied field, and it becomes advantageous to use a *dressed-atom* representation for the free-atom states. The collision dynamics is nevertheless retained field free. This is in fact the approach used by many authors when extending their discussion to strong fields (see, e.g., Mollow,[14] Courtens and Szöke,[15] and Cohen-Tannoudji and Reynaud,[16] the last ones dealing only with radiative damping). These works are equivalent to the "impact" theory calculation of Cooper *et al.*[17] in which the usual atomic rather than dressed-state basis is used. There is, however, the strong-coupling limit in which the collision dynamics itself becomes affected by the field, and this is the regime that coincides with the works of Refs. 4–6. The only exception in which such modified collisions had been

studied in the context of the redistribution problem prior to Ref. 12 is the work of Light and Szöke.[7]

Although the reference to "coupling" may allude to the radiative coupling strength (i.e., the on-resonance Rabi frequency Ω), it is really the optical nutation frequency $\Omega'=(\Omega^2+\Delta^2)^{1/2}$ (where Δ is the detuning of the incident laser frequency off resonance) that delineates the various coupling regimes. Letting γ stand for a typical linewidth parameter, and τ_c be the duration of a typical strong collision (with $\gamma\tau_c << 1$ in dilute gases)

$$\gamma \lesssim \Omega' << \tau_c^{-1}$$

specifies the medium-coupling regime, whereas

$$\Omega' \gtrsim \tau_c^{-1}$$

specifies the strong-coupling regime. The use of Ω' (rather than Ω) explains why the collision dynamics can be modified in the line wings even in weak fields[8-10] (and in fact $\Delta < \tau_c^{-1}$ is the usual "impact" criterion).

A similar distinction between the two regimes was made more recently by Reynaud and Cohen-Tannoudji.[18] The latter authors use the names impact and "nonimpact" for the medium- and strong-coupling regimes, respectively. These names were improperly chosen for, as we are going to show below, in the secular approximation used here (and in Ref. 17), in which the emission spectrum is made out of sharp isolated lines, each individual linewidth can nevertheless be calculated in the impact approximation, with dressed-atom states (in contrast to atomic states) used as the asymptotic states of the pair-collision dynamics.

We shall derive below expressions for the strong-collision regime using a time-dependent formalism as established in the series of papers referred to hereafter as I–III.[8-10] This approach enables one to directly obtain equations of motion for the density matrix and for the correlation function in the presence of the field. It is also particularly suitable for extension to time-resolved phenomena under pulsed laser fields.[19] In deriving the equation of motion we actually reduce the density matrix to the degrees of freedom of a single "active" atom whose dipole couples to the scattered radiation field, using the dressed-atom basis for the active atom in the applied radiation field. In this manner we limit the discussion to foreign-gas broadening phenomena, and the modified collision dynamics—to "optical" rather than "radiative" collisions (using the terminology of Lisitsa and Yakovlenko[1]). The extension to self-broadening, where both collision partners are "active" (before *and* during the collision) was formally outlined elsewhere.[20,21]

The derivation of the equations of motion below is simplified by using the binary-collision[8-10] and the secular (or isolated-line)[12] approximations. As already stated, the line shapes in the latter approximation can be calculated in the impact, or Markovian, approximation. This means that the linewidths can be calculated using S-matrix scattering theory, with dressed-atom states in the asymptotic collision states, and the coupling to the strong radiation as part of the collision Hamiltonian. In the simple two-level model (neglecting space degeneracy) the present results reconfirm the results of Ref. 12 for the linewidths and produce explicit expressions for the line intensities of the resonance-fluorescence spectrum.

II. THE EQUATION OF MOTION OF THE DENSITY MATRIX

A. The dressed frame transformation

The general theory of light scattering by atoms undergoing collisions has been given elsewhere. In paper I (Ref. 8) an equation of motion is derived for the density matrix of an atomic system being driven by a near resonant classical electromagnetic field and at the same time undergoing collisions. The binary-collision approximation (BCA) was used in I—as we do here also—and also it was assumed in that paper that the field was weak, i.e., $\Omega\tau_c << 1$. (Here Ω is the on-resonance Rabi frequency, defined via $\Omega=\vec{E}\cdot\vec{d}/\hbar$ where $\vec{E}$ is the electric field strength, $\vec{d}$ is the magnitude of the transition dipole moment, and τ_c is the duration of a strong collision.)

This weak-field approximation can be avoided if we make a transformation to dressed states of the atom plus driving radiation, and this is what we shall accomplish here, using the notation and terminology of paper I. Since we want to work with the dressed states we shall make the transformation to dressed states *before* we "eliminate" the collision partner variables by averaging over the "bath" of perturbers.

We shall for simplicity consider the following example (the generalization is straightforward): a two-level atom whose excited and ground states are $(2j_e+1)$ and $(2j_g+1)$ fold degenerate, respectively. Following Courtens and Szöke[15] and Cooper *et al.*[21] we define the following atomic operators:

$$D_A^+ = \sum_{m_e m_g} |m_e\rangle\langle m_e|\vec{d}|m_g\rangle\langle m_g| \ , \tag{1}$$

$$D_A^- = \sum_{m_e m_g} |m_g\rangle\langle m_g|\vec{d}|m_e\rangle\langle m_e| \ , \tag{2}$$

$$I_A = \sum_{m_e m_g} \{ |m_e\rangle\langle m_e| + |m_g\rangle\langle m_g| \} \ , \tag{3}$$

$$S_A^z = \sum_{m_e m_g} (|m_e\rangle\langle m_e| - |m_g\rangle\langle m_g|) \ . \tag{4}$$

These are operators in the atomic subspace only; the total space of course includes the perturber variables. Thus we can write the above operators for the complete space of the system, assuming for convenience structureless perturbers, in the following form:

$$D^+ = D_A^+ I_P \ , \tag{5}$$

$$D^- = D_A^- I_P , \tag{6}$$

etc., where

$$I_P = \sum_{\vec{p}\,l} |\vec{p}\,l\rangle\langle\vec{p}\,l| \ ,$$

and where $\vec{p}$ labels the momentum of the lth perturber. A general atom-perturber state may be expanded in the following basis (ignoring velocity states of the absorber):

$$|j_k m_k;\vec{p}\,l\rangle = |j_k m_k\rangle\,|\vec{p}\,l\rangle \ . \tag{7}$$

The Liouville operator, $\tilde{L}$, that determines the evolution of the complete system, atom plus perturbers, may be expressed as the commutator of the Hamiltonian $\hat{H}$,

$$\tilde{L}O = \frac{1}{i\hbar}[\hat{H},O] \ , \tag{8}$$

$$\hat{H} = \hat{H}_{\text{atom}} + \hat{H}_{\text{atom-rad}} + \sum_l \hat{V}_{\text{atom-}l\text{th pert}} + \hat{H}_{\text{pert}}$$

$$\equiv \hat{H}_A + \hat{H}_{AR} + \sum_l \hat{V}_{Al} + \hat{H}_P \ , \tag{9}$$

neglecting here cooperative effects between similar atoms (consistent with our assumption of foreign gas broadening). We shall assume that each perturber is independent. ($\hat{V}_{lj}$, the interaction between perturbers is therefore omitted from the Hamiltonian.) Since in this paper we are mainly interested in collisional phenomena, we will also assume that radiative damping is included in the Liouville operator for the atom $\tilde{L}_A$ (i.e., $\tilde{L}_A = \tilde{L}_A^0 + \tilde{S}$, where $\tilde{S}$ is the damping operator of paper I: we will, in fact, later ignore radiative damping during a collision). $\hat{H}_{AR}$ then describes the laser interaction alone.

We now make the following unitary transformation on the system

$$|\Psi_{\text{rot}}\rangle = \hat{U}_R(t)\,|\Psi_{\text{fixed}}\rangle \ , \tag{10}$$

where

$$\hat{U}_R = e^{i\omega_L t(S_A^z - 1)/2} \ . \tag{11}$$

Then if we use the rotating wave approximation[15] to the atom-radiation interaction Hamiltonian we obtain the following time-independent interaction Hamiltonian in the rotating frame:

$$\hat{H}_{AR}^{\text{rot}} = -\tfrac{1}{2}\hbar S_A^z \Delta + \tfrac{1}{2}\hbar(\omega_0+\omega_L) - (D^+\epsilon_0 - D^-\epsilon_0^*) \ . \tag{12}$$

Here, $\hbar\omega_0$, is the difference in the energies of the ground and excited states (ignoring the effects of radiative widths). ϵ_0 is the amplitude of the assumed classical driving field and $\Delta = \omega_L - \omega_0$.

The advantage of using the rotating frame is apparent, since in this frame the Hamiltonian and Liouville operators are now time independent. Construction of the eigenvectors (i.e., the dressed states) in this frame is now quite straightforward. For our example this procedure is discussed in detail (for the pure atomic states) by Cooper *et al.*[21] Since (neglecting correlation between Doppler and pressure broadening) the perturber variables commute with the dipole moment, i.e., D^+ and D^- are diagonal in perturber labels, the procedure we need is precisely the same. [Note that we have implicitly assumed that we are using a basis in which the dipole moment is not a function of atom-perturber separation (see Ref. 6).] The only new step is to transform the atom-perturber interaction to the dressed frame. The dressed states are simply superpositions of the excited and ground states that are coupled (in pairs) by the field. For convenience we will assume that the perturber-atom interaction $\hat{V}_{Al}$ [of Eq. (9)] is an effective interaction[22] which couples the excited states or the ground states but does not couple ground to excited states (e.g., van der Waals interaction). If this were not the case, as we will see later, the Hamiltonian in the rotating frame introduced here may not be time independent. (The use of an effective interaction will be valid for most atom-atom interactions since energies associated with transitions in the perturber are usually large compared to $\hbar\Omega$.) Even with this assumption, in the dressed frame the collisional interaction couples dressed states that are superposi-

tions of ground and excited states and has, therefore, a more complex form. (For details of the transformations involved for $j_e=1$, $j_g=0$ we refer the reader to Ref. 7.) In spite of this complexity the average over perturber variables is straightforward, since the projection operator that projects the full density matrix[8] onto the factorized atom plus perturber subspace commutes with the rotating wave transformation. Let the transformation to dressed states, in the rotating frame, be given by U_D. Then we can write the equation of motion for the density matrix in the dressed frame, $\hat{\rho}_D(t)$, in the following form:

$$\partial_t\hat{\rho}_D(t)=(\tilde{L}_D^A+\tilde{V}_D+\tilde{L}_P)\hat{\rho}_D(t)\ . \tag{13}$$

Here

$$\tilde{L}_D^A\hat{\rho}_D(t)\equiv\frac{1}{i\hbar}[\hat{H}_D^A,\hat{\rho}_D(t)]\ , \tag{14}$$

$$\tilde{V}_D\hat{\rho}_D(t)\equiv\frac{1}{i\hbar}[\hat{V}_D,\hat{\rho}_D(t)]\ , \tag{15}$$

$$\tilde{L}_P\hat{\rho}_D\equiv\frac{1}{i\hbar}[\hat{H}_P,\hat{\rho}_D]\ , \tag{16}$$

$$\hat{H}_D^A=\hat{U}_D(\hat{H}_{A+R}^R)\hat{U}_D^{-1}\ , \tag{17}$$

$$\hat{V}_D=\hat{U}_D\hat{U}_R(t)\left[\sum_l\hat{V}_{Al}\right]\hat{U}_R^{-1}(t)\hat{U}_D^{-1}\ ,$$

$$=\hat{U}_D\left[\sum_l\hat{V}_{Al}\right]\hat{U}_D^{-1}\ . \tag{18}$$

Note that $\tilde{L}_D^A$ is diagonal in the dressed frame, since this is, after all, the definition of the dressed frame. The second time-independent form of $\hat{V}_D$ in Eq. (18) follows from the assumption that $\hat{V}_{Al}$ is diagonal in excited or ground states. Since the Liouville operator is time independent we can use the standard procedure for obtaining an equation of motion for the reduced density matrix of the atom. We define, as usual,

$$\hat{\sigma}_D(t)\equiv\mathrm{Tr}_{\mathrm{pert}}[\hat{\rho}_D(t)]\ . \tag{19}$$

An equation of motion for $\hat{\sigma}_D(t)$ may be obtained in precisely the same manner as was done in paper I. We use the $\tilde{P}_c$ Zwanzig-Fano projection superoperator that projects onto the factorized subspace of the dressed atom plus perturber system and recall the definition here for the convenience of the reader. $\tilde{P}_c$ is defined by its action on an arbitrary operator $\hat{O}$, thus

$$\tilde{P}_c\hat{O}=\hat{\rho}_{\mathrm{pert}}\mathrm{Tr}_{\mathrm{pert}}[\hat{O}]\ , \tag{20}$$

and its complement is $\tilde{Q}_c=1-\tilde{P}_c$. We project Eq. (13) onto the $\tilde{P}_c$ and $\tilde{Q}_c$ subspaces and solve the equation for $\tilde{Q}_c$ formally using the same assumption as we did in I, i.e., that the correlations important at any given time t are those that develop in the interval $[t,-\infty]$ and not those present at $t=-\infty$.

Then the equation of motion for $\hat{\sigma}_D(t)$ may be written thus

$$\partial_t\hat{\sigma}_D(t)=\tilde{L}_D^A\hat{\sigma}_D(t)+\mathrm{Tr}_{\mathrm{pert}}[\tilde{V}_D\hat{\rho}_{\mathrm{pert}}^D]\hat{\sigma}_D(t)$$
$$+\int_{-\infty}^t dt'\mathrm{Tr}_{\mathrm{pert}}[\tilde{V}_D\exp\{\tilde{Q}_c(\tilde{L}_D^A+\tilde{V}_D+\tilde{L}_P)(t-t')\}\tilde{Q}_c\tilde{V}_D\hat{\rho}_{\mathrm{pert}}^D]\hat{\sigma}_D(t')dt'\ . \tag{21}$$

Note that, since we are dealing with an effective interaction we do not assume that $\mathrm{Tr}_{\mathrm{pert}}[\tilde{V}_D\hat{\rho}_{\mathrm{pert}}^D]=0$.

B. The binary-collision approximation

We now make the binary-collision approximation (BCA) (Ref. 23)—i.e., that strong collisions are separated in time—on Eq. (21). For a discussion of its validity see I, II, and III. The BCA to Eq. (21) enables the $\tilde{Q}_c$ to be dropped and may be written thus

$$\partial_t\hat{\sigma}_D(t)=\tilde{L}_D^A\hat{\sigma}_D(t)+N\,\mathrm{Tr}_{1\,\mathrm{pert}}[\tilde{V}_D^1\hat{\rho}_{\mathrm{pert}}^D(1)]\hat{\sigma}_D(t)$$
$$+\int_{-\infty}^t dt'N\,\mathrm{Tr}_{1\,\mathrm{pert}}[\tilde{V}_D^1\exp\{(\tilde{L}_D^A+\tilde{V}_D^1+\tilde{L}_P^1)(t-t')\}\tilde{V}_D^1\hat{\rho}_{\mathrm{pert}}^D(1)]\hat{\sigma}_D(t')\ . \tag{22}$$

Here the (1's) refer to single perturber labels and N refers to the number of perturbers in the quantization volume V (we assume, of course, that the $N\to\infty$, $V\to\infty$, $N/V=$const limit is taken when convenient). An alternative form of Eq. (22) uses the interaction representation and may be written thus

$$\partial_t\hat{\sigma}_D(t)=\tilde{L}_D^A\hat{\sigma}_D(t)+e^{\tilde{L}_D^A t}N\,\mathrm{Tr}_{1\,\mathrm{pert}}[\tilde{V}_D^1(t)\hat{\rho}_{\mathrm{pert}}^D(1)]e^{-\tilde{L}_D^A t}\hat{\sigma}_D(t)$$
$$+N\,\mathrm{Tr}_{1\,\mathrm{pert}}\left[e^{\tilde{L}_D^A t}\tilde{V}_D^1(t)\int_{-\infty}^{t}dt'\tilde{U}_D^1(t,t')\tilde{V}_D^1(t')\hat{\rho}_{\mathrm{pert}}^D(1)\right]e^{-\tilde{L}_D^A t'}\hat{\sigma}_D(t')\,, \tag{23}$$

with

$$\tilde{V}_D^1(t)=e^{-(\tilde{L}_D^A+\tilde{L}_P^1)t}\tilde{V}_D^1 e^{(\tilde{L}_D^A+\tilde{L}_P^1)t} \tag{24}$$

and the interaction picture time development superoperator

$$\tilde{U}_D^1(t,t')=T\exp\left[\int_{t'}^{t}\tilde{V}_D^1(t'')dt''\right] \tag{25}$$

(with T the time-ordering operator). This form explicitly displays the memory kernel $M(t,t')=\tilde{V}_D^1(t)\times\tilde{U}_D^1(t,t')\tilde{V}_D^1(t')$, and consideration of the dynamics of collisions indicates it is nonzero only for times $t-t'\lesssim\tau_c$ where τ_c is the "duration of a collision."

Splitting the integral $\int_{-\infty}^{t}\cdots$ in Eq. (22) into $\int_{-\infty}^{1}+\int_{0}^{t}\cdots$ it is then obvious that for times of interest greater than τ_c, the $\tilde{V}^1(t)\int_{-\infty}^{1}\cdots$ term is negligible. Further due to stationarity[24]

$$\mathrm{Tr}[e^{\tilde{L}_D^A t}\tilde{V}_D^1(t)\tilde{U}_D^1(t)\tilde{U}_D^1(t,t')\tilde{V}_D^1(t')e^{-\tilde{L}_D^A t'}\cdots]=\mathrm{Tr}[e^{\tilde{L}_D^A(t-t')}\tilde{V}_D^1(t-t')\tilde{U}_D^1(t-t',0)\tilde{V}_D^1(0)\cdots]$$

so that the Laplace transform of Eq. (23) may be obtained as

$$s\hat{\sigma}_D(s)-\hat{\sigma}_D(t=0)=\tilde{L}_D^A\hat{\sigma}_D(s)+\tilde{\gamma}_D^c(s)\hat{\sigma}_D(s)\,, \tag{26}$$

where

$$\tilde{\gamma}_D^c(s)=N\int_0^\infty d\tau\,\mathrm{Tr}_{1\,\mathrm{pert}}[e^{\tilde{L}_D^A\tau}\tilde{V}_D^1(\tau)\tilde{U}_D^1(\tau,0)\tilde{V}(0)+\tilde{V}_D^1(\tau)\delta(\tau)]e^{-s\tau}\,. \tag{27}$$

Steady state of course corresponds to $s\to 0$. In light of the nature of the memory kernel, $s\to 0$ should be a good approximation for times greater than τ_c, when using γ_D^c in the equations of motion.

C. The secular approximation

Certain of the tetradic elements of $\tilde{\gamma}_D^c$ [of Eq. (27)], do not produce an appreciable effect on the equations of motion. This is because the frequencies of the different elements of $\hat{\sigma}_D(t)$ are not all degenerate. Specifically, if the off-diagonal (nonzero) elements of $\tilde{L}_D^A$ in Eq. (26) are large compared to the corresponding elements of $\tilde{\gamma}_D^c$, then the $\tilde{\gamma}_D^c$ elements will be unimportant. This condition, namely, $\tilde{L}_D^A>>\tilde{\gamma}_D^c$, implies that the nondegenerate splittings, δ_D (say), of the levels in the dressed frame should be large compared to the damping rates, i.e., the levels should be "well separated." This is essentially the secular approximation.

It means that, to order γ_D/δ_D, only elements of the density matrix that have degenerate or nearly degenerate frequencies are coupled. This has an important consequence as the tetradic elements of the collisional operator that couple degenerate elements of the density matrix can be expressed in terms of S matrices. This implies, in turn, that if collisions only couple elements of the density matrix having degenerate frequencies (i.e., the secular approximation holds), one only has to solve Markovian equations of motion in order to obtain the density operator for the dressed atom.

To specifically establish the region of validity of the secular approximation we shall consider a simple case, i.e., a $j_g=0$ to $j_e=1$ transition (see Fig. 1), in which some of the elements have degenerate frequencies. The smallest splitting (corresponding to off-diagonal elements of $\tilde{L}_D^A$), apart from those that are zero, is that between the frequencies of $\rho_{1\,II}$ (or $\rho_{II\,1}$) and the populations. This splitting is equal to

$$\frac{(\Omega^2+\Delta^2)^{1/2}-|\Delta|}{2}=\delta_D\,, \tag{28}$$

whereas the coupling between states is given by the tetradic elements of $\tilde{\gamma}_D^c$. We can say, therefore, that if this coupling is much smaller than δ_D the

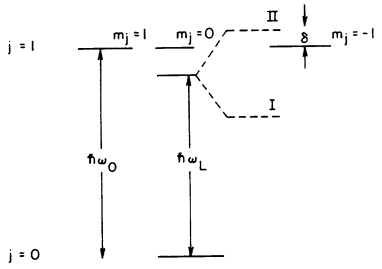

FIG. 1. Atomic and dressed states for $j=0\rightarrow j=1$ transition in the presence of linearly polarized light. — — —, dressed states; ——, pure atomic states.

coupling of the coherence between $|II\rangle$ and $|1\rangle$ to the other populations can be ignored. Actually, up to this point, radiative damping (γ_N via operator $\tilde{S}$) has been included in $\tilde{L}_D^A$, however, since Eq. (26) is linear, we will find it more convenient from now on to include it with γ_D^c. Thus, defining

$$\gamma_D(1\,II,\,11)=\langle\langle 1\,II\,|\,\tilde{\gamma}_D^c\,|\,11\rangle\rangle + \langle\langle 1\,II\,|\,\tilde{S}\,|\,11\rangle\rangle\,, \tag{29}$$

the couplings will have a negligible effect on the equations of motion if

$$\gamma_D(1\,II,\,11)<<\frac{(\Omega^2+\Delta^2)^{1/2}-|\Delta|}{2}\,. \tag{30}$$

Let us take the reasonable condition, say

$$10\gamma_D\leq\frac{(\Omega^2+\Delta^2)^{1/2}-|\Delta|}{2}\,, \tag{31}$$

i.e., so the condition

$$\Omega\geq[(20\gamma_D)^2+(40\gamma_D\,|\,\Delta\,|\,)]^{1/2}$$

defines the region of validity of the secular approximation in the absence of any other selection rules. This approximate region of validity overlaps the regions of validity of the other methods available for the problem. This is shown in Fig. 2 for different values of $\gamma_D\tau_c^{-1}$. [For the other splittings between density operator components the condition on Ω is always well satisfied within the region defined by (31).]

The reader will see that for $\gamma_d\tau_c\lesssim 5\times10^{-4}$ the secular approximation region essentially fills in all of the $[\Omega,\Delta]$ plane that other techniques cannot reach. For higher values of γ_D a gap opens up. Figure 2 certainly shows that the secular approximation in the dressed frame is useful over a very wide range of the $[\Omega,\Delta]$ plane and greatly simplifies the equations of motion.

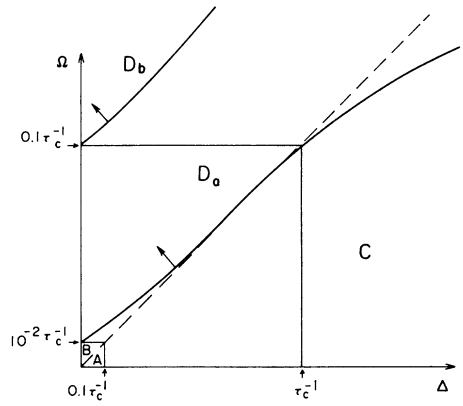

FIG. 2. Region of validity of the secular approximation (and other related approximations). *A*, weak-field Markov; *B*, strong-field Markov; *C*, weak-field non-Markov; D_a, secular $\gamma_c\sim5\times10^{-4}\tau_c^{-1}$ ($\sim$50 Torr for van der Waals broadening); D_b, secular $\gamma_c\sim5\times10^{-3}\tau_c^{-1}$ ($\sim$500 Torr for van der Waals broadening).

D. Linear polarization

When the driving field is linear, the dressed states are still eigenfunctions of the component of angular momentum along the driving field's direction.[21,25] The average collisional operators then have cylindrical symmetry, which means they can only couple elements of the density matrix with the same value of $q=(m_j-m_i)$,[25] where the density-matrix elements are labeled $\rho_{m_jm_i}$. Along with the secular approximation this means that for the case of linear polarization populations are only coupled to populations and coherences only to coherences—a considerable simplification.

E. The Markov approximation

In papers I—III an issue was made of the concepts of absorption and emission during collisions, whereas here the dressed states have eliminated the need to consider this problem separately (albeit with much more complex collisional calculations and more difficult physical interpretation, as outlined below). This does not, of course, change the physics of "absorption during a collision" that was discussed in I and II. To see this we recall that for $\Omega/\Delta<<1$ we can write the dressed states as a power series in Ω/Δ. This, in turn, implies that the off-diagonal matrix elements of the potential between dressed states will be small ($\sim\Omega/\Delta$). In Sec. III D below we shall show the precise relationship of the weak-field limits of our present calcula-

tion to the weak-field results obtained in I. Let us consider, for the purposes of illustration, the case where the interatomic potential is attractive and we detune our weak field far to the red. The dressed-state picture would, in this limit, lead us, if we used semiclassical wave functions, to calculate the lowest-order Landau-Zener transition probability for the coupling between the dressed states during a collision: the transition being localized at the curve crossing between the states (see also Light and Szöke[7] for details). We see, therefore, that our "absorption in the middle of a collision" is still in the calculation due, in the same limit, to equivalence of Landau-Zener and quasistatic (based on Franck-Condon) approximations. (We shall discuss the relation of the present approach to the conventional theory of far wing absorption further in Sec. III C.) In the weak-field case, we believe that the dressed-state approach is not as fruitful as the approach used in I–III since in I–III it was possible to obtain closed forms for scattered spectra. Moreover, using spherical tensor methods, it was possible, because of spherical symmetry, to reduce the collisional calculation to one in a single simple collision frame. If we use the dressed-state approach, since we can only have cylindrical symmetry, *we have to perform the full calculation for all the relevant collision directions and afterwards perform the angular averages.* In the strong-field case this is unavoidable, but it does lead to complex and time-consuming calculations.

The Markov approximation to Eq. (23) is

$$\partial_t \hat{\sigma}_D^I(t) = \tilde{L}_D^A \hat{\sigma}_D^I(t) + N \,\mathrm{Tr}_{1\,\mathrm{pert}}[\tilde{V}_D^1(0)\hat{\rho}_{\mathrm{pert}}^D(1)]\hat{\sigma}_D(t) + N \,\mathrm{Tr}_{1\,\mathrm{pert}}\left[\int_0^\infty d\tau\, \tilde{V}_D^1(\tau)\hat{U}_D^1(\tau,0)\tilde{V}_D^1(0)\hat{\rho}_{\mathrm{pert}}^D(1)\right]\hat{\sigma}_D(t) \,. \tag{32}$$

For elements combining degenerate (or near-degenerate) states, this is the same as the $s \to 0$ (or $s << 1/\tau_c$) limit of Eq. (27). With times of interest at least of order $(\gamma_D^c)^{-1}$, this is true if $\gamma_D^c \tau_c << 1$, which is precisely the same as the BCA.

The relevant elements of the collisional operator $\tilde{\gamma}_D^c(0)$ can now be reduced to on-the-energy-shell T-matrix elements by the standard techniques developed for Liouville-space relaxation operators by Fano[23] and Ben-Reuven.[26]

If we ignore the translational dynamical variables of the atom then we find we can write $\tilde{\gamma}_D^c$ in the following form, in terms of *dressed-state eigenfunctions,*

$$\begin{aligned}\langle\langle ij \mid \tilde{\gamma}_D^c \mid lm \rangle\rangle = -Ni\hbar^{-1}\sum_{\delta\gamma}\rho_\gamma^1\{ &[\langle l\gamma \mid T(E_l+E_\gamma+i0)l\gamma\rangle - \langle m\delta \mid T(E_m+E_\delta+i0) \mid m\delta\rangle] \\ &\times \delta_{il}\delta_{jm}\delta_{\delta\gamma} + 2\pi i\delta(E_l+E_\gamma-E_i-E_\delta)\langle i\delta \mid T(E_l+E_\gamma+i0) \mid l\gamma\rangle \\ &\times \langle j\delta \mid T(E_m+E_\delta+i0) \mid m\gamma\rangle^*\} \,.\end{aligned} \tag{33}$$

Here ρ_γ^1 is the distribution function for the perturbers where γ labels their momentum and internal state—if they are structureless ρ_γ^1 is just the Boltzmann velocity distribution (see Ref. 13). T is the Lippmann-Schwinger T-matrix of quantum-mechanical scattering theory.[27]

An alternative form of Eq. (33) is useful for classical path calculations, namely,[24]

$$\langle\langle ij \mid \tilde{\gamma}_D^c \mid lm \rangle\rangle = \{S_{il}^D S_{mj}^{+D} - \delta_{il}\delta_{mj}\}_{\mathrm{av}} \,, \tag{34}$$

where the classical path *dressed-state* matrix elements must be averaged (through $\{\cdots\}_{\mathrm{av}}$) over impact parameter, velocity, and all directions relative to the laser field. It is in this form that the calculations of Light and Szöke[7] were performed. Again, we stress that the resultant Eqs. (33) are good for any near-degenerate pairs ij and lm, in particular also for the near-degenerate elements of the density matrix used in Eq. (26).

We should stress that the secular approximation is a sufficient condition for obtaining simple rate equations. When the secular approximation is not valid, i.e., $\delta_D \lesssim \gamma_D$, the important elements of the collision operator $\tilde{\gamma}_D^c(s)$ which couple the dressed states can still be written in terms of S^D-matrix elements, since the BCA ($\gamma_D^c \tau_c << 1$) implies that $\delta_D \tau_c << 1$ too, and therefore the term $e^{\tilde{L}_D^A \tau}$ in Eq. (27) can be replaced by unity (noting that δ_D is an

eigenvalue of $\tilde{L}_D^A$). The density-matrix equations now have a much more complicated structure with coupling between populations and coherences.

III. THE CORRELATION FUNCTION

A. Formal considerations

We shall now calculate the spectrum emitted by the atom in the presence of driving field and collisions using the equation of motion for the correlation function in the dressed-state representation. We shall see that the equation of motion for the correlation function in the dressed frame is closed and Markovian for timescales $t >> \tau_c$ after any initial condition. This implies that as long as we do not consider the emission that a given dressed-state component produces at detunings $\Delta\omega_D \gtrsim \tau_c^{-1}$ from its center then we can use this closed Markovian form of the equation of motion. To show this we start with the exact expression for the correlation function from which the spectrum is derived by Fourier transformation, i.e.,

$$C(t,t_0)=\mathrm{Tr}[\hat{\rho}_H d^+(t) d^-(t_0)] , \tag{35}$$

where $\hat{\rho}_H$ is the density matrix in the Heisenberg picture (chosen to coincide with the Schrödinger picture at $t=-\infty$). This may be written in the form

$$C(t,t_0)=\mathrm{Tr}[e^{\tilde{L}(t-t_0)}(\hat{\rho}(t_0)d^+)d^-] . \tag{36}$$

We can derive an equation of motion for $C(t,t_0)$ just as we did in III. We first transform the quantity $\hat{g}_D(\tau)=e^{\tilde{L}\tau}\hat{\rho}(t_0)d^+$ into the rotating frame and then into the dressed frame [just as we did with the density operator; $e^{\tilde{L}\tau}\hat{\rho}(t_0)$]. For convenience we will put $t_0=0$ in the remainder of this section, however, we stress that in order to derive the spectrum, $\hat{\rho}(t_0)$ represents the *steady-state* value of the density matrix. After applying the BCA, the resulting equation of motion for $\hat{G}_D(\tau)$ $=\mathrm{Tr}_{\mathrm{pert}}[\hat{g}_D(\tau)]$ is (using a derivation exactly as in paper III)

$$\begin{aligned}\partial_\tau \hat{G}_D(\tau)=&\tilde{L}_D^A\hat{G}_D(\tau)+N\int_0^\tau dt'\mathrm{Tr}_{1\,\mathrm{pert}}[e^{\tilde{L}_D^A\tau}\tilde{V}_D^1(\tau)\tilde{U}_D^1(\tau,t')\tilde{V}_D^1(t')e^{-\tilde{L}_D^A t'}\hat{\rho}_{\mathrm{pert}}^D(1)]\hat{G}(t')\\&+N\,\mathrm{Tr}_{1\,\mathrm{pert}}[\tilde{V}_D(0)\hat{\rho}_{\mathrm{pert}}^D(1)]\hat{G}_D(\tau)\\&+N\,\mathrm{Tr}_{1\,\mathrm{pert}}\left[e^{\tilde{L}_D^A\tau}\tilde{V}_D^1(\tau)\tilde{U}_D^1(\tau,0)\left\{\left[\int_{-\infty}^0 d\tau'\tilde{U}_D^1(0,\tau')\tilde{V}_D^1(\tau')e^{-\tilde{L}_D^A\tau'}\hat{\rho}_{\mathrm{pert}}^D(1)\right]\hat{\sigma}_D(\tau')d_D^+\right\}\right] ,\end{aligned} \tag{37}$$

where d_D^+ is evaluated in the dressed frame. This equation is very similar to Eq. (23). The last term of Eq. (37)—the "destruction term"[28] due to a collision in progress at the initial time of the radiative process must, however, be considered in detail.

We first of all note that the observed scattered spectrum is (as examined in more detail in Sec. III B) obtained from $\hat{G}_D(\omega)$, the Fourier-Laplace transform of $\hat{G}_D(\tau)$; $[\hat{G}_D(\omega)=\hat{G}(s=i\omega)]$. This transform implies that, associated with a frequency separation $\Delta\omega_D$ of the scattered frequency ω from a dressed-atom frequency, there is a time of interest $1/\Delta\omega_D$. The memory kernel in the last term of Eq. (37) is zero if $\tau>\tau_c$, thus this term is obviously unimportant for $\Delta\omega_D << \tau_c^{-1}$ and may therefore be neglected in the equations of motion. This is reasonable, since as said above the last term of Eq. (37) represents the effect of the collision *that are in progress at time* $\tau=0$ on the dipole at later times. In fact, more detailed estimates of the destruction term (compare D_0 of paper III) show that in this "impact" ($\Delta\omega_D << \tau_c^{-1}$) limit, its contribution is at most of order $\gamma_D^c\tau_c(<<1)$. Having shown that for $\Delta\omega_D << 1/\tau_c$ the last (destruction) term in Eq. (37) is unimportant, then it is apparent that Eq. (37), can be brought to a form similar to the equations for the density matrix [$(\tilde{L}_D^A - s) < 1/\tau_c$ being equivalent to $\Delta\omega_D < 1/\tau_c$]. The condition $\Delta\omega_D < 1/\tau_c$ is sufficient to ensure[24] that $\tilde{\gamma}_D^c(\Delta\omega_D)$ reduces to the S-matrix (impact) limit, and the equations can be cast in a Markovian form. It is important to notice (as we demonstrated in Ref. 12) that Eqs. (32) and (37) involve different classes of elements of the supermatrix $\tilde{\gamma}_D^c$. The elements in (37), that determine the *shape* of the spectrum of the scattered radiation, are defined as *coherences* between initial and final dressed-atom states produced by coupling to the scattered field (the ω_S-dependent terms of Ref. 12), and have the form $\langle\langle if|\tilde{\gamma}_D^c|i'f'\rangle\rangle$, rather than the population-decay terms of the type $\langle\langle ii|\tilde{\gamma}_D^c|jj\rangle\rangle$ that appear in (32), and have an important role in obtaining the line intensities. It is easy to see that in the secular approximation, in which lines $|if\rangle\rangle$

and $|i'f'\rangle\rangle$ are well isolated, the off-diagonal elements connecting them can be neglected (this is, after all, what the secular approximation is all about).

Thus, the considerations with regard to the equation of motion for the density matrix such as secular approximation, BCA, etc., then apply in exactly the same way to the equation of motion for correlation function, which as we have seen amounts to calculating the equation of motion for (ρd^+). So the same tetradic elements that we calculate for the equation of motion for the density matrix [i.e., Eq. (26)] are needed for the equation of motion for (ρd^+) and the correlation function. This result is equivalent to the well-known quantum regression "theorem" which is strictly valid for Markovian processes. In particular, apart from different initial conditions, the same set of equations in the dressed frame are used. To reiterate, the necessary condition (in addition to secular and BCA approximations) is that we are only interested in frequency separations from the dressed frequencies such that $\Delta\omega_D << 1/\tau_c$.

B. The correlation function for the two-level atom

As we have shown above the correlation function can be calculated via the equation of motion of ρd^+, since we shall restrict ourselves to the impact region around dressed-state components, $\Delta\omega << \tau_c^{-1}$. Here $\hat{\rho} d^+$, or $\hat{G}_D$, play with respect to the scattered field the same role that a coherence element of the density matrix plays with respect to the incident field in weak-field absorption spectra (whereas σ plays the role of population elements). Then we only need the projected part of ρd^+, i.e., $\hat{\sigma}_D d_D^+$ which obeys a closed equation of motion

$$\partial_\tau \hat{G}_D(\tau) = \tilde{L}_D^A \hat{G}_D(\tau) + \tilde{\gamma}_D^c(0)\hat{G}_D(\tau) , \tag{38}$$

with initial condition $\hat{G}(\tau=0)=\hat{\sigma}_D(0)d^+$ (again note $\tau=0$ corresponds to steady state).

To give a concrete example of the technique we shall consider a two-level atom. First we note that this closed equation of motion gives us precisely

$$\begin{aligned}\hat{G}_D(\tau) &= \mathrm{Tr}_{\mathrm{pert}}[\exp(\tilde{L}\tau)]\hat{\sigma}_D(t_0)d_D^+ \\ &\equiv \tilde{U}_D^{\mathrm{av}}(\tau)[\hat{\sigma}_D(t_0)d_D^+] ,\end{aligned} \tag{39}$$

in the rotating and dressed frames (remember that $t_0=0$ was used above). We need to transform this back to the laboratory and free-atom frame since we need the quantity

$$\begin{aligned}C(\tau) &= \mathrm{Tr}[e^{\tilde{L}\tau}(\hat{\rho}d^+)d^-] \\ &= \mathrm{Tr}[\hat{U}_R^{-1}(\tau)\tilde{U}_R(\tau)(\hat{\rho}d^+)\tilde{U}_R^{-1}(\tau)\tilde{U}_R(\tau)d^-] \\ &= \mathrm{Tr}_{\mathrm{atom}}[\tilde{U}_D^{\mathrm{av}}(\tau)(\hat{\sigma}_D^I(t_0)d_D^+)U_R(\tau)d^-\tilde{U}_R^{-1}(\tau)] \\ &= \mathrm{Tr}_{\mathrm{atom}}[\hat{G}_D(\tau)d^-(\tau)] ,\end{aligned} \tag{40}$$

where $d^-(\tau)$ is d^- in the rotating frame. We now write $\hat{\sigma}_D(t_0)$ in terms of the basis vectors $|I\rangle$ and $|II\rangle$ [see, e.g., Ref. 21]

$$\hat{\sigma}_D(t) = \sum_{i\&j=I\&II} \sigma_{ij}^D |i\rangle\langle j| . \tag{41}$$

Using the transformation from atomic to dressed states

$$|I\rangle = -b_2|1\rangle + b_1|0\rangle , \tag{42}$$

$$|II\rangle = b_1|1\rangle + b_2|0\rangle . \tag{43}$$

Here

$$b_1 = \left[\frac{\Omega'+\Delta}{2\Omega'}\right]^{1/2} \tag{44}$$

and

$$b_2 = \mp\left[\frac{\Omega'-\Delta}{2\Omega'}\right]^{1/2} , \tag{45}$$

where $-(+)$ should be used when Δ is positive (negative). In the dressed-state basis the dipole operator d_D^+ may be written in the following form:

$$\begin{aligned}[d_D^+] &= \begin{bmatrix} b_1 & b_2 \\ -b_2 & b_1 \end{bmatrix}\begin{bmatrix} 0 & d_{10} \\ 0 & 0 \end{bmatrix}\begin{bmatrix} b_1 & -b_2 \\ b_2 & b_1 \end{bmatrix} \\ &= \begin{bmatrix} b_1 b_2 d_{10} & b_1^2 d_{10} \\ -b_2^2 d_{10} & -b_2 b_1 d_{10} \end{bmatrix} ,\end{aligned} \tag{46}$$

i.e., $[d_D^+] = d_{10}\{|II\rangle\langle II|b_1b_2 + |II\rangle\langle I|b_1^2 - |I\rangle\langle II|b_2^2 - |I\rangle\langle I|b_2b_1\}$. So our initial condition is, using steady-state values of $\hat{\sigma}_D$ for $t_0=0$,

$$\begin{aligned}[\hat{\sigma}_D(0)d_D^+] = d_{10}[&|II\rangle\sigma_{II\,II}(0)b_1b_2\langle II| + |II\rangle\sigma_{II\,II}(0)b_1^2\langle I| - |II\rangle\sigma_{II\,I}(0)b_2^2\langle I| \\ &- |II\rangle\sigma_{II\,I}(0)b_1b_2\langle I| - |I\rangle\sigma_{I\,II}(0)b_1b_2\langle II| + |I\rangle\sigma_{I\,II}(0)b_1^2\langle I| \\ &- |I\rangle\sigma_{I\,I}(0)b_2^2\langle II| - |I\rangle\sigma_{I\,I}(0)b_1b_2\langle I|]\end{aligned} \tag{47}$$

and in matrix form the initial condition is

$$[\hat{\sigma}_D(0)d_D^+]=d_{10}\begin{bmatrix} b_1b_2\sigma_{II\,II}(0) & \sigma_{II\,II}(0)b_1^2-\sigma_{II\,I}(0)b_1b_2-\sigma_{II\,I}(0)b_2^2 \\ \sigma_{I\,II}(0)b_1b_2-\sigma_{I\,I}b_2^2 & b_1b_2\sigma_{II\,I}(0)+b_1^2\sigma_{I\,II}(0) \end{bmatrix}. \tag{48}$$

Now in the steady state the off-diagonal elements of the density operator in the dressed basis all vanish since, having no driving term, all they can do is decay. They do not couple to the populations. So our steady-state initial condition is

$$[\hat{\sigma}_D(0)d_D^+]=d_{10}\begin{bmatrix} b_1b_2\sigma_{II\,II}(0) & \sigma_{II\,II}(0)b_1^2 \\ -b_2^2\sigma_{I\,I}(0) & -\sigma_{I\,I}(0)b_1b_2 \end{bmatrix}. \tag{49}$$

Equation (40) says that we require

$$C(\tau)=\langle 1\,|\,\tilde{U}_D^{\rm av}(\tau)(\sigma_D(0)d_D^+)\,|\,0\rangle d_{01}e^{i\omega_L\tau} \tag{50}$$

for the evaluation of the correlation function. Since

$$\hat{G}_D(\tau)\equiv\tilde{U}_D^{\rm av}(\tau)(\hat{\sigma}_D(0)d_D^+)\,, \tag{51}$$

we can express the matrix element of $\hat{G}_D(t)$ we need, i.e., $\langle 1\,|\,\hat{G}_D(t)\,|\,0\rangle$, in the following dressed-state form:

$$\langle 1\,|\,\hat{G}_D(t)\,|\,0\rangle=\begin{bmatrix} b_1 & b_2 \\ -b_2 & b_1 \end{bmatrix}\begin{bmatrix} G_{II\,II}(t) & -G_{II\,I}(t) \\ G_{I\,II}(t) & G_{I\,I}(t) \end{bmatrix}\begin{bmatrix} b_1 & -b_2 \\ b_2 & b_1 \end{bmatrix}$$

$$=b_1b_2[-G_{II\,II}(t)+G_{I\,I}(t)]+b_1^2G_{II\,I}(t)-b_2^2G_{I\,II}(t)\,. \tag{52}$$

Now the equation of motion for $\hat{G}_D(t)$ has the following form, where all zero elements are due to the secular approximation,

$$\frac{d}{dt}\begin{bmatrix} G_{I\,I} \\ G_{I\,II} \\ G_{II\,I} \\ G_{II\,II} \end{bmatrix}-\begin{bmatrix} -\Gamma_{I\,I} & 0 & 0 & \Gamma_{I\,II} \\ 0 & i\Delta_{I\,II}+\Sigma_{I\,II} & 0 & 0 \\ 0 & 0 & i\Delta_{II\,I}+\Sigma_{II\,I} & 0 \\ +\Gamma_{I\,II} & 0 & 0 & -\Gamma_{II\,II} \end{bmatrix}\begin{bmatrix} G_{I\,I} \\ G_{I\,II} \\ G_{II\,I} \\ G_{II\,II} \end{bmatrix}, \tag{53}$$

$$\Gamma_{I\,I}=\langle\langle II\,|\,\tilde{\gamma}_D^c\,|\,I\,I\rangle\rangle+\gamma_N^{II}\,, \tag{54}$$

$$\Gamma_{II\,II}=\langle\langle II\;II\,|\,\tilde{\gamma}_D^c\,|\,II\;II\rangle\rangle+\gamma_N^{II\,I}\,, \tag{55}$$

$$\Gamma_{I\,II}=\langle\langle II\,|\,\tilde{\gamma}_D^c\,|\,II\;II\rangle\rangle+\gamma_N^{II\,I}\,, \tag{56}$$

$$\Gamma_{II\,I}=\langle\langle II\;II\,|\,\tilde{\gamma}_D^c\,|\,I\;I\rangle\rangle+\gamma_N^{I\,II}\,, \tag{57}$$

$$\Sigma_{I\,II}=\langle\langle I\;II\,|\,\tilde{\gamma}_D^c\,|\,I\;II\rangle\rangle+\frac{\gamma_N}{2}(b_1^4+b_2^4+4b_1^2b_2^2)\,, \tag{58}$$

$$\Delta_{I\,II}=\frac{E_{II}-E_I}{\hbar}=\Omega+2\delta=-\Delta_{II\,I}\,, \tag{59}$$

$$\gamma_N^{I\,II}=\frac{\gamma_N}{4}\left[\frac{\Omega^2+2\Delta^2-2\Omega'\Delta}{Q'^2}\right], \tag{60}$$

$$\gamma_N^{II\,I}=\frac{\gamma_N}{4}\left[\frac{\Omega^2+2\Delta^2+2\Omega'\Delta}{\Omega'^2}\right]. \tag{61}$$

Here γ_N is the natural decay rate. These collisional rates in Eqs. (54)–(58) are the rates of coupling between states in the dressed frame as calculated, e.g., by Light and Szöke for $j_g=0\rightarrow j_e=1$. The coupled pair of equations we have to solve is for $G_{I\,I}(t)$ and $G_{II\,II}(t)$. The initial conditions are given by Eq. (49). The observable quantity is proportional to

$$\int_0^\infty e^{i\omega_L\tau}\langle 1|\hat{G}_D(\tau)|0\rangle e^{-i\omega\tau}d\tau=\hat{G}_D(i(\omega-\omega_L))$$
$$=b_1b_2[G_{II}(i\Delta')-G_{III}(i\Delta')]+b_1^2G_{III}(i\Delta')-b_2^2G_{III}(i\Delta')$$
$$=\frac{b_1^2b_2^2}{(i\Delta')(i\Delta'-\Gamma_{II}-\Gamma_{III})}[(\Gamma_{II}+\Gamma_{III})\sigma_{III}(0)+(\Gamma_{III}+\Gamma_{III})\sigma_{II}(0)+i\Delta']$$
$$+\frac{b_1^4}{i\Delta'+i\Delta_{III}+\Sigma_{III}}\sigma_{II\,II}(0)+\frac{b_2^4\sigma_{II}(0)}{i\Delta'-i\Delta_{III}+\Sigma_{III}^*}\cdot \tag{62}$$

Here $\Delta'=\omega-\omega_L$ and,

$$\sigma_{II}(0)=\frac{\Gamma_{III}}{(\Gamma_{III}+\Gamma_{II})};\qquad \sigma_{III\,II}(0)=\frac{\Gamma_{III}}{(\Gamma_{III}+\Gamma_{III})}\cdot \tag{63}$$

This has precisely the form of the Mollow triplet (Refs. 29 and 30). We must emphasize that this spectrum in the strong-field limit has been derived without making any phenomenological assumptions about the form of the damping operator. The linewidths of the three components of the triplet are the same as derived by Rabin and Ben-Reuven.[12] The latter authors, however, have not given explicit expressions for the line intensities. In weaker fields (the intermediate coupling case $\Omega\tau_c<<1$) we get the corresponding results of Refs. 12, 21, and 17. General expressions for the evaluation of these microscopically derived collision operators in the dressed frame are given by [Eqs. (33) and (34)]. The analysis used in this example can, of course, be *easily* extended to the more general $j_g\rightarrow j_e$ transition case—if the driving field is linearly polarized. For the case of $j_g=0\rightarrow j_e=1$ transition interacting with perturbers via a van der Waals potential, the collision operators in the dressed frame have been calculated by Light and Szöke.[7] The explicit equations of motion for the $j_g=0\rightarrow j_e=1$ case including a full solution for a time-dependent field (important for the analysis of many experiments) will be presented elsewhere.[18]

C. Evaluation of collision operators in the weak-field limit

It is instructive to relate the collision operators we have defined above to the conventional line-broadening operators discussed elsewhere. In this way we shall show how Eqs. (62) and (63) give, in the weak-field limit (in the BCA, of course), the exact linear response result. To show this we start with the definition of Γ_{III}, i.e., from Eq. (33),

$$\Gamma_{III}=Nh^{-1}\times\sum_{\vec{p}_\gamma\vec{p}_\delta}\rho_\gamma^1|\langle II\vec{p}_\delta|T(E_I+E_\gamma+i0)|I\vec{p}_\gamma\rangle|^2\times\delta(E_I+E_\gamma-E_{II}-E_\delta)\,. \tag{64}$$

We shall consider as we did in paper I that only the lower level interacts with perturbers. In the weak-field limit, i.e., $\Omega/\Delta<<1$ the part of the potential that couples the two dressed levels, i.e., $|I\vec{p}\rangle$ and $|II\vec{p}\rangle$ may be treated as a perturbation. The full effect of the interaction of the perturber with ground state must of course be retained. This is precisely the situation where we can use the distorted-wave born approximation (DWBA) (see Ref. 27, p. 271). The perturbation that couples $|I\vec{p}\rangle$ and $|II\vec{p}'\rangle$ is given by Eq. (18). In this case it gives

$$\langle II\vec{p}'|\hat{V}_D|I\vec{p}\rangle=b_1b_2\langle 0\vec{p}'|\hat{V}_g|0\vec{p}\rangle\,. \tag{65}$$

Here $\hat{V}_g$ is just the interaction with the perturber in the ground state. If we denote the scattering state formed by an incoming ground state in the absence of the driving field by $|0\vec{p}_\gamma+\rangle$, then the DWBA gives

$$\Gamma_{III}=Nh^{-1}\sum_{\vec{p}_\gamma\vec{p}_\delta}\rho_\gamma^1|\langle 0\vec{p}_\delta|\hat{V}_g|0\vec{p}'_\gamma+\rangle|^2\times\delta(E_I+E_\gamma-E_{II}-E_\delta)b_1^2b_2^2\,. \tag{66}$$

Note that in the weak limit $E_I-E_{II}=\Delta$ so that we

can write, for $\Omega/\Delta << 1$,

$$\Gamma_{II} I = Nh^{-1}\Omega^2 \sum_{\vec{p}_\gamma \vec{p}_\delta} |\langle 0\vec{p}_\delta | 0\vec{p}_\gamma +;\rangle|^2 e^{-E(\vec{p}_\gamma)/kT} . \tag{67}$$

This is the exact BCA far wing absorption rate that includes the effect of the ground-state potential on the perturber distribution: through the Boltzmann factor in (67) (see paper I). In case there is an upper-level interaction, $\hat{V}_e$, the only modification necessary is to replace $\hat{V}_g$ in Eq. (66) by $\hat{V}_g - \hat{V}_e$. The reduction of (66) to (67) is not possible when we have spatial degeneracy since in that case we cannot use the BO approximation for the atom plus perturber wave function.[6]

We want to emphasize that we have shown here that the dressed state and free atomic state bases give exactly the same results in the weak-field limit and contain exactly the same physics of absorption during collisions. In the weak-field limit, as emphasized above, the collisional calculation for the degenerate case is considerably simplified by exploiting the spherical symmetry of the perturber distribution. If, however, an experiment is done using a crossed-beam arrangement[3] rather than a thermal cell the dressed-state approach is by and large the most direct and suffers only from the limits of the secular approximation.

IV. SUMMARY

We have shown how the spectrum emitted by an atom in the presence of collisions and a driving field may be calculated even when the driving field significantly alters the mechanism of the collision with the atom. In particular, the equations of motion derived here for the density matrix and the autocorrelation functions are simple Markovian equations in the dressed-state basis (the coefficients of which can be directly related to single-collision S^D-matrix elements calculated in the dressed frame). The conditions necessary for obtaining these equations are the following: (1) The binary collision approximation should be valid (requiring $\gamma_D^c \tau_C << 1$); (2) the secular approximation should be valid (requiring that the energy splittings δ_D between nondegenerate components in the dressed frame be large compared to γ_D^c, i.e., isolated components); and (3) scattering frequencies of interest must be in the impact region in the dressed frame around each separate resonance peak (requiring frequency separations $\Delta\omega_D << 1/\tau_c$).

[Conditions (1) and (2) are sufficient for obtaining simple decoupled Markovian equations. When this is not valid, i.e., $\delta_D \lesssim \gamma_D^c$, the important elements of the collision operator can still be written in terms of S^D-matrix elements, but the density-matrix equations now have more complicated couplings, as in the problem of overlapping-line band spectra.]

We thus reiterate the conclusions of Rabin and Ben-Reuven that the measurement of the spectral components emitted by the dressed states can be used to study the detailed variation of the collisions in the dressed frame as functions of the driving field strength and detuning of the laser from the atoms natural frequency. This should prove a powerful technique in the study of the mechanism of laser induced processes in atomic collisions.

This work was supported in part by NSF Grant No. PHY79-04928 and in part by NASA Grant No. NGL-06-003-057 (both through the University of Colorado), and also by the Research Corporation and by the Atomic and Plasma Radiation Division of the NBS.

---

*1979–80 Joint Institute for Laboratory Astrophysics Visiting Fellow.

[1]V. S. Lisitsa and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. 68, 479 (1975) [Sov. Phys.—JETP 41, 233 (1975)].

[2]R. W. Falcone, W. R. Green, J. C. White, J. F. Young, and S. E. Harris, Phys. Rev. A 15, 1333 (1977).

[3]P. R. Brooks, R. F. Curl, Jr., R. S. Judson, and R. S. Lowe, Phys. Rev. Lett. 44, 10, 587 (1980).

[4]S. I. Yakovlenko, Kvant. Elektron. (Moscow) 5, 259 (1978) [Sov. J. Quantum Electron. 8, 151 (1978)].

[5]T. F. George *et al.*, in *Chemical and Biochemical Applications of Lasers,* edited by C. B. Moore (Academic, New York, 1979), Vol. IV.

[6]F. H. Mies, *Theoretical Chemistry: Advances and Perspectives,* edited by D. Henderson (Academic, New York, 1980), Vol. 8.

[7]J. C. Light and A. Szöke, Phys. Rev. A 18, 1363 (1978).

[8]K. Burnett, J. Cooper, R. J. Ballagh, and E. W. Smith, Phys. Rev. A 22, 2205 (1980) (paper I).

[9]K. Burnett and J. Cooper, Phys. Rev. A 22, 2027 (1980) (paper II).
[10]K. Burnett and J. Cooper, Phys. Rev. A 22, 2044 (1980) (paper III).
[11]J. B. Yelnik and D. Voslamber, Astrophys. J. 230, 184 (1979).
[12]Y. Rabin and A. Ben-Reuven, J. Phys. B 13, 2011 (1980).
[13]A. Ben-Reuven and Y. Rabin, Phys. Rev. A 19, 2056 (1979).
[14]B. R. Mollow, Phys. Rev. A 15, 1023 (1977).
[15]E. Courtens and A. Szöke, Phys. Rev. A 15, 1588 (1977); erratum 17, 2119 (1978).
[16]C. Cohen-Tannoudji and S. Reynaud, J. Phys. B 10, 345 (1977).
[17]J. Cooper, R. J. Ballagh, and K. Burnett, Phys. Rev. A 22, 535 (1980).
[18]S. Reynaud and C. Cohen-Tannoudji, *Proceedings of the Fifth International Conference on Laser Spectroscopy* (Springer, New York, 1981).
[19]P. D. Kleiber, J. Cooper, M. G. Raymer, and K. Burnett (unpublished).
[20]A. Ben-Reuven, Phys. Rev. A 22, 2572 (1980); 22, 2585 (1980).
[21]A. Ben-Reuven, in *Spectral Line Shapes,* edited by B. Wende (de Gruyter, Berlin, 1981), pp. 867–884.
[22]J. Callaway and E. Bauer, Phys. Rev. 140, A1072 (1965).
[23]U. Fano, Phys. Rev. 131, 259 (1963).
[24]E. W. Smith, J. Cooper, and C. R. Vidal, Phys. Rev. 185, 140 (1969).
[25]A. Omont, Prog. Quantum Electron. 5, 69 (1977).
[26]A. Ben-Reuven, Adv. Chem. Phys. 33, 235 (1975).
[27]J. R. Taylor, *Scattering Theory* (Interscience, New York, 1970).
[28]R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, New York, 1974).
[29]B. R. Mollow, Phys. Rev. 188, 1969 (1969).
[30]P. L. Knight and P. W. Milonni, Phys. Rep. 66, 21–107 (1980).