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Theory of two-atom coherence in gases. II. Continuous-wave spectra

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General expressions are derived for the spectral line shapes of resonance absorption and scattering of coherent radiation in collision-broadened gases, taking into account effects of coherent excitation of two or more atoms (or molecules), as steady-state solutions of a hierarchy of master equations described in a previous publication (paper I). Coupling between the coherent motions of the atoms, provided by a Bethe-Salpeter–type effective interaction, in the binary-collision approximation, forms the essential mechanism for introducing cooperative coherent effects into the steady-state spectra. Explicit expressions are given for the effects of two-atom coherence in the binary-collision approximation, in which the Bloch-type dressed-atom self-energy superoperator is modified by the presence of collisions in which both atoms retain memory of their coherent propagation before the collision. The self-energies include the effects of resonance exchange symmetrization in self-broadening, and are renormalized by the coincidence of radiative transitions during the collisions. The impact (near-resonance) and the quasistatic (line-wing) limits of the applied-frequency detunings are discussed. In the quasistatic limit, coherent many-atom excitations become irrelevant; however, interactions of both collision partners with the radiation during the collision accounts for such phenomena as collision-induced absorption or radiative collisions. In the impact limit, the inclusion of the Bethe-Salpeter interactions allows for the appearance of two-atom resonances. Magnitude estimates of these effects are discussed. Effects of higher-rank (many-body) coherences are formally discussed with the help of a diagrammatic method, leading into implicit bootstrap equations that can be solved by iterative or other procedures.

I. INTRODUCTION

In a previous publication (Paper I),[1] a hierarchy of master equations was derived describing the coherent excitation of a many-atom nonreactive gas system by an arbitrarily strong applied coherent radiation, under the influence of binary collisions.[2]

In this publication, a general expression derived in Sec. II for photon-counting rates and applicable to both resonance absorption and resonance scattering of radiation, is brought into a form related to the steady-state solution of the master equations, in the case of continuous-wave spectra. As in Paper I, coherence effects are introduced gradually, beginning with the one-atom case (in Sec. III), going through the two-atom case (in Sec. V), and culminating in a brief formal discussion of many-atom effects (in Sec. VI). Explicit expressions are derived for the two-atom coherence case, using a diagrammatic method described in Sec. IV, in the binary-collision approximation. The spectral shape is expressed in terms of self-energy (collision broadening and shifting) superoperators, related to the binary-collision scattering matrix, and including such effects as resonance exchange in self-broadening and coincidence of radiative transitions during the collisions. The effects of collisions between two atoms, both retaining memory of their coherent excitation before the collision, are introduced as modifications to the self-energy, related to the Bethe-Salpeter effective interaction of Paper I. In Secs. VII and VIII, the impact and the quasistatic approximations are derived as limit cases, using the method of Burnett *et al.* for treating the initial correlations in the density matrix.[3] In the *impact* limit, where the evolution of the system extends over many collisions, the modifications involving the Bethe-Salpeter diagrams introduce frequency-dependent features that allow, in principle, the appearance of cooperative two-atom resonance peaks in resonance fluorescence.[2,4] Rough estimates of the cooperative effects are discussed. In the *quasistatic* limit, where the time evolution extends over one collision at most, such cooperative effects cannot be felt. However, introducing self-energies renormalized by the interaction of both atoms with radiation coincident with the collision, allows one to incorporate in this limit such phenomena as *radiative* collisions.[5,6] This relation is discussed in Sec. VIII. A more detailed study of the two-level-atom resonance fluorescence will follow in a forthcoming article of this series. For terminology and notation used here consult Paper I. Here, too, wherever "atoms" are referred to, they can be replaced by "molecules."

II. PHOTON-COUNTING RATES

The rate at which photons are emitted (or absorbed) in the kth mode of the radiation field, from a coherently driven gas system of N_A atoms, can be obtained by calculating the time derivative of the mean photon number in the kth mode. This

mode can be one of the incident field modes (self-attentuation) or a scattered mode (resonance scattering or resonance fluorescence). In the Schrödinger picture, the emission (or minus absorption) rate can be written as[7]

$$\langle \dot{N}_k \rangle = -i\hbar^{-1}\,\mathrm{tr}\{[a_k^\dagger a_k, V_k^R]\rho(t)\}\,, \tag{1}$$

using a second-quantized description of the fields. Here $\rho(t)$ is the density matrix of the *entire* system (gas plus radiation). The interaction of the gas with the kth radiation mode (considered here in the electric-dipole approximation) can be written as

$$V_k^R = \sum_{j=1}^{N_A} V_k^{j,R} = V_k^{R+} + V_k^{R-}\,, \tag{2}$$

where the $+(-)$ term is proportional to the annihilation (creation) operator $a_k(a_k^\dagger)$ for k-mode photons.

The annihilation and creation operators obey the boson commutation relations

$$[a_k, a_k^\dagger] = 1\,, \tag{3}$$

etc., and therefore

$$[a_k^\dagger a_k, V_k^{R\mp}] = \pm V_k^{R\mp}\,. \tag{4}$$

Hence

$$\begin{aligned}\langle \dot{N}_k \rangle &= \mp i\hbar^{-1}\,\mathrm{tr}[V_k^{R\mp}\rho(t) - \rho(t)V_k^{R\pm}] \\ &\equiv \mp i\,\mathrm{tr}[\mathcal{V}_k^{R\mp}\rho(t)]\,,\end{aligned} \tag{5}$$

with both signs applicable. In the last equality we used the definition of Liouvillian superoperators[8]

$$\hbar\mathfrak{K}X = (HX - XH^\dagger) \equiv (HI^* - IH^*)X \tag{6}$$

[where H is an ordinary (dyadic) Hamiltonian operator], as operators in double space,[9] with

$$\langle\langle ab\,|AB^*\,|cd\rangle\rangle = \langle a|A|c\rangle\langle b|B|d\rangle^*. \tag{7}$$

Note the appearance of the Hermitian-conjugate dagger symbol in (6). $V_k^{R\mp}$ is *not* a Hermitian operator. If it were, then by the use of (6), Eq. (5) would be turned into a trace of a commutator and thus vanish.

The time evolution of $\rho(t)$ can be related to a specified initial condition at t_0 by

$$\rho(t) = U(t,t_0)\rho(t_0)U^\dagger(t,t_0) \equiv \mathcal{U}(t,t_0)\rho(t_0)\,, \tag{8}$$

where U is the ordinary time-evolution operator (in the Schrödinger picture), and $\mathcal{U}$ is the corresponding superoperator

$$U(t,t_0) = \exp[-i\mathfrak{K}(t-t_0)]\,, \tag{9}$$

where $\mathfrak{K}$ is related to the Hamiltonian H of the entire system by (6).

Steady-state emission rates, under continuous-wave irradiation conditions, can be obtained either by specifying the initial conditions at a fixed time (for example, $t_0 = 0$) and letting $t \to \infty$, or by letting $t_0 \to -\infty$, and reckoning $\rho(t)$ at a fixed time (for example, $t = 0$). Following the latter lead, we now *postulate* for the initial conditions an equilibrium state of the sample on which the coherent incident beam is superimposed[7] by a Glauber displacement transformation,

$$\rho(t_0) = D(\alpha(t_0))\rho_{eq}D^\dagger(\alpha(t_0)) \quad (t_0 \to -\infty)\,, \tag{10}$$

where

$$D(\alpha) = \exp\Big(\sum_{k\in\text{beam}} (\alpha_k a_k^\dagger - \alpha_k^* a_k)\Big)\,, \tag{11}$$

assuming the incident beam is a discrete set of coherent monochromatic fields, each described by a Glauber coherence state $|\alpha_k\rangle$,[10] and

$$\alpha_k(t) = \alpha_k e^{-i\omega_k t}\,, \tag{12}$$

with ω_k being the (angular) frequency of the kth mode.

The displacement operators can be removed at the cost of adding a time-dependent *classified-field interaction* to the Hamiltonian, in the manner shown in Appendix A to Paper I. The time dependence can be removed by the Floquet method, extending the basis of double-space vectors in which $\rho(t)$ is expanded,[1,7] by introducing the Floquet numbers $\hat{n}$ describing the harmonics of the incident-field frequencies in the response of the system. With $\mathfrak{K}$ replaced by

$$\mathfrak{L} = \mathfrak{K} + \mathcal{V}^{R,\mathrm{cl}} + \mathfrak{L}^R\,, \tag{13}$$

where $\mathcal{V}^{R,\mathrm{cl}}$ is the superoperator corresponding to the classical-field (time-independent) interactions, and $\mathfrak{L}^R$ is a supermatrix of frequency harmonics in Floquet space,[1,7]

$$\mathfrak{L}^R|\hat{n}\rangle\rangle = -\sum_{k\in\text{beam}} \hat{n}_k\omega_k|\hat{n}\rangle\rangle \quad \hat{n}\equiv\{\hat{n}_k\};\ \hat{n}_k = 0, \pm 1, \ldots \tag{14}$$

we can write

$$\begin{aligned}\langle \dot{N}_k \rangle &= \mp i\,\mathrm{tr}[\mathcal{V}_k^{R\mp}\mathcal{U}'(t,-\infty)\rho_{eq}] \\ &\equiv \mp i\langle\langle I\,|\mathcal{V}_k^{R\mp}\mathcal{U}'(t,-\infty)\,|\rho_{eq}\rangle\rangle\,,\end{aligned} \tag{15}$$

with the end-point interaction $\mathcal{V}_k^{R\mp}$ including now the classical-field interaction, and

$$\mathcal{U}'(t,t_0) = \exp[-i\mathfrak{L}(t-t_0)]\,. \tag{16}$$

The equilibrium average is expressed here as an expectation value in double space, using the definition of the metric in this space[9]

$$\langle\langle A\,|B\rangle\rangle = \mathrm{tr}\{A^\dagger B\}\,, \tag{17}$$

with the identity operator I as the bra conjugate to the equilibrium-state ket ρ_{eq} (both belonging to $\hat{n}$

$=0$ in Floquet space).

The equilibrium state, being a stationary state of the system when the incident radiation is switched off, obeys

$$\mathfrak{U}_e(t,t_0)\rho_{eq}=\rho_{eq}\,, \tag{18}$$

where $\mathfrak{U}_e$ is obtained from $\mathfrak{U}'$ by removing the classical-field interactions ($\mathfrak{L}\to\mathfrak{L}_e$). Using a box normalization in a macroscopic box of length L, we can also omit from $\mathfrak{U}_e$ the interaction with the scattered mode k_s, in case (15) refers to resonance scattering, within an error of $O(L^{-3})$. Using the integral identity

$$\mathfrak{U}'(t,t_0)=\mathfrak{U}_e(t,t_0) - i\int_{t_0}^{t}\mathfrak{U}'(t,t')\mathfrak{V}^R\mathfrak{U}_e(t',t_0)dt'\,, \tag{19}$$

where, from now on, $\mathfrak{V}^R$ refers to only the relevant ("dressing") field modes (all incident plus the single scattered modes), and the definition of the (retarded) resolvent superoperator,

$$\mathcal{G}(z)=-i\int_{-\infty}^{t}e^{iz(t-t')}\mathfrak{U}'(t,t')dt' =(z-\mathfrak{L})^{-1}\quad(\mathrm{Im}\,z>0)\,, \tag{20}$$

we finally get

$$\langle\dot N_k\rangle=\mp i\,\mathrm{tr}[\mathfrak{V}_k^{R\mp}\mathcal{G}(i0)\mathfrak{V}^R\rho_{eq}] \tag{21}$$

for the steady-state emission rates. Here $z=i0$ implies the limit as z approaches the origin from above the real axis. A term involving $\mathfrak{V}_k^{R\mp}\rho_{eq}$ alone was omitted, since transition rates require an *even* number of applications of the interaction superoperator.

The resolvent in (21) can be expanded as an infinite series in the coupling to the beam modes, allowing for their effects to arbitrary strength. In self-attenuation, reference to the second-quantized part in $\mathfrak{V}_k^{R\mp}$ can be omitted, to $O(L^{-3})$, and the expansion involves explicitly only the classical-field interactions. All couplings to other field modes are relegated to the role of radiative-bath relaxation effects. In resonance scattering, the coupling strength is proportional to $L^{-3/2}$ in box normalization, and therefore the resolvent should also be expanded to first power in the relevant coupling to the k_s mode. (The resulting L^{-3} dependence is canceled on calculating the differential rate of scattering into a finite solid angle.) The scattering rate can therefore be expressed as

$$\langle\dot N_{k_s}\rangle=\mp i\,\mathrm{tr}\{\mathfrak{V}_{k_s}^{R\mp}\mathcal{G}_{\hat n_s=\pm1}(i0)\mathfrak{V}_{k_s}^{R}[1+\mathcal{G}_{\hat n_s=0}(i0)\mathfrak{V}^{R,\mathrm{cl}}]\rho_{eq}\}\,. \tag{22}$$

Here $\hat n_s=0$ and ±1 specify two different representations of the resolvent operator in double space (in the limit $\mathfrak{V}_{k_s}^{R}\to0$). The first one is independent of the scattered-mode frequency ω_{k_s}; the second one involves $\pm\omega_{k_s}$ in the denominator and hence determines the spectrally resolved features of the scattered radiation. The two terms in the square brackets in (22) thus split the expression into two parts. The first part represents *spontaneous* emission, with the atoms initially in thermal equilibrium, but the emission spectrum is modified by the presence of the coherent beam. The second part describes *induced* emission, with the density matrix of the atoms initially driven by the applied fields, affecting both intensity and shape of the scattering spectrum. This part is therefore more likely to be influenced by cooperative coherent excitation in the gas.[11]

The scattering rate, being quadratic in $\mathfrak{V}_{k_s}^{R}$, is essentially proportional to the spectral resolution (Fourier transform) of the *first-order* correlation function of the scattered field.[12] A *second-order* correlation function can be related to the coincidence rate of two photons in modes s and s'. This rate is quartic in the scattered-field amplitude.

The equilibrium distribution ρ_{eq} includes all statistical correlations between constituent particles (atoms and photons). The transformation of Burnett *et al.*,[3] relates it to the separable (ideal-gas) canonical distribution ρ_0 by[13]

$$\rho_{eq}=\mathfrak{U}_e(0,-\infty)\rho_0=[1+\mathcal{G}_e(i0)\mathfrak{V}^B]\rho_0\,. \tag{23}$$

Here $\mathcal{G}_e$ is obtained from $\mathcal{G}$ by setting $\mathfrak{V}^R=0$ (where R refers to the relevant dressing modes) and $\mathfrak{V}^B$ is the "thermal bath" interaction, incorporating all interactions within the sample (atom-atom and atom-photon). The square brackets in (23) serve as a superoperator analog of the Möller wave operator in scattering theory,[14] or the Gell-Mann and Low transformation in quantum field theory,[15] transforming ρ_0 as the "bare-vacuum" state into the "interacting-vacuum" state ρ_{eq}. As the final state involves a trace over a complete basis, no such modification is required, strictly speaking, in the final state (represented by the identity operator). However, in resonance scattering or absorption, we generally limit the final-state summation only to those atomic levels lying close to resonance with one of the dressing field modes. We then practically replace the identity operator in (15) by a projection P^R on a limited subset (the "resonance set").[7] However, these levels are modified by collisions in the gas, which may mix them with other (nonresonant) states. Therefore P^R, too, must represent a set of real (interacting) gas states, and a Burnett *et al.*[3] transformation must be applied, again, to relate it to the ideal-gas resonance set (P_0^R):

$$P^R = P_0^R \mathfrak{u}_e(\infty, 0) = P_0^R[1 + \mathcal{V}^B \mathcal{G}_e(i0)] \,. \tag{24}$$

Using the identity

$$[1 + \mathcal{G}(z)\mathcal{V}^R][1 + \mathcal{G}_e(z)\mathcal{V}^B] = 1 + \mathcal{G}(z)(\mathcal{V}^R + \mathcal{V}^B) \,, \tag{25}$$

and a similar one transposing resolvents and interactions, we can now write

$$\langle \dot{N}_k \rangle = \mp i \,\mathrm{tr}[(\mathcal{V}_k^{R\mp} + \mathcal{V}^B)\mathcal{G}(i0)(\mathcal{V}^R + \mathcal{V}^B)\rho_0] \,, \tag{26}$$

omitting explicit reference to the resonance-set projection P_0^R. The last $\mathcal{V}^B$ on the left will anyhow vanish on summing over a complete basis as it contributes a commutator to the trace. However, it produces a much better approximation when the sum is limited to the resonance set.

III. ONE-ATOM COHERENCE

At this point, Zwanzig's method of projection operators[8,16] can be introduced in order to obtain reduced expressions for the emission rates. Consider first the existence of only one-atom coherences,[1] as in the foreign-gas broadening problem, assuming the N_A identical atoms in the sample have no knowledge of each other's coherent excitation. The trace in (26) can then be written as N_A times a single-atom expression, where $\mathcal{V}^R$ is replaced by $\mathcal{V}^{1,R}$. The calculation of the trace is accomplished in two steps, summing first over all "bath" degrees of freedom, and leaving out the "dressed" atom (single atom plus relevant field modes) to the next step. Let

$$\rho_0 = \rho_0^1 \rho_0^B \,, \tag{27}$$

where 1 and B stand for the dressed-atom and the bath, respectively, and let

$$\mathcal{P} = |\rho_0^B\rangle\rangle\langle\langle I^B| \tag{28}$$

(where I^B implies a trace over bath degrees of freedom) be the corresponding Zwanzig projection operator. Inserting $\mathcal{P} + \mathcal{Q}$ (where $\mathcal{Q} = 1 - \mathcal{P}$) at every intermediate step in a power-series expansion of $\mathcal{G}$ in powers of $\mathcal{V}^R$ and $\mathcal{V}^B$, and bunching together all terms with intermediate $\mathcal{Q}$'s between a $\mathcal{P}$ at the edges, we get

$$\langle \dot{N}_k \rangle = \mp i N_A \,\mathrm{tr}_1(\{\delta\Sigma_k^{1\mp}(i0) + [\mathcal{V}_k^{1,R\mp} + \delta\Sigma_k^{1\mp}(i0)]\, g^1(i0)[\mathcal{V}^{1,R} + \Sigma^1(i0)]\}\rho_0^1) \,. \tag{29}$$

Here

$$\Sigma^1(z) = \mathrm{tr}_B\{[\mathcal{V}^{1,B} + \mathcal{V}^{1,B}\mathcal{Q}(z - \mathcal{Q}\mathfrak{L}\mathcal{Q})^{-1}\mathcal{Q}\mathcal{V}^{1,B}]\rho_0^B\} \tag{30}$$

is the self-energy superoperator, and

$$\delta\Sigma_k^{1\mp} = \mathrm{tr}_B[\mathcal{V}^{1,B}\mathcal{Q}(z - \mathcal{Q}\mathfrak{L}_e\mathcal{Q})^{-1}\mathcal{Q}\mathcal{V}_k^{1,R\mp} \times \mathcal{Q}(z - \mathcal{Q}\mathfrak{L}\mathcal{Q})^{-1}\mathcal{Q}\mathcal{V}^{1,B}\rho_0^B] \tag{31}$$

is the contribution to the self-energy in which $\mathcal{V}_k^{1,R\mp}$ appears as the last radiative coupling on the left. Also g^1 is the reduced resolvent

$$g^1(z) = [z - \mathfrak{L}^1 - \Sigma^1(z)]^{-1} \,, \tag{32}$$

where $\mathfrak{L}^1$ is the dressed-atom Liouvillian superoperator, including coupling to the relevant field modes.

In the binary-collision approximation we can write

$$\Sigma^1(z) = N_B \,\mathrm{tr}_2[\mathcal{T}_R^{1,2}(z)\rho_0^2] \,. \tag{33}$$

Similarly,

$$\delta\Sigma_k^{1\mp} = N_B \,\mathrm{tr}_2[\mathcal{T}^{1,2}(z)(z - \mathfrak{L}_0)^{-1} \times \mathcal{V}_k^{1,R\mp}(z - \mathfrak{L}_0)^{-1}\mathcal{T}_R^{1,2}(z)\rho_0^2] \,. \tag{34}$$

Here N_B is the number of perturbers, and $\mathcal{T}^{1,2}(z)$ and $\mathcal{T}_R^{1,2}(z)$ are the field-independent and field-renormalized binary-collision scattering superoperators defined by Eqs. (22) and (21) of Paper I, respectively, and $\mathfrak{L}_0$ is the interaction-free two-atom Liouvillian superoperator.

In self-broadening where the perturbing and driven atoms are identical, we can still use the one-atom coherence picture provided *one* of the two atoms, before or after the collision, is not coherently excited (i.e., it is in the coherence-vacuum state[1] described by the ideal-gas thermal-equilibrium distribution). We should then play a game of "follow the ball carrier," labeling the one atom marked by coherent excitation as "1," even though resonance exchange may occur in collisions. All intermediate binary-collision self-energies Σ^1 appearing in the resolvent (32) should be replaced by the symmetrized forms Σ_S^1 obtained by replacing

$$\mathcal{T}_R^{1,2} \to \mathcal{T}_R^{1,2}\mathcal{S}_2 \,, \tag{35}$$

where $\mathcal{S}_2$ is a symmetrization operation[1] implying a summation over the two permutations of particle labels. Furthermore, the replacement

$$\mathcal{V}^{1,R} \to \mathcal{V}^{1,R} + \mathcal{V}^{2,R} \equiv \mathcal{V}^R \tag{36}$$

should be made in the definition of $\mathcal{T}_R^{1,2}$, since both atoms can interact with the radiation during the binary collision. Also, N_B is replaced by N_A.

Special care is needed in handling the sole $\delta\Sigma_k^{1\mp}$ term, appearing in (29) as a vacuum-expectation value (in the terminology of Paper I), and the two end-point insertions, Σ^1 and $\delta\Sigma_k^{1\mp}$ acting as vertex

functions, raising and lowering the coherence rank (from 0 to 1 and vice versa), respectively, together with the accompanying bare radiative couplings. The first two of these three self-energy terms operator on the coherence vacuum, defined by Eq. (57) of Paper I, and therefore should appear in the *nonsymmetrized* form,[1] provided (36) is still used. The last of the three terms is different, however. It carries, as last radiative coupling during the collision, the terms $\mathcal{V}_k^{1,R\mp}$, in which the label "1" comes from replacing the N_A-atom radiative couplings by N_A times the single-atom interaction. This serves as an "identity tag," by which the atom carrying the coherent excitation before this terminal collision can be identified. Therefore the *symmetrized* form, with (35), should be used. Hence

$$\langle \dot{N}_k \rangle = \mp i N_A \operatorname{tr}_1(\{\delta\Sigma_k^{1\mp}(i0) + [\mathcal{V}_k^{1,R\mp} + \delta\Sigma_{S,k}^{1\mp}(i0)]\, g_S^1(i0)[\mathcal{V}^{1,R} + \Sigma^1(i0)]\}\rho_0^1) \tag{37}$$

in self-broadening, with

$$g_S^1(z) = [z - \mathfrak{L}^1 - \Sigma_S^1(z)]^{-1} \tag{38}$$

as the symmetrized propagator, using (35) and (36) in the definition of Σ_S^1, and (36) only in that of Σ^1.

The addition of the end-point vertices represents, according to Burnett *et al.*,[3] radiative processes that commence or culminate *during* a collision, whereas the bare radiative couplings refer to intercollisional transitions. The sole vacuum-averaged term represents a complete process occuring *within* a single collision, i.e., a collision-induced absorption[17] (or scattering) process, or a radiative collision.[5,6] In strongly allowed line spectra (i.e., spectra in which the intensity is dominated by the bare radiative vertices), under moderately strong radiation intensity, the effects of these collision-induced interactions will be felt only in the line wings,[3] and can be neglected under near-resonance conditions (in the so-called impact limit, to be discussed below). Only under stronger radiation, in which the Rabi nutation frequencies become comparable to the inverse collision-duration time, will the self-energies in the resolvent be appreciably affected,[18] and the domain of optical collisions (discussed by Lisitsa and Yakovlenko[5]) be reached.

IV. DIAGRAMMATIC REPRESENTATION

The results of Sec. III, as well as further modifications resulting from higher-rank coherences, can be translated into a diagrammatic representation, forming a one-to-one correspondence between algebraic elements and graphic symbols. In this construction we should recall that resolvent operators describing the propagation of disjoint components of the system, represented here by vertical lines, can be convoluted into a single resolvent (or propagator), represented by a pair of parallel lines, by using the identity

$$(z - \mathfrak{L}^1 - \mathfrak{L}^2)^{-1} = \int (z - z' - \mathfrak{L}^1)^{-1}(z' - \mathfrak{L}^2)^{-1} dz' . \tag{39}$$

Integration in (39) is carried along a straight line parallel to the real axis, with $\mathrm{Im}z > \mathrm{Im}z' > 0$.

Let a solid untruncated vertical line represent the propagation of a bare atom (with no radiative or collisional couplings). Let a parallel dotted line represent the dressing relevant free-radiation modes. The dressed-atom propagator, including radiative coupling, is then represented by a solid double bar obeying the Dyson equation illustrated in Fig. 1, with the wavy horizontal bar representing the radiative coupling $\mathcal{V}^{1,R}$. The dotted vertical bars, representing free-radiation propagators, are not shown explicitly in later diagrams. Reduced propagators, such as (32), modified by foreign-gas collisions are represented by Fig. 2, where an "improper" self-energy insertion (using the conventional terminology of many-body theories[15]), represented by a crosshatched block, is related to the "proper" self-energy (simply hatched block) by the Dyson equation illustrated in Fig. 2. A self-energy diagram, in the foreign-gas binary-collision approximation, is represented by the "ladder" diagram of Fig. 3, with the dashed horizontal bar representing an intermolecular coupling $\mathcal{V}^{1,2}$. All closed loops and truncated particle lines, representing a projection onto a lower coherence rank, signify a thermal averaging over particle states, and multiplication by particle number, implying the separable (ideal-gas) distribu-

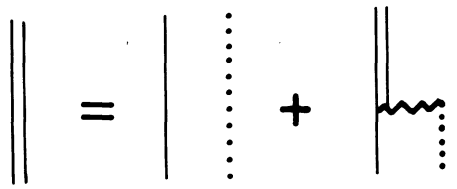

FIG. 1. A dressed-atom coherence propagator in double space (a double bar) in absence of a thermal bath, the solid and the dotted bars representing free propagators of the bare atom and the relevant ("dressing") field modes, respectively. The horizontal wavy line represents a radiative coupling.

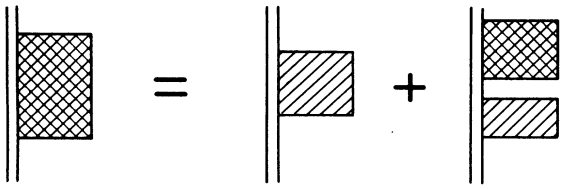

FIG. 2. A dressed-atom coherence propagator in double space with coupling to a thermal bath, the singly hatched block representing a "proper" self-energy insertion.

tion in the averaging. Self-energy diagrams for self-broadening, with resonance exchange (in the binary-collision approximation) are shown in Fig. 4. In this fashion the two atoms are treated symmetrically, labeling the one-atom coherence by "1," irrespective of the identity of the atom it belongs to.

The complete spectrum produced by one-atom coherences is represented by Fig. 5, where the crossed blocks signify a radiative vertex modified by collision-induced processes (Fig. 6). The uppermost vertex is labelled $k\mp$, to denote the emission (absorption) of a k-mode photon as the final radiative process. Processes completed within a single collision are represented by the sole (vacuum-contracted) block in Fig. 5, more explicitly shown in Fig. 7. The collisional contributions to the lower-end vertex, and the vacuum-contracted block of Fig. 7, have no resonance-exchange counterpart, as on the "vacuum" side, there is no particle line to be labeled.

An effective interaction of the Bethe-Salpeter-type, introduced in Sec. IV of Paper I, is represented by Fig. 8. On each side it has a pair of protruding double bars representing a two-atom coherence. The two sets of labels at the outgoing bars, representing resonance exchange, should be used when the symmetrized form of the effective interaction is required. Having no truncated vertical bars, this diagram involves no bath average, neither does it carry a particle-number factor. Its role in creating nonvanishing contributions of two-atom coherences to the steady-state spectra is exemplified by Fig. 9. Without the effective interaction providing a lateral link, the evolution of two independently driven atoms would produce the disconnected diagram of Fig. 9. Such diagrams involve products of factors, each independently implying a trace over a complete set of dressed-atom states. However, only one such factor carries the distinctive mark $k\mp$, hence all other traces vanish, leading to the vanishing of the whole diagram. This constitutes the *law of disconnected diagrams* familiar from other diagrammatic methods.[15]

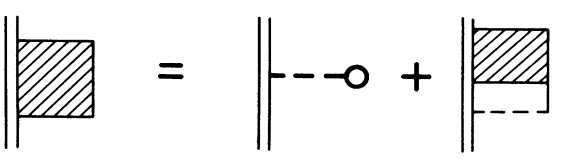

FIG. 3. A self-energy (Σ^1) diagram in the foreign-gas binary collision approximation, with dressed-atom propagators renormalized by radiative coupling. The horizontal dashed line represents a two-atom interaction.

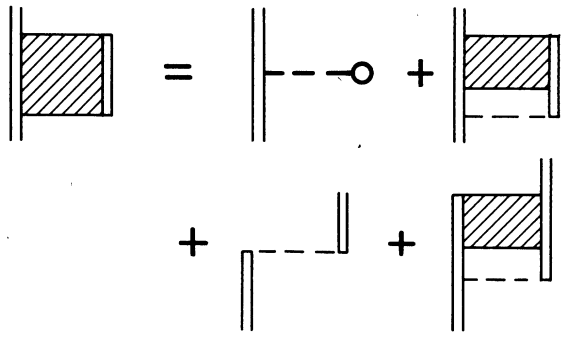

FIG. 4. A symmetrized self-energy diagram in resonance broadening, with resonance-exchange collisions.

V. TWO-ATOM COHERENCE

The effective interaction of the Bethe-Salpeter-type,[1]

$$\Phi^{1,2} = \mathcal{P}^{1,2}(\vec{k})\, \mathcal{T}_R^{1,2}\, \mathcal{P}^{1,2}(\vec{k}), \tag{40}$$

where $\mathcal{P}^{1,2}(\vec{k})$ is the projection onto the subspace of two-atom coherences (in double space), provides a link between two disjoint one-atom coherence propagation diagrams. However, owing to the L^{-3} factor in (40) in box normalization, in the binary-collision approximation, once such a link appears, one of the particle propagators must be truncated (providing the extra factor N_A) without the two coherently driven atoms colliding again. This can be repeated any number of times, with *both* atoms

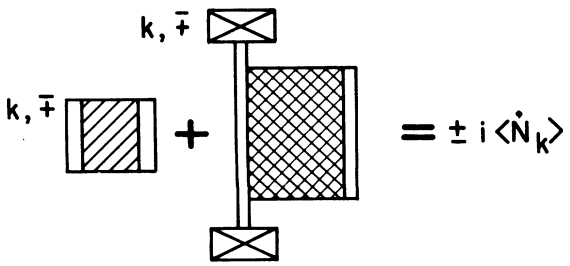

FIG. 5. A k-mode photon emission rate, including a single collision-induced term, and a multiple-collision term with collision-modified end-point vertices.

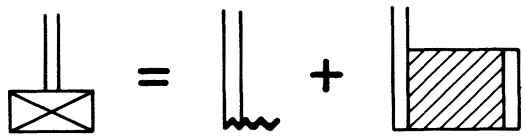

FIG. 6. A collision-modified right-end (initial) vertex, including a bare radiative vertex, and a collision-induced vertex.

in each case retaining memory of their coherent propagation before the collision. As a result, the self-energy diagrams of the one-atom coherence should be replaced by the diagram shown in Fig. 10, in which such memory-retaining effects are incorporated. Similar memory effects extended *after* the collision vanish on taking the trace. In binary-collision self-broadening, Σ^1_S is replaced by

$$\Xi^1(z) = N_A \,\mathrm{tr}_2(\Phi^{1,2}_S(z)\{1 + g^{1,2}_S(z)[\mathcal{V}^{2,R} + \Sigma^2(z)]\}\rho_0^2)\,, \tag{41}$$

where

$$g^{1,2}_S(z) = [z - \mathfrak{L}^1 - \mathfrak{L}^2 - \Sigma^1_S(z) - \Sigma^2_S(z)]^{-1} \tag{42}$$

is the reduced propagator of the two independent dressed atoms. Note that the end-point vertex

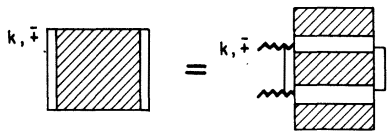

FIG. 7. A single-collision diagram for collision-induced k-mode photon emission rate.

operators $\Sigma^2(z)$ are not symmetrized, as they are projected onto the coherence vacuum.

Two-atom coherences will also affect the final end-point vertex, by adding similar memory-retaining terms as shown in Fig. 11. Therefore

$$\delta\Xi^{1\mp}_k(z) = N_A \,\mathrm{tr}_2(\delta\Phi^{1,2\mp}_{S,k}(z)\{g^{1,2}_S(z)[\mathcal{V}^{2,R} + \Sigma^2(z)] + 1\}\rho_0^2)\,, \tag{43}$$

replaces $\delta\Sigma^{1\mp}_{S,k}$ in the final vertex. Here $\delta\Phi^{1,2\mp}_{S,k}$ is defined the same way $\delta\Sigma^{1\mp}_{S,k}$ was, with $\mathcal{V}^{1,R\mp}_k$ as the last radiative coupling on the left. The arguments behind using the nonsymmetrized self-energy and the symmetrized effective interaction in (43) are the same as those that lead to Eq. (37).

The sole vacuum-averaged collision-induced term has no protuding memory extensions, and is therefore unaffected by higher-order coherences. Hence

$$\langle \dot{N}_k \rangle = \mp\, iN_A \,\mathrm{tr}_1(\{\delta\Sigma^{1\mp}_k(i0) + [\mathcal{V}^{1,R\mp}_k + \delta\Xi^{1\mp}_k(i0)]\, g^1_R(i0)[\mathcal{V}^{1,R} + \Sigma^1(i0)]\}\rho_0^1)\,, \tag{44}$$

with

$$g^1_R(z) = [z - \mathfrak{L}^1 - \Xi^1(z)]^{-1}. \tag{45}$$

Equation (44) is the continuous-wave emission rate, modified by the presence of two-atom coherences, in the binary-collision approximation.

This scheme can be readily adapted to a *mixture* of several distinct gases, all of which participate actively in the radiative process in the spectral region under study, either independently, or by forming radiatively responsive complexes during collisions (radiative collisions[5]). In this case, each dressed-atom propagator should carry a particle-type label, and upper truncation of such a propagator—the appropriate particle number. The self-energy insertions Σ^1 or Ξ^1 form "matrices" in particle-label space; foreign-gas-like

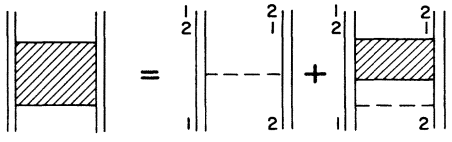

FIG. 8. A Bethe-Salpeter–type binary-collision effective interaction, with two pairs of particle labels representing symmetrization by resonance exchange.

contributions forming diagonal elements, and resonance-exchange terms forming off-diagonal elements. Radiative collisions are represented by the sole vacuum-contracted collision-induced term. Emission rates,

$$\langle \dot{N}_k \rangle_{rc} = \mp\, iN_A N_B \,\mathrm{tr}_{1,2}[\delta\Phi^{1,2\mp}_k(i0)\rho_0^{1,2}]\,, \tag{46}$$

form one aspect of such radiative collisions. Another aspect is formed by the radiation-induced transition rates from two-atom state $\alpha = \alpha_1\alpha_2$ to $\beta = \beta_1\beta_2$,

$$\langle W_{\alpha\to\beta}\rangle_{rc} = -\,iN_A N_B \,\mathrm{tr}_{1,2}[P_\beta\, \delta\Phi^{1,2}(i0)P_\alpha \rho_0^{1,2}] \tag{47}$$

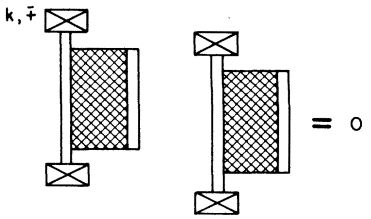

FIG. 9. An identically vanishing disconnected two-atom diagram.

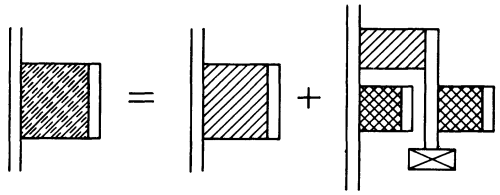

FIG. 10. An effective self-energy insertion (Ξ^1) in the presence of two-atom coherences, in the binary-collision approximation.

(P_α being a projection on the state α, etc.), where $\delta\Phi^{1,2}$ is the modification of the effective interaction by the incident radiation. The partial collision cross sections are obtained by (47) on dividing by $N_A N_B L^{-3}\bar{v}$, where $\bar{v}$ is the mean relative speed of the colliding pair.

VI. MANY-ATOM COHERENCE

The effect of higher-rank coherences ($N > 2$), with N varying indefinitely, can be worked out formally in the binary-collision approximation. Each of the one-atom propagators in Fig. 10 should be modified by coupling to other one-atom coherences, in the same fashion the self-energy itself was modified. The improper (crosshatched) self-energy diagrams in Figs. 10 and 11 should then be modified with Ξ^1 replacing Σ^1. As a result, the explicit expression (41) for Ξ^1 is replaced by the implicit equation

$$\Xi^1_R(z) = N_A \operatorname{tr}_2(\Phi^{1,2}_S(z)\{1 + g^{1,2}_R(z) \times[\mathcal{V}^{2,R} + \Sigma^2(z)]\}\rho_0^2), \quad (48)$$

where

$$g^{1,2}_R(z) = [z - \mathcal{L}^1 - \mathcal{L}^2 - \Xi^1_R(z) - \Xi^2_R(z)]^{-1}. \quad (49)$$

The unmodified vertex in the last term of Fig. 11 should be modified accordingly, replacing Eq. (43) by

$$\delta\Xi^{1\mp}_{R,k}(z) = N_A \operatorname{tr}_2(\delta\Phi^{1,2\mp}_{S,k}(z)\{g^{1,2}_R(z)[\mathcal{V}^{2,R} + \Sigma^2(z)] + 1\}\rho_0^2). \quad (50)$$

This "bootstrap" situation, in which $\Xi^1_R(z)$ depends on itself, may be resolved by a self-consistent iteration procedure (e.g., continued fractions). A truncation after a finite number of iterations is equivalent to a consideration of N-atom

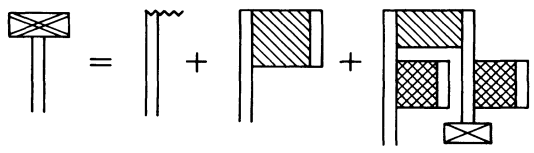

FIG. 11. A left-end (final) vertex modified by the presence of a two-atom coherence.

coherences with a finite value of N. The first step in such iteration processes would most likely be the nonrenormalized version (41), incorporating only rank-two coherences. A solution of these bootstrap equations should provide a general theory of resonance broadening in the binary-collision approximation.

The response of a gas sample in a finite cavity may drastically change, and its spectrum altered, as a result of the onset of optical bistabilities.[19] The preceding discussion suggests, however, that cooperative coherence effects may exist even in the "one-atom" branch, as a result of the combined effect of collisions and coherent radiation.

VII. IMPACT LIMIT

The impact limit in binary-collision broadening[20] is obtained whenever the field modes are tuned sufficiently close to resonance, so that the pertinent eigenvalues of $\mathcal{L}^1$ are sufficiently small:

$$\|\mathcal{L}^1\|\tau_c \ll 1, \quad (51)$$

where $\|\mathcal{L}^1\|$ represents the magnitude of the eigenvalues of $\mathcal{L}^1$, and τ_c is the correlation time of the memory kernel $\tilde{\Sigma}(t)$ which, in binary collisions, is a measure of the duration of a collision ($\sim 10^{-12}$ sec in thermal collisions). In this limit, the self-energy can be approximated by its on-resonance value, where the collision integral $\mathcal{T}^{1,2}_R$ can be expressed in terms of on-the-energy-shell T-matrix (or S-matrix) elements, or asymptotic scattering wave functions.

This approximation (regarding the dependence on the eigenvalues of $\mathcal{L}_1$) should not be confused with the Markovian approximation (regarding the dependence on the real part of the complex variable z in time-resolved phenomena), as some authors fail to observe, although their criteria of validity are similar, given the self-energies vary smoothly as functions of these variables.

Under impact conditions [unless the radiative coupling is so strong that it becomes comparable to the inverse of τ_c (Ref. 18)] one may neglect radiative corrections to the self-energy[3] (substituting $\mathcal{T}^{1,2}$ for $\mathcal{T}^{1,2}_R$) and replace the collision-modified end-point vertices of Fig. 11 by the free dressed-atom radiative vertices. The effect of collisions will be felt only through the repetitive occurrence of the self-energy diagrams in the resolvent $g^1(z)$. Furthermore, if Doppler shifts are negligible, and the collision integrals do not depend too strongly on the velocities, the molecular-chaos approximation will generally hold, and velocity-averaged self-energies can be used. Under these conditions, the molecular-chaos approximation can be applied to the Bethe-Salpeter

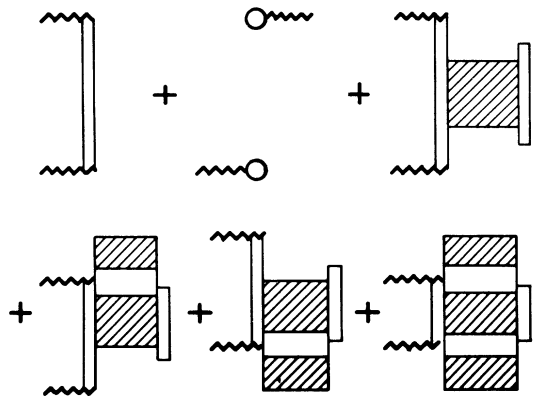

FIG. 12. The single-collision diagrams reckoned in the quasistatic limit, including the identically vanishing disconnected diagram for symmetry's sake. The uppermost radiative coupling is tagged $k\mp$ in all diagrams.

effective interactions, too.

The modified resolvent of Eq. (45) can be split by the Dyson equation

$$g^1_R = g^1_S(z) + g^1_S(z)[\Xi^1(z) - \Sigma^1_S(z)]\, g^1_R(z), \tag{52}$$

into a part representing pure contributions of one-atom coherences, and another part representing the added effects of two-atom coherences. An order-of-magnitude estimate of the corrections involved in the two-atom coherences can be made as follows. In sufficiently weak radiation (in the under-saturation case), where

$$\Omega \lesssim \gamma_C, \tag{53}$$

$\Omega = |2\mu \mathcal{E}^+/\hbar|$ being a magnitude of the radiative coupling (Rabi frequency) and $-i\gamma_C$ a typical coherence-damping ("T_2") element of Σ^1_S (in the velocity-averaged molecular-chaos approximation), the propagator $g^1_S(i0)$ has the approximate magnitude

$$\| g^1_S(i0) \| \approx (\Delta\omega^2 + \Omega^2 + \gamma_C^2)^{-1/2}, \tag{54}$$

where $\Delta\omega$ is a frequency detuning off a bare-atom resonance frequency. As $N_A \Phi^{1,2}$ is of the order of γ_C, we then have

$$\| \Xi^1 - \Sigma^1_S \| \approx \gamma_C \Omega (\Delta\omega^2 + \Omega^2 + \gamma_C^2)^{-1/2}; \tag{55}$$

i.e., the modifications increase with the applied field amplitude and (off-resonance) with the gas density, through γ_C. In stronger radiation (in the over-saturation case), in which

$$\Omega \gg \gamma_C, \tag{56}$$

the self-energy insertions in the extension attached to the modified self-energy diagram Ξ^1 in Fig. 10 can be neglected. This extension is then represented by

$$1 + \mathcal{G}_0(z) \mathcal{V}^{2,R} = 1 + (z - \mathfrak{L}^1_0 - \mathfrak{L}^2_0 - \mathcal{V}^{1,R} - \mathcal{V}^{2,R})^{-1} \mathcal{V}^{2,R}. \tag{57}$$

This double-space analog of a Möller wave operator transforms states of interacting-dressed-atom 1 and noninteracting-dressed-atom 2 into states of the two atoms interacting with the dressing fields (i.e., states modified by the dressing radiation) in double space. In a closed basis in double space, such transformations are unitary, and therefore the magnitude of the elements of Ξ^1 remains bounded by the maximum eigenvalue of Σ^1_S,

$$\| \Xi^1 \| \lesssim \gamma_C(\max). \tag{58}$$

The major novelty introduced upon replacing Σ^1_S by Ξ^1 is the possible appearance of new transitions, that were forbidden in the one-atom case. It is easy to see that in the case of over saturation, the further modification introduced by higher-rank coherences will not alter the magnitude of Ξ^1_R appreciably, but it will allow still further forbidden transitions to occur.

The second part of (52) contains all the information on the structural changes in the spectrum as a result of two-atom coherences, such as the appearance of new resonance peaks. The positions and widths of these peaks in self-attenuation spectra depend mostly on the poles of the two-atom coherence propagator $g^{1,2}_S(z)$ of Eq. (42); namely, on the roots of

$$| \mathfrak{L}^1 + \mathfrak{L}^2 + \Sigma^1_S(i0) + \Sigma^2_S(i0) | = 0 \tag{59}$$

as functions of the frequency ω_{k_i} of the attenuated incident mode, treated as a complex variable. In resonance scattering, these roots are shifted by

$$\Delta\omega_s = \omega_{k_s} - \omega_{k_i} \tag{60}$$

(the detuning of the scattered-mode off the incident-mode frequency). The emission peaks then depend on the eigenvalues of the inverse of $g^{1,2}_S(i0)$; namely, on the roots of the secular equation

$$| \mathfrak{L}^1 + \mathfrak{L}^2 + \Sigma^1_S(i0)\mathcal{I} - \Delta\omega_s \mathcal{I} | = 0 \tag{61}$$

($\mathcal{I}$ being the identity superoperator), with ω_{k_i} fixed and $\Delta\omega_s$ a complex variable. Consider, for example, a nondegenerate two-level atom. In the limit of well-separated resonances, i.e.,

$$\Omega' \gg \gamma_C, \tag{62}$$

where

$$\Omega' = (\Omega^2 + \Delta\omega^2)^{1/2}, \tag{63}$$

the first-order (one-atom) resonances lie around the eigenvalues of $\mathfrak{L}^1$, namely

$$\Delta\omega_s = n\Omega' \quad (n = 0, \pm 1). \tag{64}$$

Second-order (two-atom) additional peaks, pro-

vided they are strong enough to be detected, are expected around

$$\Delta\omega_s = \pm 2\Omega' \tag{65}$$

(the additional eigenvalues of $\mathfrak{L}^1 + \mathfrak{L}^2$), as claimed by several authors.[2,4] From the preceding discussion, we can see that

$$\gamma_C(\Delta\omega^2 + \Omega^2 + \gamma_C^2)^{-1/2} \approx \gamma_C/\Omega' \tag{66}$$

is an upper-bound estimate for the relative magnitude of the additional peaks (compared to the one-atom sidebands), when (62) holds. The relative intensity of the additional peaks should thus *diminish* on increasing the applied field intensity beyond a certain value, pointing to the possibility of reconciling between the conflicting opinions on the existence of these features.[4,21,22]

In many cases, a real (frequency-shift) term δ_C should be added to the imaginary self-energy $(-i\gamma_C)$, such as the dipole-dipole resonance exchange shift discussed in Sec. V of Paper I. In this case γ_C should be replaced by $(\gamma_C^2 + \delta_C^2)^{1/2}$ in our upper-bound estimates.

It is important to note that, provided the scattered-light spectrum is made of well-separated sharp $(\gamma_C \tau_C \ll 1)$ resonance peaks, the impact limit *always* prevails for widths of resonance-scattering peaks, notwithstanding how large Ω' is. The description in terms of complete collisions (on-the-energy-shell scattering amplitudes) should then refer to the dressed-atom states (modified by radiative couplings) as the asymptotic collision states.[23] In this manner, the variation of the linewidth with the incident-radiation frequency can be attributed to changes in the dressed-atom states, rather than to a nonimpact behavior. However, line intensities, as in the one-atom case,[3,24] may still depend on self-energy elements outside the impact region.

VIII. QUASISTATIC LIMIT

The quasistatic limit[25] in weak fields generally refers to line-wing excitations where the exciting radiation is tuned sufficiently off resonance so that

FIG. 13. A truncated double-bar diagram with a protruding collisionless one-atom coherence.

$$\Delta\omega\tau_c \gg 1\,, \tag{67}$$

where τ_c is the duration of a collision. The obvious generalization to strong fields is to replace $\Delta\omega$ by an eigenvalue of $\mathfrak{L}^1 + \mathfrak{L}^2$; e.g., in self-attenuation,

$$n\Omega'\tau_c \gg 1 \quad (n = 1, 2)\,, \tag{68}$$

with Ω' defined by (63). The magnitude of the self-energy, compared to the eigenvalues of $\mathfrak{L}^1$, is then sufficiently small to let us retain it only to lowest order in the rate expressions. This is equivalent to considering only one collision, at most, along the time evolution of the system. It then becomes obvious that many-particle coherence effects, requiring a succession of collisions, are unimportant. The single-collision terms include, nevertheless, cooperative two-atom processes owing to the interaction of the radiation with both atoms.

The dominant term in this limit is the sole $\delta\Sigma_k^{1\mp}$ term. Add to it the relatively insignificant terms that end or begin with collisionless dressed-atom propagators and incorporate, at most, only one collision. Those additional terms vanish in case the transitions are forbidden outside the collision (as in collision-induced absorption, or radiative collisions). All the terms considered here are shown diagrammatically in Fig. 12, with the truncated double-bar diagrams explained in Fig. 13. Adding the identically vanishing disconnected diagram in Fig. 12, we can replace the sign-carrying last radiative coupling by one-half the sum of the two atomic couplings, expressing the emission rate in terms of the more symmetrical form of (36). Combining all these terms under the two-particle trace, the quasistatic limit for self-broadening is then

$$\langle \dot{N}_k \rangle_{qs} = \mp i\,\tfrac{1}{2} N_A^2 \mathrm{tr}_{1,2}\{\mathfrak{M}^{(-)\dagger}(i0)\mathcal{V}_k^{R\mp}(i0 - \mathfrak{L}_0 - \mathcal{V}^R)^{-1}[1 + \mathcal{T}_R^{1,2}(i0)(i0 - \mathfrak{L}_0 - \mathcal{V}^R)^{-1}]\mathcal{V}^R\mathfrak{M}^{(+)}(i0)\rho_0^{1,2}\}\,. \tag{69}$$

Here, following the method of Burnett *et al.*,[3]

$$\mathfrak{M}^{(+)}(z) = 1 + \mathcal{G}_e(z)\mathcal{V}^{1,2}\,, \tag{70}$$

$$\mathfrak{M}^{(-)\dagger}(z) = 1 + \mathcal{V}^{1,2}\mathcal{G}_e(z)\,, \tag{71}$$

are introduced as the superoperator analogs of the Möller wave operators for the binary collision, where

$$\mathcal{G}_e(z) = (z - \mathfrak{L}_0 - \mathcal{V}^{1,2})^{-1} \tag{72}$$

(with $\mathfrak{L}_0 = \mathfrak{L}_0^1 + \mathfrak{L}_0^2$) is the pair propagator in the absence of interaction with the dressing fields. The two Möller superoperators operating on the initial and the final state produce, respectively, the results[3]

$$\mathfrak{M}^{(+)} |\rho_0^{1,2}\rangle\rangle = |\rho_{eq}^{1,2}\rangle\rangle , \tag{73}$$

$$\langle\langle bb|\mathfrak{M}^{(-)\dagger} = \langle\langle b^{(-)} b^{(-)}| , \tag{74}$$

where $\rho_{eq}^{1,2}$ is the equilibrium pair distribution function (unaffected by third-body correlations in the binary-collision approximation), and $|b^{(-)}\rangle$ is a stationary scattering state asymptotically evolving into the free-particle state $|b\rangle$ of the dressed-atom pair.

In the quasistatic limit, at frequency detunings larger than the inverse collision duration, kinetic-energy contributions to the Hamiltonian can ordinarily be neglected under certain conditions (the Landau-Zenner case). The scattering states and equilibrium distribution can then be treated by the Born-Oppenheimer approximation, with the interatomic radius-vector $\vec{r}$ serving as a "good" quantum number. Then

$$\langle \dot{N}_k \rangle = \mp i \tfrac{1}{2} N_A^2 L^{-3} \sum_{\alpha,\beta} \int d\vec{r}\, \langle\langle \beta(\vec{r})\beta(\vec{r}); \hat{0} | \upsilon_k^{R\mp} (i0 - \mathfrak{L}_0 - \upsilon^R)^{-1} [1 + \mathcal{T}_R^{1,2}(i0)(i0 - \mathfrak{L}_0 - \upsilon^R)^{-1}] \upsilon^R | \alpha(\vec{r})\alpha(\vec{r}); \hat{0}\rangle\rangle \rho_\alpha(\vec{r}) , \tag{75}$$

where $|\alpha(\vec{r})\rangle\rangle$ is a Born-Oppenheimer two-atom state (or two-molecule state in a molecule-molecule collision, with $\vec{r}$ connecting the centers of mass).

Equation (75) involves matrix elements between double-space vectors $|aa\rangle\rangle$ (representing projection operators in the ordinary wave-vector space) of the superoperator obeying the Lippmann-Schwinger equation

$$\mathfrak{F}(z) = \upsilon^R + \upsilon^R G_e(z) \mathfrak{F}(z) . \tag{76}$$

This is the superoperator analog of a scattering operator (F) describing radiative scattering by the two-atom system.[26] The linear term υ^R vanishes, as transition rates, expressed in the double-space formalism, require that the coupling to each radiation mode υ_k^R appear an even number of times. Elements of $\mathfrak{F}$ between states $|aa\rangle\rangle$, etc., are related to elements of F by the law[24]

$$-i\langle\langle bb | \mathfrak{F}(i0) | aa\rangle\rangle = 2\pi\hbar^{-2} |\langle b | F(E_a + i0) | a\rangle|^2 \delta(\omega_{ab}) . \tag{77}$$

Hence (75) can be expressed in terms of the ordinary law relating transition rates to the Lippmann-Schwinger scattering matrix. In order to accomplish this goal, it is necessary to introduce an ordinary Hilbert-space analog of the Floquet space vectors $|\hat{n}\rangle\rangle$. This is accomplished, following Shirley[27] and Cohen-Tannoudji and co-workers,[28] by using the dressed-atom representation. To each atomic state $|a\rangle$ is associated in this representation an infinite set of dressed-atom states $|a;n\rangle$ ($n = \{n_k\}$; $n_k = 0, \pm 1, \dots$), a free-radiation Hamiltonian H^R, with

$$H^R |a; n_k\rangle = n_k \omega_k \hbar |a; n_k\rangle , \tag{78}$$

and an interaction $V^{R\mp}$ that raises (lowers) n by unity (but its magnitude is independent of n). It is then possible to associate with each double-space vector, with a given Floquet number $\hat{n}$, the infinite subset

$$|ab;\hat{n}\rangle\rangle \rightarrow \{|a;n\rangle\langle a;n+\hat{n}|\} \quad (n_k = 0, \pm 1, \dots) . \tag{79}$$

This multiplicity should not unduly worry us since $n = 0$ can be chosen for the initial state, and the final-state n value is taken care of by the delta function in (77).

Application of (77) to (75) should take into consideration the requirement that *one* of the two F elements must end up with $V_k^{R\mp}$. Therefore,

$$\langle \dot{N}_k \rangle = \pm \pi \hbar^{-1} N_A^2 L^{-3} \sum_{\alpha\beta} \sum_n \int d\vec{r}\, \rho_\alpha^{1,2}(\vec{r})\, \mathrm{Re} \langle \beta(\vec{r}); n | F_k^{\mp}(E_\alpha(\vec{r}) + i0) | \alpha(\vec{r}); 0\rangle \times \langle \beta(\vec{r}); n | F(E_\alpha(\vec{r}) + i0) | \alpha(\vec{r}); 0\rangle^* \delta(E_\alpha(\vec{r}) - E_\beta(\vec{r}) - n\hbar\omega) . \tag{80}$$

Here

$$F(z) = V^R [1 + G_e(z) F(z)] \tag{81}$$

and

$$F_k^{\mp}(z) = V_k^{R\mp} [1 + G_e(z) F(z)] \tag{82}$$

are radiative-transition Lippman-Schwinger operators, and

$$G_e(z) = (z - H_e)^{-1} \tag{83}$$

is the corresponding resolvent operator, all defined on the dressed-atom representation with

$$H_e = H^1 + H^2 + V^{1,2} + H^R, \quad V^R = V^{1,R} + V^{2,R}. \tag{84}$$

In self-attenuation spectra, $\alpha(\vec{r})$ stands now for a bare collision pair (without interaction with the radiation modes). In resonance scattering we must add to it the scattered mode. Equation (80) can be simplified in the optical limit ($\hbar\omega_s \gg k_B T$, where k_B is Boltzmann's constant and T the gas temperature). We can then choose $|0_s\rangle$ for the initial state and $|1_s\rangle$ for the final. The two states being distinct, the positioning of $V_{k_s}^{R\mp}$ becomes inmaterial. Hence

$$\langle \dot{N}_{k_s} \rangle = \pi\hbar^{-1} N_A^2 L^{-3} \sum_{\alpha\beta} \sum_n \int d\vec{r}\, \rho_\alpha^{1,2}(\vec{r}) |\langle \beta(\vec{r}); 1_s; n | F(E_\alpha(\vec{r}) + i0) | \alpha(\vec{r}); 0_s; 0 \rangle|^2 \times \delta(E_\alpha(\vec{r}) - E_\beta(\vec{r}) - \hbar\omega_s - \hbar n\omega), \tag{85}$$

with H^R and V^R now incorporating the scattered mode, and F incorporating $V_{k_s}^{R-}$ once only. Introducing the eigenstates of the dressed-atom pair *with* radiative coupling to the applied field,

$$|\alpha^R(\vec{r}); n\rangle = (1 + G_e F_{-s}) |\alpha(\vec{r}); n\rangle \tag{86}$$

(where F_{-s} is defined without the scattered-mode coupling), and their energy eigenvalues $E_\alpha^R(\vec{r}) + n\hbar\omega$, we get

$$\langle \dot{N}_{k_s} \rangle = \pi\hbar^{-1} N_A^2 L^{-3} \sum_{\alpha\beta} \sum_n \int d\vec{r}\, \rho_{\alpha,R}^{1,2}(\vec{r}) |\langle \beta^R(\vec{r}); 1_s; n | V_{k_s}^{R-} | \alpha^R(\vec{r}); 0_s; 0 \rangle|^2 \times \delta(E_\alpha^R(\vec{r}) - E_\beta^R(\vec{r}) - \hbar\omega_s - n\hbar\omega). \tag{87}$$

where $\rho_{\alpha,R}^{1,2}$ is the interacting-dressed-atom pair equilibrium distribution, by using a procedure similar to the one yielding Eqs. (73) and (74). The kinetic motion effectively "smears" the delta function in (87). This effect is, however, negligible at frequencies where the bulk of the contribution of the spatial integral in (87) comes from.

Defining a one-atom radiative-transition operator

$$F^{(j)} = V^{j,R} + V^{j,R} G_e F^{(j)} \quad (j = 1, 2), \tag{88}$$

we can extract from (80) a pure atom-j contribution by inserting into (80) $F^{(j)}$ instead of F (and multiplying by two in case of identical atoms). The remaining mixed terms in the equation

$$F = F^{(1)} + F^{(2)} + F^{(2)} G_e V^{1,R} (1 + G_e F), \tag{89}$$

and the cross products in FF^*, express the cooperative effects of the combined two-atom process. Obviously, in weak fields, where perturbation expansions hold, these cooperative effects involve higher-order perturbation terms.

Generalization to the case of two *distinct* atoms is straightforward. Here $\mathcal{V}^{1,R}$ and $\mathcal{V}^{2,R}$ imply distinct matrix elements and, as either atom can contribute to the last sign-carrying interaction,

$$\tfrac{1}{2} N_A^2 \to N_A N_B \tag{90}$$

should be substituted in the preceding analysis.

Qualitative analysis of resonances in the quasistatic limit (both in similar-atom and different-atom collisions) is rather complicated, depending generally on the shape of the interatomic potentials used. The quasistatic limit is explicitly (or implicitly) used in most theories dealing with the combined interaction of two atoms with a strong coherent radiation, in the vastly expanding bibliography on radiative collisions,[6, 29, 30] to which (80) or (87), with (90) in different-atom pairs, may serve as the connecting link. Little, however, is known on the line shapes of of such gas systems in the impact limit, under cooperative excitation conditions, for the analysis of which the previous sections may prove useful.

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