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# Theory of two-atom coherence in gases. I. Master equations

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The response of a collision-broadened gas sample to driving coherent radiation is studied theoretically, taking into account effects of coherent excitations of two or more atoms (or molecules). In analogy to the Bloch-type master equation for one-atom coherences, describing the motion of a single atom "dressed" by the relevant (incident and detected) field modes, a master equation is derived for two-atom coherences, including an effective interaction of the Bethe-Salpeter–type, accounting for the mutual interaction of the coherently driven pair. The master equation includes also all symmetrization effects owing to resonance exchange between identical atoms, and is limited to nonreactive gas atoms (or molecules) undergoing binary collisions, including otherwise all (internal and translational) relaxation effects. The self-energy kernels are expressed in a nonperturbative fashion, in terms of binary-collision scattering amplitudes, and include renormalization effects due to coincidence of radiative couplings with the collisions (optical and radiative collisions). The concept of two-atom coherences is generalized to higher coherence ranks by constructing a hierarchy of master equations, including vertex operators that upgrade or downgrade the coherence rank, as a prelude to a diagrammatic method for calculating continuous-wave spectra. This hierarchy is compared with prevalent Agarwal-type master equations, based on the Dicke pseudospin method, and used in the study of two-level atoms.

## I. INTRODUCTION

Resonance fluorescence from a group of coherently driven atoms has become the subject of considerable theoretical interest in the last few years. Though this problem was originally suggested in order to provide a proof of the quantum nature of light,[1] attention was turned later on to the spectral features of collective fluorescence. A debate is going on as to whether, in addition to the two sidebands in Rayleigh scattering predicted by Mollow[2] (and verified by experiments[3]), an additional pair of overtone sidebands should appear[4,5] or not.[6-8] Similar arguments apply to the problem of weak-probe absorption.[9] The debate is not settled yet, and even if extra sidebands will eventually be discovered, other possible sources for their appearance (such as dynamic Stark effects beyond the rotating-wave approximation) should not be ruled out. However, certain questions have been raised with regard to the present treatments of collective coherence phenomena. The common attitude is to use a Hamiltonian,[10] or derive a master equation,[6,11] that depend on the collective (resultant) pseudospin operators, based on Dicke's[12] pseudospin method of treating the two-level-atom model. Such Hamiltonians have the property of conserving the resultant total pseudospin quantum number $J$ (i.e., the corresponding collective Bloch vector's motion is confined to a sphere in pseudospace[13]). In Agarwal's[11] master equation, even radiative decay and transfer processes appear as coherent ($J$-conserving) processes.

Recently, two major objections have been raised to this approach. Walls[14] has pointed out the importance of relaxation processes in which the individual atoms decay incoherently, thus breaking $J$ conservation. Mavroyannis[15] and Freedhoff[16] have studied certain effects of electrostatic interactions between the participating atoms (collision broadening and shifting) which may lead to the splitting and shifting of resonance peaks. Though their treatments of collision effects are far from being complete (collisions are treated only in the quasistatic limit, with a fixed intermolecular separation, without averaging over a distribution of separations, and taking into account only first-order dipole-dipole[15] and dispersion[16] interactions), they nevertheless claim that collisions produce significant effects. In particular, first-order dipole-dipole interactions cannot be discarded even at molecular-beam densities as their range extends over distances comparable to the wavelength of the radiation. Collisions, providing a "thermal bath," will generally affect the rank of coherence of the atomic system.

A third objection can be raised regarding the inherent reflection symmetry in the two-level model between the "least-coherent" ground state and the "most-coherent" state in which all atoms in the sample are excited. Although this is strictly legitimate in a two-level model, the moment any internal or translational dynamical processes enter the picture this symmetry must collapse. There is hardly any similarity between a chaotic equilibrium state of a true atomic (or molecular) gas system and a state of maximum coherent excitation.

We therefore set out to look for another approach that stresses the intrinsic asymmetry between equilibrium (as a coherence "vacuum") and coherent excitations. The basic idea is to replace the Bloch equations for the coherent propagation of individual atoms, by a hierarchy of equations for $N=1,2,\ldots,$ atoms collectively driven (using the concept of vertex operators to form couplings between the various equations in the hierarchy). In doing so, we treat collision effects to all powers of the interactions, by using a scattering-matrix approach to the self-energies, restricting, however, the discussion to the binary-collision approximation (neglecting recollisions of the same pair after third-body collisions). The driving fields, supposed to consist of a discrete set of coherent modes, are considered to arbitrary power, both in the secular part of the equations (dynamic Stark effects[2,17,18]) and in the self-energy (incorporating such effects as optical and radiative collisions[19]). Finally, we make use of the method proposed recently by Burnett *et al.*[20,21] for dealing with the initial (statistical) correlations in an interacting (real) gas, allowing the use of the uncorrelated (ideal-gas) equilibrium distribution in the projection operators of the hierarchy.

A major feature of the equations for $N$-atom coherence (with $N>1$) is the inclusion, in addition to the secular and self-energy parts of the ordinary ($N=1$) Bloch equation, of an effective interaction of the Bethe-Salpeter-type, correlating the motion of the participating atoms.

The hierarchy of coherences allows us (even in macroscopic samples where the total number of atoms is extremely large) to restrict the discussion to any finite number of coherently excited atoms by approximately truncating the hierarchy. In particular, effects of two-atom coherence can be discussed by considering only $N=0$, 1, and 2. We can therefore apply the thermodynamic limit to the sample volume, and use the methods of thermodynamics of irreversible phenomena in deriving the master equations. In particular, we follow here the methods of Zwanzig[22] and Fano,[23] with the realization that the reduction of the equations by projection operators should be carried out on the "dressed" atoms (including the relevant radiation modes, i.e., the incident modes and the scattered mode in resonance scattering).[24,25] In the form presented here, this formalism considers the state of thermal equilibrium as the asymptotic condition of the gas (as the applied radiation is switched off); however, with due modifications it can be adjusted to other asymptotic conditions (e.g., molecular beams). Although our discussion is generally focused upon short-range binary-collision phenomena, it can be extended to include radiative damping and long-range radiative-transfer phenomena (as argued briefly in Sec. V).

The reader is led from a reconstruction of the one-atom Bloch equation, using projection-operator methods, in Sec. II, through modifications for atom indistinguishability in self-broadening in Sec. III, to two-atom coherences in Sec. IV, and, finally, to the hierarchy of equations in Sec. VI. This hierarchy is compared with pseudospin master equations in Sec. VII.

This hierarchy is used in a subsequent article[26] (Paper II), with the help of a diagrammatic technique, to construct the steady-state (continuous-wave) spectrum of any of the relevant field modes, be it the exciting (pump) mode, a weak probe, or a resonance fluorescence (or Raman) mode. This theory is generally applicable to any number of resonance transitions and relaxation channels, restricted only by the requirement that the participating molecules be inert (i.e., neglecting chemical reactions or ionization phenomena). Wherever the word "atom" appears it can be equally well replaced by the word "molecule." The problem of resonance fluorescence from a "two-level atom" will be dealt with as a special case in a third article of this series.

## II. ONE-ATOM COHERENCE–FOREIGN-GAS BROADENING

One-atom coherence generally refers to a state of an atomic (molecular) gas system driven by a coherent radiation, in which we can single out individual atoms as being independently affected by the radiation. All other atoms, at the time they interact with a coherently excited atom, are initially in an equilibrium state, acting as a thermal bath, with a resulting damping (or relaxation) of the coherent excitation (the *foreign-gas broadening* problem). This notion of one-atom coherence (which will later be given a more quantitative definition), can be extended by proper symmetrization[27] to a gas of identical molecules, provided no collisions occur between two coherently excited atoms, however, taking into account the possibility of transferring the excitation from one atom to the other (*resonance-exchange broadening*).

The time evolution of one-atom coherences is traditionally described by a Bloch-type generalized master equation,[28] having the form

$$i\frac{\partial}{\partial t}\rho^1(t)=\mathcal{L}^1\rho^1(t)+\int_{-\infty}^{t}\tilde{\Sigma}^1(t-t')\rho^1(t')dt' . \qquad (1)$$

Here $\rho^1(t)$ is a reduced density matrix for the relevant degrees of freedom (the atom plus relevant field modes), $\mathcal{L}^1$ is the linear superoperator describing the secular part of its motion (including interaction with the relevant field modes), and $\tilde{\Sigma}^1(t)$

is a self-energy (or memory) kernel, representing the mean effect of coupling to the rest of the system (the thermal bath). The Markovian approximation is obtained upon assuming an infinitesimally short memory time, replacing the memory kernel by

$$\tilde{\Sigma}^1(t) \approx \Sigma^1(i0)\delta(t+\tau) \quad (\tau \to 0+), \tag{2}$$

where $\Sigma^1(z)$ [or $\Sigma^1(is)$] is the one-sided Fourier transform (Laplace transform) of $\tilde{\Sigma}^1(t)$, taken here in the limit $z \to i0$ $(s \to 0+)$. Thus

$$i\frac{\partial}{\partial t}\rho^1(t) \approx [\mathcal{L}^1 + \Sigma^1(i0)]\rho(t), \tag{3}$$

where the real and the imaginary parts of $\Sigma^1(i0)$ serve as shifting and damping (relaxation) superoperators, respectively.

It is essential to specify more explicitly the "relevant" degrees of freedom on which $\rho^1$ is defined, as a preliminary to the discussion of higher-rank coherences. These consist of all one-atom degrees of freedom (internal and translational), all applied-field modes, and the scattered mode ideally singled out by the detector in resonance scattering. In other words, (1) is an equation of motion for the dressed atom.[24]

The superoperators $\mathcal{L}^1$ and $\Sigma^1$ can be represented in matrix form by providing a Hilbert-space basis on which $\rho^1$ can be expanded. This is best done with the help of the double-space (or Liouville-space) representation.[23,29] In this representation, ordinary (dyadic) operators are expanded in a Hilbert-space basis,

$$X \longleftrightarrow |X\rangle\rangle = \sum_{ab} X_{ab}|ab\rangle\rangle, \tag{4}$$

where $|ab\rangle\rangle$ is the double-space vector (in Baranger's[30] notation) representing the operator $|a\rangle\langle b|$. The metric of this space is defined by

$$\langle\langle X|Y\rangle\rangle = \mathrm{tr}\,\{X^\dagger Y\}. \tag{5}$$

Each of the two labels, $a$, $b$, represents a complete set of quantum numbers for the relevant degrees of freedom (the dressed atom). A slightly modified notation can be used in the case of excitation by coherent radiation modes, represented by Glauber coherence states. It can be shown that having such states as initial states of the applied beam is exactly equivalent to perturbing the molecules by a classical time-dependent coherent field[31,32] (also see Appendix A). The time dependence can then be removed with the help of the Floquet method.[33] Instead of using the ordinary double-space expansion,

$$|\rho^1\rangle\rangle = \sum_{ab}\rho^1_{ab}|ab\rangle\rangle, \tag{6}$$

we can use an extended basis,

$$|\rho^1\rangle\rangle = \sum_{\hat{n}=-\infty}^{\infty}\sum_{ab}\rho^{1(\hat{n})}_{ab}|ab;\hat{n}\rangle\rangle, \tag{7}$$

where the Floquet number $\hat{n}$ denotes the $\hat{n}$th harmonic response $[\sim \exp(i\hat{n}\omega_k t)]$ to the applied-field frequency $\omega_k$, and $a$, $b$, refer now to the remaining (quantized) degrees of freedom (not including the classicallike applied field). We can then write

$$\mathcal{L}^1 = \mathcal{H}^1 + \mathcal{V}^{1,R} + \mathcal{L}^R, \tag{8}$$

where $\mathcal{H}^1$ is the Liouvillian superoperator for the quantized part of the system, $\mathcal{L}^R$ is a diagonal supermatrix of frequency harmonics,

$$\mathcal{L}^R|\hat{n}\rangle\rangle = -\hat{n}\omega_k|\hat{n}\rangle\rangle \quad (\hat{n} = 0, \pm 1, \ldots), \tag{9}$$

and $\mathcal{V}^{1,R}$ is the (now time-independent) interaction with the applied field, acting as a raising or lowering operator on the Floquet numbers. We should recall that Liouvillian quantum superoperators ($\mathcal{H}$), generating the motion of dynamic variables, are related to Hamiltonian operators ($H$) by[23]

$$\hbar\mathcal{H}X = (HX - XH^\dagger) \equiv (HI^* - IH^*)X, \tag{10}$$

($I$ being the identity operator) where we have used the shorthand notation[29]

$$\langle\langle ab|AB^*|cd\rangle\rangle \equiv A_{ac}B^*_{bd}. \tag{11}$$

The self-energy superoperator $\Sigma(z)$ depends on the interaction of the reduced system with all remaining (atomic and radiative) degrees of freedom, and can be derived by the help of Zwanzig's projection-operator method. Let

$$\rho_0 = \rho^1_0\rho^B_0 \tag{12}$$

be the separable (ideal-gas) equilibrium density matrix for the entire system in the limit where correlations between constituents are neglected ($B$ here denoting the bath degrees of freedom. The Zwanzig projection operator is defined by

$$\mathcal{P} \equiv |\rho^B_0\rangle\rangle\langle\langle I^B|, \tag{13}$$

where $I^B$ is the identity operator in bath degrees of freedom. Application of $\mathcal{P}$ to the density matrix of the entire system, forms a bath-averaged density matrix for 1, multiplied by $\rho^B_0$:

$$\mathcal{P}\rho(t) = \rho^B_0\,\mathrm{tr}_B[\rho(t)]. \tag{14}$$

In Liouville-space terminology, (13) projects on a product space consisting of the complete space of the reduced system 1, and the one-dimensional subspace of $B$ specified by $\rho^B_0$.

Let $\mathcal{L}^B_0$ and $\mathcal{V}^{1,B}$ be the Liouvillian superoperators for the free bath and its interaction with 1, respectively. In the foreign-gas problem we treat only atom 1 as interacting with the relevant radiation modes. Then, according to Zwanzig's method,[22]

$$\Sigma^1(z)=\mathrm{tr}_B\{\mathcal{P}[\mathcal{V}^{1,B} + \mathcal{V}^{1,B}\mathcal{Q}(z-\mathcal{Q}\mathcal{L}\mathcal{Q})^{-1}\mathcal{Q}\mathcal{V}^{1,B}]\mathcal{P}\}, \tag{15}$$

where

$$\mathcal{L}=\mathcal{L}^1+\mathcal{L}_0^B+\mathcal{V}^{1,B}=\mathcal{L}_0^1+\mathcal{V}^{1,R}+\mathcal{L}_0^B+\mathcal{V}^{1,B}, \tag{16}$$

with $\mathcal{V}^{1,R}$ being the interaction with the relevant modes, and

$$\mathcal{Q}=1-\mathcal{P}. \tag{17}$$

In the case of perturbations by binary collisions (as in not-too-dense gases), $\Sigma(z)$ can be approximated by[23]

$$\Sigma(z)=N_B\,\mathrm{tr}_2\{\mathcal{P}\mathcal{V}^{1,2}[1+(z-\mathcal{L})^{-1}\mathcal{V}^{1,2}]\mathcal{P}\}, \tag{18}$$

where $N_B$ is the number of perturber atoms, and with $\mathcal{V}^{1,2}$, $\mathcal{L}$, and the trace referring now to a one-perturber "bath." The omission of the intermediate $\mathcal{Q}$ projections from (15) is explained later on. The pair Liouvillian superoperator in (18),

$$\mathcal{L}=\mathcal{L}_0^1+\mathcal{L}_0^2+\mathcal{V}^{1,2}+\mathcal{V}^{1,R}\equiv\mathcal{L}_0+\mathcal{V}^{1,2}+\mathcal{V}^{1,R}, \tag{19}$$

includes the radiative couplings $\mathcal{V}^{1,R}$, i.e., it incorporates radiative transitions coincident with the collision. We can, however, reexpress the resolvent in (18) in terms of the undriven resolvent (at $\mathcal{V}^{1,R}=0$); i.e.,

$$\Sigma^1(z)=N_B\,\mathrm{tr}_2[\mathcal{T}_R^{1,2}(z)\rho_0^2], \tag{20}$$

where

$$\mathcal{T}_R^{1,2}(z)=\mathcal{T}^{1,2}(z) +\mathcal{T}^{1,2}(z)(z-\mathcal{L}_0)^{-1}\mathcal{V}^{1,R}(z-\mathcal{L}_0)^{-1}\mathcal{T}_R^{1,2}(z) \tag{21}$$

and

$$\mathcal{T}^{1,2}(z)=\mathcal{V}^{1,2}[1+(z-\mathcal{L}_0-\mathcal{V}^{1,2})^{-1}\mathcal{V}^{1,2}]. \tag{22}$$

Expression (22) is Fano's tetradic (Liouville-space) analog of the Lippmann-Schwinger binary-collision scattering ($T$) matrix.[23] It can be explicitly expressed in terms of the ordinary (dyadic) $T$ matrix,[23,29] and generalized to the dressed-atom case.[33] Expression (21) represents a *renormalized* tetradic scattering matrix,[34] describing the collision of a dressed atom (with radiative couplings) with a perturber atom. The more familiar linear-response approximation[22,23] is obtained by replacing

$$\mathcal{T}_R^{1,2}(z)\approx\mathcal{T}^{1,2}(z) \tag{23}$$

in the binary-collision self-energies.

Expression (20) is proportional to the number of perturbers ($N_B$), but $\mathcal{V}^{1,2}$ (and hence $\mathcal{T}_R^{1,2}$) introduces an extra inverse-volume factor ($L^{-3}$), if we use box normalization (in a cube of length $L$), in order to introduce a denumerable basis. The box normalization procedure can also serve to explain why the intermediate $\mathcal{Q}$ operators inserted in (15) were omitted in the binary-collision approximation. Momentum states for the translation degrees of freedom form with box normalization a denumerable manifold of Hilbert-space vectors $|\vec{p}\rangle$ whose density is proportional to $L^3$. The corresponding manifold of Liouville-space vectors $|\vec{p}\vec{q}\rangle\rangle$ has therefore a density, or measure, proportional to $L^6$:

$$m(\{|\vec{p}\vec{q}\rangle\rangle\})=O(L^6). \tag{24}$$

Application of $\mathcal{V}^{1,2}$ to this basis set spreads it further out onto a two-particle manifold which (owing to translational invariance, or momentum conservation) has a measure $O(L^9)$. Therefore, discarding the $\mathcal{P}$ in $\mathcal{Q}=1-\mathcal{P}$ at all intermediate steps in the expansion of (15) in a power series will have a negligible effect [to $O(L^{-3})$].

This measure-spreading effect of the pair interaction becomes even more marked if we note that the projection onto the $O(L^6)$ manifold created by Zwanzig's projection operator is still too big for our purpose of describing coherent excitation. Regard, for example, the ideal-gas separable equilibrium distribution (12) as an intial state. $\rho_0^1$ represents a one-dimensional "vacuum" ket in double space,

$$|\rho_0^1\rangle\rangle=\sum_{\alpha}\sum_{\vec{p}}f_\alpha(\vec{p})\,|\alpha\alpha;\vec{p}\vec{p};\hat{0}\rangle\rangle, \tag{25}$$

with the Boltzmann-Maxwell distribution $f_\alpha(\vec{p})$ providing the expansion coefficients ($\alpha$ denoting the discrete quantum numbers of the dressed atom, besides the Floquet numbers). Its corresponding bra vector is the one-atom identity operator

$$\langle\langle I^1|=\sum_{\beta}\sum_{\vec{q}}\langle\langle\beta\beta;\vec{q}\vec{q};\hat{0}\,|. \tag{26}$$

Consider now the interaction of a classicallike field mode $j$ on such a state. In the electric-dipole approximation we have

$$\begin{aligned}\mathcal{V}_j^{1,R}X&=-\hbar^{-1}\sum_{\pm}[\mathcal{C}_j^{\pm}\mathcal{E}_j^{\pm}(\vec{\mu}\cdot\vec{\epsilon}_j)\exp(\pm i\vec{k}_j\cdot\vec{r}^1)X - \mathcal{C}_j^{\mp}X\mathcal{E}_j^{\mp}(\vec{\mu}\cdot\vec{\epsilon}_j)\exp(\mp i\vec{k}_j\cdot\vec{r}^1)]\\ &\equiv\sum_{\pm}\mathcal{V}^{1,R\pm}X,\end{aligned} \tag{27}$$

where $X$ is an arbitrary (dyadic) dressed-atom operator. Here $\vec{\mu}^1$ and $\vec{r}^1$ are the dipole moment, and center-of-mass position of atom 1; $\vec{\epsilon}_j$, $\vec{k}_j$, and $\mathcal{E}_j$ are the polarization, wave vector, and complex amplitude of the $j$ mode $(\mathcal{E}_j^- = \mathcal{E}_j^{+*})$; $\mathfrak{C}^\pm$ is a raising (lowering) operator in Floquet space:

$$\mathfrak{C}_j^\pm |\hat{n}_j\rangle\rangle = |\hat{n}_j \pm 1\rangle\rangle . \tag{28}$$

The plus (minus) part of (27) traces its origin to the photon-annihilating (creating) part of a second-quantized field interaction.

Thanks to the momentum-conserving spatial phase factors in (27), successive applications of $\mathfrak{V}^{1,R}$ to (25) can only produce double-space vectors of the type

$$|\alpha\beta; \vec{p} + \hat{n}\vec{k}, \vec{p}; \hat{n}\rangle\rangle \quad (\hat{n} = \{\hat{n}_j\};\ \hat{n}_j = 0, \pm 1, \ldots), \tag{29}$$

where

$$\hat{n}\vec{k} = \sum_j \hat{n}_j \vec{k}_j , \tag{30}$$

summing over all applied field modes. This is easily generalized to the case of resonance scattering, where the scattered ($s$) mode is included in the dressed atom, by letting

$$\hat{n}\vec{k} = \sum_j \hat{n}_j \vec{k}_j + (n_\beta - n_\alpha)\vec{k}_s , \tag{31}$$

where

$$(n_\beta - n_\alpha) \equiv \hat{n}_s \quad (\hat{n}_s = 0, \pm 1) \tag{32}$$

serves as a Floquet number for the scattered mode ($n_\alpha$ being the $s$-mode photon occupation number in state $\alpha$, etc.).

The manifold of vectors represented by (29) is only a *subset* of (24), because of the $\vec{k}$-dependent constraints on the momenta. One can assign to this manifold of one-atom coherences a projection operator $\mathcal{P}^1(\vec{k})$. Its measure is

$$m(\{\mathcal{P}^1(\vec{k})\}) = O(L^3) . \tag{33}$$

The meaning of distributions confined to this subspace is made more transparent by transforming to the Wigner representation.[35] Let

$$\rho_W^1(\vec{x}, \vec{p}) = \sum_{\vec{q}} e^{-i\vec{q}\cdot\vec{x}} \langle \vec{p} + \vec{q} | \rho^1 | \vec{p} \rangle \tag{34}$$

define the Wigner representation for the one-atom density matrix. An appropriate basis in Liouville space is defined by

$$|\vec{x}\vec{p}\rangle\rangle = \sum_{\vec{q}} e^{i\vec{q}\cdot\vec{x}} |\vec{p} + \vec{q}, \vec{p}\rangle\rangle , \tag{35}$$

so that

$$|\rho^1\rangle\rangle = \int \frac{d\vec{x}}{L^3} \sum_{\vec{p}} \rho_W^1(\vec{x}, \vec{p}) |\vec{x}, \vec{p}\rangle\rangle . \tag{36}$$

Distributions belonging to the manifold of one-atom coherences attain in this representation the form

$$\rho_W^1(\vec{x}, \vec{p}) = \rho_W^{1(\hat{n})}(\vec{p}) e^{-i\hat{n}\vec{k}\cdot\vec{x}} , \tag{37}$$

with a coherent spatial phase factor.

The self-energy superoperator $\Sigma^1$, also, is projected onto this subspace of one-atom coherences. In its field-renormalized form (20), it is generally not diagonal in the Floquet $\hat{n}$ numbers. However, in the more familiar linear-response approximation, assuming the perturbing-gas distribution is translationally invariant, $\Sigma^1$ is diagonal in $\hat{n}$ as a label specifying an irreducible representation of the translational group. Similar arguments apply to rotational invariance. Bases for the irreducible representations of the rotation group are formed by applying a vector-subtraction scheme to the contragradient states forming the double-space vector.[36] Whereas the linear-response self-energy is invariant under rotations, the field-renormalized form is not.

A frequently encountered approximation is one in which translational effects are neglected. Although this approximation cannot apply to Doppler-limited saturation spectra,[37] it may be quite broadely applicable to homogeneously broadened spectra. This approximation requires either that the absorbing molecule be much heavier than the perturbers (the resting molecule, or Brownian particle, approximation), or that collisions completely randomize the velocity distribution. We shall therefore refer to it here as *the molecular-chaos approximation.* In this approximation, we may further reduce the density matrix by taking the trace over the translational states, noting that in this approximation the momentum dependence in (37) always remains the Maxwellian equilibrium distribution. The resulting Bloch equations refer now only to internal (discrete) degrees of freedom, with $\Sigma^1$ replaced by the velocity-averaged

$$\langle\langle \alpha\beta; \hat{n}' | \langle \Sigma^1 \rangle | \gamma\delta, \hat{n} \rangle\rangle = \sum_{\vec{p}, \vec{q}} \langle\langle \alpha\beta; \vec{p} + \hat{n}'\vec{k}, \vec{p}; \hat{n}' | \Sigma^1 | \gamma\delta; \vec{q} + \hat{n}\vec{k}, \vec{q}; \hat{n} \rangle\rangle f(\vec{q}) , \tag{38}$$

where

$$f(\vec{q}) = \sum_\alpha f_\alpha(\vec{q}) \tag{39}$$

is the (box-normalized) Maxwellian momentum distribution. Obviously, this approximation is inadequate when velocity or position-dependent coherence effects are studied explicitly. In these cases it may be most advantageous to use the Wigner representation.

## III. ONE-ATOM COHERENCE–SELF-BROADENING

The dressed-atom master equation, in which the driven atom has been so far singled out as distinct from all other atoms with which it collides (the *foreign-gas* problem), can be readily extended to self-broadening, taking into account resonance exchange between identical atoms, as long as no two coherently excited atoms collide. All that is required then is to augment the foreign-gas-like self-energy by a resonance-exchange term[2,7]; i.e.,

$$\Sigma_S^1 = \Sigma_{fg}^1 + \Sigma_{ex}^1 . \tag{40}$$

Having now $N_B \equiv N_A$ (the number of driven atoms),

$$\langle\langle ab;\hat{n}' \,|\, \Sigma_{fg}^1(z) \,|\, cd;\hat{n}\rangle\rangle = N_A \sum_{ee'} \langle\langle ae', be';\hat{n}' \,|\, \mathcal{T}_R^{1,2}(z) \,|\, ce, de;\hat{n}\rangle\rangle f_e \tag{41}$$

[where $f_e = f_\epsilon(\vec{p})$ is the ideal-gas distribution of perturbers] is the foreign-gas-like contribution. Similarly,

$$\langle\langle ab;\hat{n}' \,|\, \Sigma_{ex}^1(z) \,|\, cd;\hat{n}\rangle\rangle = N_A \sum_{ee'} \langle\langle e'a, e'b;\hat{n}' \,|\, \mathcal{T}_R^{1,2}(z) \,|\, ce, de;\hat{n}\rangle\rangle f_e \tag{42}$$

is the resonance-exchange contribution, with the roles of perturber and emitter exchanged in the final state. Furthermore, even though only one of the atoms is assumed to be coherently driven, before or after the collision, there is no point in distinguishing betweem them during the collision. Therefore, in the renormalization scheme (21), the replacement

$$\mathcal{V}^{1,R} \rightarrow \mathcal{V}^{1,R} + \mathcal{V}^{2,R} , \tag{43}$$

should be made in self-broadening.

This situation is radically changed when two coherently excited atoms collide, both particle propagating coherently with well-defined relative phases determined by the driving fields. Such collisions provide a correlating mechanism for the motion of the two otherwise independent atomic coherences.

## IV. TWO-ATOM COHERENCE

Consider the manifold of dressed-two-atom (two atoms plus relevant field modes) states in double space,

$$|\,\alpha_1\alpha_2, \beta_1\beta_2; \vec{p}_1 + \hat{n}_1\vec{k}, \vec{p}_2 + \hat{n}_2\vec{k}, \vec{p}_1, \vec{p}_2; \hat{n}\rangle\rangle \quad (\hat{n} = \hat{n}_1 + \hat{n}_2) , \tag{44}$$

where the subscripts 1, 2, refer to the two coherently excited atoms (or molecules), treated as two *distinct* particles. These vectors form a basis for the two-atom coherences, which attain the form

$$\rho_{\alpha_1\alpha_2,\beta_1\beta_2}^{1,2(\hat{n}_1,\hat{n}_2)}(\vec{p}_1, \vec{p}_2) \exp[-i(\hat{n}_1\vec{k}\cdot\vec{x}_1 + \hat{n}_2\vec{k}\cdot\vec{x}_2)] , \tag{45}$$

in the Wigner representation. Define a projection operator $\mathcal{P}^{1,2}(\vec{k})$ projecting onto this subspace of dressed-two-atom states. The measure of this subspace in box normalization is

$$m(\{\mathcal{P}^{1,2}(\vec{k})\}) = O(L^6) . \tag{46}$$

In deriving the appropriate self-energy for the two-atom coherences we first apply a Zwanzig projection operator (13), with $\rho_0^B$ now referring to the remaining atoms (plus all nonrelevant radiation modes), and then further reduce to the subspace of coherences by $\mathcal{P}^{1,2}(\vec{k})$. In the course of this reduction we end up with two distinct types of contributions (in the binary-collision approximation): One in which $\mathcal{V}^{1,B}$, in the two end-point interactions $\mathcal{Q}\mathcal{V}\mathcal{P}$ and $\mathcal{P}\mathcal{V}\mathcal{Q}$ in (15), is the interaction with the "true" bath (all remaining atoms, less two, in collision broadening), and another in which $\mathcal{V}^{1,B}$ is replaced by $\mathcal{V}^{1,2}$, the interaction between the two participating atoms. The first contribution gives the sum of one-atom self-energies

$$\Sigma^{1,2} = \Sigma^1 + \Sigma^2 , \tag{47}$$

in which $\Sigma^1$ is diagonal in (and independent of) all quantum numbers of particle 2 (including $\hat{n}_2$), etc., and is proportional (in binary-collision broadening) to the perturber density. The additional term involving $\mathcal{V}^{1,2}$ provides a coupling between the two participating atomic coherences.

The interaction superoperator $\mathcal{V}^{1,2}$ spans a manifold of intermediate states of measure $O(L^9)$ during the collision, as in the calculation of the self-energy terms. Therefore, even though we project here on a manifold of higher measure, $O(L^6)$, than the one we had in the case of one-atom coherences, it still has a lower measure than the set of intermediate states. So, we can omit again the intermediate-state $\mathcal{Q}$ operators, to $O(L^{-3})$. We are then left with

$$\Phi^{1,2}(z)=\mathcal{P}^{1,2}(\vec{k})\mathcal{T}_R^{1,2}(z)\mathcal{P}^{1,2}(\vec{k}) \tag{48}$$

as the contribution of the collision between the two atoms. There is no summation here over perturbers (and therefore no $N_B$ factor); $\Phi^{1,2}$, like $\mathcal{V}^{1,2}$, is proportional to $L^{-3}$ in box normalization. It replaces $\mathcal{V}^{1,2}$ as an effective interaction, in the reduced space of two-atom coherences. This interaction is similar in nature to the one encountered in the Bethe-Salpeter equation for the correlated motion of two particles.

Letting $\rho^{1,2}$ denote, in general, two-atom coherences (or rather their part orthogonal to the one-atom coherences), we therefore obtain a master equation (in the Markovian approximation) of a mixed Bloch and Bethe-Salpeter-type

$$i\frac{\partial}{\partial t}\rho^{1,2}(t)=[\mathcal{L}^1+\mathcal{L}^2+\Sigma^1(i0)+\Sigma^2(i0) + \Phi^{1,2}(i0)]\rho^{1,2}(t)\,, \tag{49}$$

with an obvious generalization (introducing a memory-kernel integral) to the non-Markovian case. Here again we can use the molecular-chaos approximation whenever appropriate, replacing $\Phi^{1,2}$ by its velocity average $\langle\Phi^{1,2}\rangle$, defined as in (38), with one-particle states (29) replaced by two-particle states (44), and $f(\vec{q})$ replaced by

$$f(\vec{q}_1)f(\vec{q}_2)=f(\vec{q})f(\vec{Q})\,, \tag{50}$$

where $\vec{q}$ and $\vec{Q}$ are the momenta for the relative and center-of-mass motions of the pair. With this substitution, Eq. (49) is reduced to the set of internal (discrete) atomic states. It should be kept in mind, however, that this reduction follows *after* the projection onto the subset of coherences, with all the measure-dependent considerations of the previous discussion still prevailing.

The effective interaction $\Phi^{1,2}$ is the only term in (49) which may have nondiagonal elements in both atom 1 and atom 2 (and in $\hat{n}_1$ and $\hat{n}_2$ as well). It forms a necessary step in the creation of many-atom coherence effects in continuous-wave (steady-state) spectra.[26] Without it, the reduced density matrix in (49) would simply factorize into a product of two uncoupled one-atom coherences. In the diagrammatic language of Paper II, this would lead to the appearance of disconnected diagrams, of vanishing contribution. Of course, in transient phenomena, many-atom coherent excitations can occur without the mediation of collisions, with the coherent radiation providing the phase-locking mechanism.

So far the two atoms were treated as distinct particles. In self-broadening we have to take into account the effects of indistinguishability of the particles. Let

$$s_j\equiv a_jb_j;\hat{n}_j \quad (j=1,2) \tag{51}$$

specify all the quantum numbers of the one-atom coherences. The two-atom density matrix should remain invariant to exchange of the labels 1 and 2; i.e.,

$$\rho^{1,2}=\tfrac{1}{2}\mathcal{S}_2\rho^{1,2}\,, \tag{52}$$

where an $N$-particle symmetrization operation is defined by

$$\mathcal{S}_N|s_1,\ldots,s_N\rangle\rangle=\sum_{\text{perm}}|s_{j_1},\ldots,s_{j_N}\rangle\rangle\,, \tag{53}$$

summing over all $N!$ permutations. In other words, a further reduction of the basis is required, replacing $\mathcal{P}^{1,2}(\vec{k})$ by $\mathcal{P}_S^{1,2}(\vec{k})$, projecting onto the symmetrized subset of two-atom coherences. So, Eq. (49) is replaced in self-broadening (in the binary-collision Markovian approximation) by

$$i\frac{\partial}{\partial t}\rho^{1,2}(t)=\left(\sum_{j=1}^{2}[\mathcal{L}^j+\Sigma_S^j(i0)] + \tfrac{1}{2}\Phi_S^{1,2}(i0)\right)\rho^{1,2}(t)\,, \tag{54}$$

where

$$\tfrac{1}{2}\Phi_S^{1,2}=\tfrac{1}{2}\Phi^{1,2}\mathcal{S}_2\,. \tag{55}$$

Note that when (55) is contracted over one-particle states in order to produce the self-energy, we project on both sides with $\mathcal{P}^1(\vec{k})$. In self-broadening, this means picking up any of the two particles and labeling it "1." Therefore we must distinguish between the case in which the same particle is picked up on both sides and the case in which the two particles are different. The $\frac{1}{2}$ factor in (55) then drops out and

$$\Sigma_S^1=N_A\,\mathrm{tr}_2(\Phi_S^{1,2}\rho_0^2) \tag{56}$$

results as the self-energy modified by resonance exchange.

We shall later on encounter situations where the effective interaction is further contracted on either side (or on both sides) by projecting onto the one-dimensional coherence vaccum state described by

$$\mathcal{P}_0=|\rho_0\rangle\rangle\langle\langle I|\,, \tag{57}$$

where $\rho_0$ and $I$ refer to the entire gas sample. In this case one may no more distinguish between two possibilities of labeling the particles, and therefore either only the foreign-gas-like part, or one-half the symmetrized form of the effective interaction should be used.

## V. RADIATIVE-BATH EFFECTS

Coupling to the radiative bath can be treated by the same formalism.[21,33] In discussing effects of the radiative bath we should distinguish between two kinds of phenomena[11]: The first kind is concerned with the interaction of individual atoms with the radiation bath, leading to radiation damping effects. These involve self-energy matrix elements such as

$$\langle\langle bb;\hat{0}\,|\,\Sigma^{1}(z)\,|\,aa;0\rangle\rangle =\langle\langle bb;\hat{0}\,|\,\mathrm{tr}_{B}[\mathcal{V}^{1,B}(z-\mathcal{L}_{0})^{-1}\mathcal{V}^{1,B}\rho_{0}^{B}]\,|\,aa;\hat{0}\rangle\rangle\,, \tag{58}$$

where $B$ stands now for the radiative bath, with $\mathcal{L}_0=\mathcal{L}_0^1+\mathcal{L}_0^B$. Elements diagonal in the internal states ($\alpha=\beta$) represent radiative ("natural") decay of the level $\alpha$ by virtual emission of photons. Elements with $\beta\neq\alpha(E_\beta<E_\alpha)$ represent cross relaxation from $\alpha$ to $\beta$ by emission of true photons (cascading).[24]

The second kind of effect is concerned with the transfer of radiation from one atom to another[11] introducing, for example, effective-interaction matrix elements such as

$$\langle\langle b_1a_2,b_1b_2;\hat{0}_1\hat{1}_2,\hat{1}\,|\,\mathrm{tr}_{B}[\mathcal{V}^{2,B}(z-\mathcal{L}_{0})^{-1}\mathcal{V}^{1,B}\rho_{0}^{B}]\,|\,a_1b_2,b_1b_2;\hat{1}_1\hat{0}_2,\hat{1}\rangle\rangle\,, \tag{59}$$

where now $\mathcal{L}_0=\mathcal{L}_0^1+\mathcal{L}_0^2+\mathcal{L}_0^B$. According to the Power-Zienau transformation[38] in quantum electrodynamics, these elements are *one and the same*, at short interatomic separations, as those of the first-order multipolar electrostatic interaction between the atoms. In the electric-dipole approximation they are equivalent to the first-order dipole-dipole ($\sim r^{-3}$) interaction. Thus, these elements should be treated as collision-broadening (rather than radiative-damping) phenomena. However, at larger interatomic separation, owing to retardation effects, the true radiative ($\sim r^{-1}$) character of these couplings is revealed. Such radiative-transfer elements play an important role in radiation trapping. In very dilute gases (where the mean interatomic separation is comparable to the transition wavelength or larger), the two-atom contributions should be augmented by higher-order $N$-atom contributions leading to a highly nonlinear density dependence of the self-energy.[39] At higher densities, these effects become completely masked by short-range (collision-broadening-proper) phenomena.

Owing to the extremely short memory (correlation) time associated with radiative decay,[21,40] the truly radiative effects, such as radiative damping, and the retarded (long-range) radiative-transfer elements, are completely dominated by the lowest-order perturbation terms, such as (58) and (59), and one need not be concerned with the incorporation of $\mathcal{V}^{1,B}$, or $\mathcal{V}^{1,R}$ (interaction with the applied modes), in the resolvents.

First-order electrostatic dipole-dipole effective-interaction elements, though properly belonging under collision broadening, should be handled with care owing to their relatively long range, and we therefore discuss them briefly here. The element described in (59) represents a resonance-exchange contribution, to be distinguished from the foreign-gas-type element

$$\langle\langle a_1b_2,b_1b_2;\hat{1}_1\hat{0}_2,\hat{1}\,|\,\mathrm{tr}_{B}[\mathcal{V}^{2,B}(z-\mathcal{L}_{0})^{-1}\mathcal{V}^{1,B}\rho_{0}^{B}]\,|\,a_1b_2,b_1b_2;\hat{1}_1\hat{0}_2,\hat{1}\rangle\rangle\,. \tag{60}$$

Owing to the nonisotropic irreducible-tensor character of the interaction,[41] the latter element vanishes on performing the integration over the interatomic radius-vector $\vec{r}$. The resonance-exchange element (59), however, does not vanish. In a two-level system, its elements (in momentum space) are independent of the initial momenta and, though the radial integral extends over magnitudes of $r$ comparable to the wavelength, it is independent of the magnitude and orientation of $\vec{k}$. It results in a (velocity-independent) frequency shift

$$\delta=-\pi N_A(c/\omega_{\alpha\beta}L)^3\gamma_N\,, \tag{61}$$

where $\gamma_N$ is the radiative decay rate (the Einstein $A$ coefficient) of the upper level. Higher-order contributions of the dipole-dipole interaction modify this value only by a few percent.[42] The long-range nature of these first-order dipole-dipole interactions makes it likely, as with the radiative-transfer terms, that they play an important role in introducing cooperative many-atom effects,[43] although unambiguous experimental evidence is still missing.

## VI. MANY-ATOM COHERENCE

As the applied radiation is made stronger, more coherently excited atoms are likely to interact with each other, and the rank $N$ of the coherent excitation may become increasingly large, by successive application of $\Phi^{1,2}$, $\Phi^{2,3}$, etc. Therefore reckoning a *fixed* number ($N$) of distinct atoms, we can write the master equation for $N$-atom coherences,

$$i\frac{\partial}{\partial t}\,\rho^{1,\ldots,N}(t)=\left(\sum_{j=1}^{N}[\mathcal{L}^{j}+\Sigma^{j}(i0)]+\sum_{j<l}\Phi^{j,l}(i0)\right)\rho^{1,\ldots,N}(t)\quad(N\geqslant 2)\tag{62}$$

in the Markovian binary-collision approximation. In denser fluids, where $M$-body collisions ($M\geqslant 2$) may occur, $\Phi^{1,2}$ is replaced by a succession of $M$-body effective interactions $\Phi^{j_1,\ldots,j_M}$ (with $M=2,\ldots,N$) expressible in terms of $M$-body scattering amplitudes.

As in the two-atom case, the density matrix in self-broadening must remain invariant to the interchange of two-particle labels; i.e.,

$$\rho^{1,\ldots,N}=(N!)^{-1}\mathcal{S}_N\rho^{1,\ldots,N},\tag{63}$$

where $\mathcal{S}_N$ is defined in (53). Therefore the symmetrized forms

$$\Phi^{j,l}\rightarrow\tfrac{1}{2}\Phi_S^{j,l},\quad\Sigma^{j}\rightarrow\Sigma_S^{j},\tag{64}$$

should replace those in (62).

Coherences of a lower rank $N'<N$ can be derived from the density matrix for rank-$N$ coherences, as subsets of a lower measure, by projecting onto the ideal-gas equilibrium state of the remaining $N-N'$ atoms. However, as the number $N_A$ of atoms in the sample is macroscopically large, $O(L^3)$, $N$ is practically unbounded in strong radiation fields. We must therefore find a way of dealing with $N$ as a varying number, rather than a fixed one.

There are various ways of dealing with the variability of $N$. One such procedure is to use a second-quantization (Fock-space) formalism, superimposed on the complete set of one-atom double-space vectors (in the extended Floquet space) as the underlying Hilbert space. As $N$ is practically unbounded from above, this quantization must obey boson commutation rules (see Appendix B).

In practice, equivalent results can be obtained by the use of projection operators. In the equation for $N$-atom coherence (with a fixed $N$), $\Phi^{1,2}$, $\Sigma^1$, and (implicitly) $\mathcal{V}^{1,R}$ are treated as isomorphic mappings, projecting the $O(L^{3N})$ coherence space onto itself. We can, however, exploit the fact that lower-rank coherences have a vanishingly small overlap with this space, to construct a hierarchy of coupled equations, with a varying $N=0,1,\ldots,$ by the help of introducing vertex operators, such as

$$\mathcal{P}^1(\vec{k})\mathcal{V}^{1,R}\mathcal{P}_0,\quad\mathcal{P}^1(\vec{k})\Sigma^1\mathcal{P}_0,\quad\mathcal{P}^{1,2}(\vec{k})\Phi^{1,2}\mathcal{P}^1(\vec{k})\tag{65}$$

or

$$\mathcal{P}^{1,2}(\vec{k})\Phi^{1,2}\mathcal{P}_0\tag{66}$$

acting as *rank upgrading* operators, the first ones raising $N$ by a unity, the last one—by two. Similarly, *rank downgrading* vertex operators are formed by interchanging the order of projection operators in (65) and (66). All these operators should join the isomorphic ones,

$$\mathcal{P}^1(\vec{k})\mathcal{V}^{1,R}\mathcal{P}^1(\vec{k}),\quad\mathcal{P}^1(\vec{k})\Sigma^1\mathcal{P}^1(\vec{k}),\quad\mathcal{P}^{1,2}(\vec{k})\Phi^{1,2}\mathcal{P}^{1,2}(\vec{k})\tag{67}$$

already included in (62). In self-broadening, all operators in (65) and (66) *not* having the vacuum projection $\mathcal{P}_0$ on either side, should be augmented by the resonance-exchange contributions.

Treating the various ranks of coherence as orthogonal subspaces, the hierarchy of coupled equations will have the general structure

$$i\frac{\partial}{\partial t}\rho_N=\sum_{M=-2}^{2}\mathcal{K}_{N,N-M}\,\rho_{N-M}\quad(N=1,2,\ldots;M\leqslant N)\tag{68}$$

in the binary-collision Markovian approximation. Here we have used $\rho_N\equiv\rho^{1,\ldots,N}$ for shortness, and $\mathcal{K}_{N,N-M}$ are the various upgrading ($M>0$), downgrading ($M<0$), and isomorphic ($M=0$) operations. Note that the ideal-gas distribution $\rho_0$ should appear in the right-hand side of (68), upgraded not only by $\mathcal{V}^{1,R}$, but also by $\Sigma^1$ and $\Phi^{1,2}$, as it is not a constant of the motion (even in the linear-response approximation). In the previous discussion we did not take note of the identities

$$\mathcal{P}_0\Sigma^1=\mathcal{P}_0\Phi^{1,2}=\mathcal{P}_0\mathcal{V}^{1,R}=0\tag{69}$$

when applying the finite-state summation to a *complete* basis of coherences, as such sums involve the trace of a commutator. In dealing with resonance processes, we generally project on a limited basis (the resonance set[23]) as, for example, in the rotating-wave approximation. We therefore should better keep these terms in the equations. This would also mean that an equation for the coherence vacuum $N=0$, with $\mathcal{P}_0\Sigma^1\mathcal{P}_0$ as the isomorphic driving term, should be added to the resonance-set hierarchy of equations. The single equation (62), for a chosen $N$, is obtained by an approximate truncation procedure, taking out all coherences of a higher rank, and incorporates all lower-rank coherences as subspaces of the rank-$N$ coherence.

Further details of the structure of (68) become relevant in constructing diagrammatic solution methods. Such a method is developed in Paper II (Ref. 26) for dealing with steady-state properties of the system. Under steady-state conditions, only the Markovian limit ($z=i0$) matters. Expressions are derived in Paper II for the continuous-wave emission (or absorption) of radiation in any (incident or scattered) mode of the dressing fields, including the effects of coherences of a rank higher than one.

## VII. DISCUSSION

Cooperative coherence effects in the two-level-atom model are usually treated with the help of pseudospin master equations.[11] In this method, the upper and lower states of the atom are treated as a spin-$\frac{1}{2}$ doublet, and the absorption and emission of radiation are related to the pseudospin raising and lowering operators, $J_+$ and $J_-$, respectively, where

$$\vec{J}=\sum_{j=1}^{N_A}\vec{J}^{j},\quad \vec{J}\equiv(J_+,J_-,J_0) \tag{70}$$

is the resultant pseudospin of the sample, obeying ordinary angular momentum commutation relations. The raising and lowering operators conserve the total pseudospin quantum number $J$ ($J$ invariance). In Agarwal's equation,[6,11] radiative damping and transfer are also treated as $J$ invariant. Also translational effects are not included, the space coordinates $\vec{x}_j$ being treated merely as parameters.

Walls's comment regarding the necessity of introducing $J$-noninvariant relaxation processes,[14] brings to mind a situation similar, in some senses, to the one we faced on introducing the $N$-varying vertex operators to the hierarchy of master equations. In order to see the analogy, recall first that the single-atom pseudospin-$\frac{1}{2}$ doublet is replaced, in the density matrix formalism, by a pseudospin-1 triplet (the Bloch triad)[13,44]

$$(R_+,R_-,R_0)\equiv(\rho_{\alpha\beta}^{(\hat{1})},\rho_{\beta\alpha}^{(-\hat{1})},\rho_{\alpha\alpha}^{(\hat{0})}-\rho_{\beta\beta}^{(\hat{0})}) \tag{71}$$

in the two-level rotating-wave approximation (in addition to an invariant singlet representing the total population). In the hierarchy of equations presented here, the Floquet numbers $\hat{n}$, obeying the sum rule

$$\hat{n}=\sum_{j=1}^{N}\hat{n}_j\,, \tag{72}$$

therefore play a role analogous to that of the $J_0$ numbers in the density-matrix formalism. The isomorphic projections of

$$\mathcal{V}^{R}=\sum_{j=1}^{N}\mathcal{V}^{j,R} \tag{73}$$

are analogous to the $J_\pm$-dependent radiative couplings in the pseudospin equations. However, it is easy to see that in a two-level model, in the rotating-wave approximation,

$$|\hat{n}|\leq N\,. \tag{74}$$

Therefore the coherence rank $N$ is analogous to the total $J$ quantum number in the density-matrix formalism. Each step (with fixed $N$) in the hierarchy is therefore analogous to a $J$-invariant subspace (a "Bloch sphere"[13]), and $J$-noninvariance is counterparted by the vertex operators.

There are, nevertheless, certain fundamental differences between the two approaches. In the pseudospin formalism, in wave vector space, the lower ($\beta$) state and upper ($\alpha$) state play a symmetric role. Calling the state of total excitation ($J_0=+\frac{1}{2}N_A$) a "maximum-coherence" state, and the ground state ($J_0=-\frac{1}{2}N_A$) a "minimum-coherence" state is, in a way, misleading. They represent two polarly opposed points on the maximum-$J$ Bloch sphere, and are therefore equally coherent. Although this is perfectly legitimate and useful in a two-level model, the moment other levels, or other degrees of freedom, enter the picture this symmetry becomes meaningless.

The starting point used here, in which the gas is in a coherence vacuum state represented by the ideal-gas distribution $\rho_0$, introduces into the problem a fundamental asymmetry of the kind essential to the treatment of irreversible phenomena. The results of this asymmetry become evident the moment we introduce into the description such effects as translational relaxation (as in Doppler-limited saturation spectroscopy[37]), or internal relaxation (as in real atomic and molecular spectra). It also becomes evident in low-frequency (far-infrared and microwave) spectra, when the upper-level equilibrium population is not negligible. Needless to say, our method is not limited in applicability to the two-level model.

Another important distinction is provided by the variability of $N$. In pseudospin methods, the total number of participating atoms ($N_A$) is treated as a fixed number, and therefore the total pseudospin $J$ has a maximum value. In our approach, one can let the thermodynamic limit ($N_A\to\infty$) be reached, and treat the coherence rank $N$ as an unbounded number, as implicated in the diagrammatic representation of Paper II.[26]

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## APPENDIX A: EQUIVALENCE OF COHERENT RADIATION TO CLASSICAL FIELDS

This equivalence is discussed in detail elsewhere,[32,33] but it shall be briefly reveiwed here for the convenience of the reader. Suppose that, in the absence of interaction between the applied beam and the sample, we can represent the coherent beam by a pure Glauber-state[45] projection operator $|\alpha_k\rangle\langle\alpha_k|$ (or a direct product of such operators in case of several-mode beams), and the sample by an equilibrium density matrix $\rho_{eq}$ defined on all degrees of freedom, including internal (spontaneously emitted) photons.

Switching on the interaction between the beam and the sample, it is *postulated* that the initial condition at $t_0 \to -\infty$ can then be represented by the "in asymptote"

$$\rho_{in} = D(\alpha(t_0))\rho_{eq} D^\dagger(\alpha(t_0)) \quad (t_0 \to -\infty)\,, \tag{A1}$$

where

$$D(\alpha) = \prod_{k\in \text{beam}} D(\alpha_k) = \prod_k \exp(\alpha_k a_k^\dagger - \alpha_k^* a_k) \tag{A2}$$

is the Glauber unitary displacement operator, and

$$\alpha(t) = \{\alpha_k(t)\} = \{\alpha_k e^{-i\omega_k t}\}\,. \tag{A3}$$

For example, an optical mode (with $\hbar\omega_k \gg k_B T$, where $k_B$ is the Boltzmann constant and $T$ the temperature), is represented in $\rho_{eq}$ by a factor $|0_k\rangle\langle 0_k|$, which is transformed into $|\alpha_k\rangle\langle\alpha_k|$ by (A1). Let

$$H = H_e + V^R \tag{A4}$$

be the Hamiltonian of the entire system, with $V^R$ representing the (second-quantized) coupling to the applied-beam modes. Then (A2) obeys the identities

$$U_e(t,t')D(\alpha(t')) = D(\alpha(t))U_e(t,t')\,, \tag{A5}$$

$$V^R D(\alpha(t)) = D(\alpha(t))[V^R + V^{R,\text{cl}}(t)]\,, \tag{A6}$$

where

$$U_e(t,t') = \exp[-iH_e(t-t')\hbar]\,, \tag{A7}$$

and

$$V^{R,\text{cl}}(t) = \langle\alpha(t)|V^R|\alpha(t)\rangle \tag{A8}$$

is the classical-field interaction. In the Schrödinger picture,

$$\rho(t) = U(t,t_0)\rho(t_0)U(t,t_0)\,, \tag{A9}$$

with $U$ obtained from (A7) on replacing $H_e$ by $H$. Letting $t_0 \to -\infty$, and using (A5) and (A6), we get

$$\rho(t) = X(t,-\infty)\rho_{eq}X^\dagger(t,-\infty)\,, \tag{A10}$$

with $X(t,t')$ obeying

$$i\hbar\frac{\partial}{\partial t}X(t,t') = [H + V^{R,\text{cl}}(t)]X(t,t')\,. \tag{A11}$$

Equation (A10) can be brought into a superoperator form,

$$\rho(t) = X(t,-\infty)X^*(t,-\infty)\rho_{eq} \equiv \mathcal{X}(t,-\infty)\rho_{eq} \tag{A12}$$

replacing ordinary Hamiltonian operators in $X$ by the equivalent superoperators in $\mathcal{X}$. The time dependence can now be removed from the classical interaction by the Floquet method, expressing $\rho(t)$ in the extended basis of Eq. (7) (using $a$ and $b$ for the states of the entire system). Then

$$i\frac{\partial}{\partial t}\rho(t) = (\mathcal{H} + \mathcal{V}^{R,\text{cl}} + \mathcal{L}^R)\rho(t)\,, \tag{A13}$$

where $\mathcal{H}$ is obtained from $H$ by (10), $\mathcal{V}^{R,\text{cl}}$ is the time-independent radiative-driving superoperator, and $\mathcal{L}^R$ is defined by (9), with $\rho_{eq}$ as the initial state (belonging to the $\hat{n}=0$ subspace).

## APPENDIX B: SECOND QUANTIZATION IN LIOUVILLE SPACE

A Fock-space second-quantization procedure can be applied directly to the Liouville space of the dressed (sample-plus-beam) system, as the underlying Hilbert space. Let

$$s = ab\,;\hat{n} \tag{B1}$$

denote all the quantum numbers of a dressed one-atom double-space vector (not necessarily limited to the momentum-constrained coherence states). The coherence rank $N$ can serve as the "occupation number" in the superimposed many-particle Fock space. As $N$ is unbounded from above (in the thermodynamic limit), the quantization field operators must obey boson commutation rules ("coherons"). One can therefore introduce a set of annihilation and creation operators, $\mathcal{A}_s$ and $\mathcal{A}_s^\dagger$, respectively, obeying

$$[\mathcal{A}_s, \mathcal{A}_t^\dagger] = \delta_{st}\,, \tag{B2}$$

$$[\mathcal{A}_s, \mathcal{A}_t] = [\mathcal{A}_s^\dagger, \mathcal{A}_t^\dagger] = 0\,. \tag{B3}$$

A second-quantized form of the coupling to the radiation $\mathcal{V}^R$ and the intermolecular couplings $\mathcal{V}^B$ is given by the usual prescription,[46]

$$\hat{\mathcal{V}}^R = \sum_{s,t} \langle\langle s|\mathcal{V}^{1,R}|t\rangle\rangle \mathcal{A}_s^\dagger \mathcal{A}_t\,, \tag{B4}$$

$$\hat{\mathcal{V}}^B = \sum_{s_1 s_2, t_1 t_2} \langle\langle s_1 s_2|\mathcal{V}^{1,2}|t_1 t_2\rangle\rangle \mathcal{A}_{s_1}^\dagger \mathcal{A}_{s_2}^\dagger \mathcal{A}_{t_2} \mathcal{A}_{t_1}\,. \tag{B5}$$

The density matrix can then be expressed as a superposition if Fock space,

$$|\hat{\rho}\rangle\rangle \equiv \sum_{N=0}^{\infty} |\rho^{1,\ldots,N};N\rangle\rangle\,, \tag{B6}$$

where $N$ is an eigenvalue of the number operator (coheron number)

$$\hat{N} = \sum_s \mathcal{A}_s^\dagger \mathcal{A}_s\,. \tag{B7}$$

The separable (ideal-gas) equilibrium distribution ($|\rho_0\rangle\rangle$) and the identity operator ($\langle\langle I|$) serve, respectively, as the "bare vacuum" ($N=0$) ket and bra double-space vectors. Therefore, steady-state rates can be expressed as vacuum-expectation values, and calculated by the method of zero-temperature Green's functions,[46] with each one-particle contraction involving a thermal averaging over the one-particle distribution $\rho_0^1$. This approach should ultimately lead to the diagrammatic analysis used in Paper II in the binary-collision (ladder) approximation, with momentum-conservation constraints, symmetrization effects, etc., automatically taken care of.

This second-quantization procedure should not be confused with theories of spectral line shape using a Fock-space formalism superimposed on the ordinary (wave-vector) Hilbert space, and employing finite-temperature (imaginary-time) Green's function methods.[47,48] In these theories, particle-hole pair propagators play the role of an individual double-space propagator in Liouville space. The use of Liouville-space methods has, however, two advantages: First, self-energies are related to familiar dynamical quantities (binary-collision scattering amplitudes). Second, the treatment of initial correlations by Burnett *et al.*[21] clearly shows how to distinguish between radiative transitions induced *during* a collision and those induced *between* collisions, thus conveniently enabling one to treat the quasistatic limit in collision broadening, collision-induced absorption, radiative collisions, etc., as distinct physical processes.

A second-quantization procedure based on the idea of converting thermal averages into vacuum-expectation values has been described by Takahashi and Umezawa.[49] Instead of using the Liouville representation in which both row and column quantum numbers represent equally "physical" states, these authors attach to each physical state in ordinary wave-vector space a fictitious image state in order to create a double-space formalism. The quantization procedure suggested in this appendix does not take into account the quantum statistics of the interacting atoms. For binary collisions, however, this can be incorporated by a proper symmetrization procedure.[50] This symmetrization should not be confused with the one introduced in Sec. III as a reflection of the two ways in which the trace over one-atom states can be taken. When states symmetrized according to the Pauli principle are used, the symmetrization indicated by the label $S$ is attained by simply multiplying the corresponding unlabeled term by 2.

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