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Theory of resonance scattering and absorption of strong coherent radiation by thermally relaxing multilevel atomic systems

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The resonant response of a multilevel atomic system to strong coherent radiation is analyzed using an extension of the methods of time-independent scattering theory, adapted to the density-matrix formalism in order to include thermal bath effects. General steady-state expressions are derived for self-attenuation and resonance scattering rates in strong saturating fields, as functions of the coupling strengths, relaxation parameters, and frequency detunings. Formal expressions are given for radiative-damping and collision-broadening relaxation parameters, relating the latter to scattering amplitudes. Modifications of collision-broadening parameters by the presence of very strong fields are discussed. The Bloch equations are derived by transformation to the time domain, under specified conditions.

I. INTRODUCTION

The response of simple atomic (or molecular) systems of two or more energy levels in resonant interaction with strong coherent monochromatic radiation fields has been studied extensively in recent years, experimentally as well as theoretically. These studies include (i) Steady-state and time-resolved spectroscopy of two- and three-level systems, including attenuation (absorption) spectra, and resonance Raman (resonance fluorescence), with homogeneous coupling to a thermal bath (radiative, collisional, etc.),[1-26] (ii) saturation absorption in Doppler-broadened line spectra (Lamb-dip spectroscopy),[27-36] (iii) transient coherent effects,[37-44] such as optical nutation, photon echo, and double resonance, and (iv) multiphoton dissociation of molecules by coherent excitation where, at least part of the process is described as a multilevel resonance absorption.[45,46]

In all these problems, the atom (or molecule) is approximated by a system of sharp resonance transitions between discrete levels, homogeneously or inhomogeneously broadened, strongly excited by the incident radiation. The customary analysis of such systems is carried out by finding time-dependent (or steady-state) solutions to the equations of motion of the density matrix for the single-molecule multilevel degrees of freedom. In homogeneously broadened systems, these equations are known as the Bloch equations.[47,48] If velocity effects, such as Doppler shifts, are introduced, these are replaced by a generalized linear Boltzmann equation (with internal states).[49]

Practically all recent work is concerned with *application* of these equations. An analytic solution of the Bloch equations has been obtained for certain simple systems. The two-level system has been solved for one strong-mode attenuation[1,3,4] for weak-probe attenuation in the presence of a strong mode[3,4,10] and for resonance fluorescence,[2,4,5,7,8,10,12] in the rotating wave approximation (RWA). Corrections owing to deviations from the RWA have been studied.[50] Attempts have been made to solve the two-level Bloch equations for certain temporal forms of variation.[51,52] Such solutions require smooth variation of the light-intensity profile with the time in order to conform with the RWA. Analytic solutions for the three-level system were available only with certain limitations on the parameters.[11,31] Numerical solutions are available, too.[9] Recently, algebraic methods were introduced as a means of solution of "ladder"-type N-level excitations in the RWA.[53] The three-level two-mode problem has been fully solved (with arbitrary T_1 and T_2 relaxations, coupling strengths, and frequency detunings).

There are, however, certain fundamental problems concerning the derivation, validity limits, and possible extensions of the dynamic equations which require more attention:

(a) Are the Bloch equations, with relaxation parameters determined by the equilibrium properties, valid in the presence of very strong saturating fields? If not, what are the necessary modifications? (b) Can weak-field (linear response) theories for the relaxation parameters (such as collision broadening) be extended to multiphoton processes? (c) Is it possible to incorporate systematically in the theory such modifications as several-photon nonresonant simultaneous transitions (such as two-photon simultaneous absorption), coupling by relaxation to radiatively inactive levels, etc.? (d) Can one develop direct (time-independent) methods for obtaining steady-state solutions? (e) How should one define attenuation rates for a particular field mode when several strong coherent modes are present? Can this problem be posed as a scattering problem?

These and related problems are studied here. The method of solution is basically an extension of the methods of time-independent scattering theory to the density matrix formalism. The following main steps are: (i) Description of attenuation and scattering as photon counting rates, (ii) displacement of the external field from the boundary conditions to the time evolution in the form of a time-dependent classical field, (iii) introduction of tetradic notation to the time evolution of the density matrix, (iv) removal of the time dependence of the interaction by the Floquet method, (v) introduction of the proper self energy by averaging over the thermal bath, (vi) distinction between radiative couplings of free molecules and couplings coincident with self-energy insertions, the latter leading to the modification of the equilibrium relaxation rates by the external field (e.g., field-enhanced collisions), (vii) reduction of the basis of the equations to a "resonance set" consisting of all levels, or coherences of level pairs, resonantly coupled by the radiation, introducing various corrections to the RWA (simultaneous several-photon transitions, Bloch-Siegert shifts, relaxation processes involving levels not actively coupled to the radiation, etc.) and (viii) finally, the relation to the equations of motion is discussed.

This work is mostly concerned with homogeneous broadening by radiative or collisional thermal baths. Velocity effects are briefly discussed. The present work is limited to single-molecule excitations, disregarding cooperative phenomena.

II. THE INITIAL STATE

Consider the scattering of a monochromatic coherent radiation (laser) beam L into a scattering mode S by resonance interaction with a closed microscopic atomic system A coupled to a large thermal bath B. Here L generally means monochromatic coherent radiation, with several distinct modes, each characterized by a macroscopically large density of photons. S stands for the scattered mode (or modes) specified by an ideally resolving detector that measures radiation fluxes (or photon counts). A is a microscopic (one-body) scatterer (e.g., an atom, a molecule, a disordered impurity in a crystal, or an intramolecular system in a large molecule) characterized by an internal set of discrete levels. The interaction of various scatterers with the radiation is assumed to be uncorrelated (i.e., we disregard cooperative excitation phenomena). Incorporated in B are all other degrees of freedom, not directly involved in the resonance interaction with L (or S), acting on A as a thermal bath. These bath modes can be molecular (e.g., binary collisions in a gas, phonons and local modes in a crystal, intersystem crossing in a large molecule) or radiative—including both virtual transitions (radiative damping) and actual fluorescence by cascading processes.

We shall use throughout the simplifying assumption that A and B, in their equilibrium state, are statistically uncorrelated. This assumption implies that their equilibrium density matrix is separable:

$$\rho_{AB}^{\mathrm{eq}}=\rho_A^{\mathrm{eq}}\rho_B^{\mathrm{eq}}, \tag{1a}$$

where

$$\rho_A^{\mathrm{eq}}=\mathrm{tr}_B\rho_{\mathrm{AB}}^{\mathrm{eq}} \tag{1b}$$

depends, at most, on average bath properties and ρ_B^{eq} is completely independent of A. This assumption is frequently applicable in dilute or weakly coupled systems (e.g., in dilute gases). Corrections due to initial correlations can be formally introduced by the methods of temperature Green functions, provided ρ^{eq} is a canonical distribution.[54,55] This would, however, exclude systems prepared in stationary but not canonical-equilibrium states.

It is further assumed that ρ_A^{eq} can be written in a diagonal form:

$$\rho_A^{\mathrm{eq}}=\sum_a \rho_a^{\mathrm{eq}}|a\rangle\langle a| \,. \tag{2}$$

Quite generally, the complete set of eigenstates of the Hamiltonian of A, H_A, is used in Eq. (2).

The equilibrium state of the various field modes (in the absence of the external beam) is likewise assumed to be separable. More particularly, we shall concern ourselves here with *optical* photons, assuming

$$\hbar\omega \gg k_B T\,, \tag{3}$$

where ω is the photon frequency and T is the bath temperature. (Modifications due to far-infrared "thermal" photons can be incorporated in the framework of the present theory.)

The equilibrium state of the field in the optical limit (3) is the photon vacuum $|0\rangle\langle 0|$.

To sum up, the state of the complete system before the external sources are "switched on" can be written approximately as

$$\rho^{\mathrm{eq}}=\rho_A^{\mathrm{eq}}\rho_B^{\mathrm{eq}}\rho_S^{\mathrm{eq}}\rho_L^{\mathrm{eq}}, \tag{4a}$$

where

$$\rho_B^{\mathrm{eq}}=\rho_M^{\mathrm{eq}}\rho_F^{\mathrm{eq}}, \tag{4b}$$

by further distinction between a molecular bath M (e.g., collisions) and a radiative bath F (fluorescence).

The initial conditions following the switching on of the external beam can be formally expressed by the "in" asymptote (extending the jargon of scattering theory to the density-matrix formalism):

$$\rho^{\text{in}} = \rho_A^{\text{eq}}\rho_B^{\text{eq}}\rho_S^{\text{eq}}\rho_L^{\text{ext}}\,, \tag{5}$$

where ρ_L^{ext} depends only on externally controlled parameters. In dealing with a coherent single-mode optical radiation, ρ_L^{ext} is simply the pure Glauber state[56]

$$\rho_L^{\text{ext}} = |\alpha_L\rangle\langle\alpha_L|\,. \tag{6}$$

Extension to several modes is straightforward. Equation (5) is related to the vacuum state by a unitary displacement operator $D(\alpha_L)$:

$$\rho_L^{\text{ext}} = D(\alpha_L)|0\rangle\langle 0|D^\dagger(\alpha_L)\,, \tag{7}$$

where

$$D(\alpha_L) = \exp(\alpha_L a_L^\dagger - \alpha_L^* a_L)\,, \tag{8}$$

$a_L^\dagger$ and a_L being, respectively, the photon creation and annihilation operators for the L mode. This unitary operator is used in the transformation of the external-field effects from the initial conditions (7) to the time-evolution operator, where they manifest themselves by the addition of a classical-field time-dependent interaction to the Hamiltonian.[7,57]

III. PHOTON-COUNTING RATES

In dealing with multiphoton processes at high intensities, it is useless to talk about cross sections. However, one can define attenuation rates of one of the beam modes, or scattering rates into an infinitesimal solid angle of an ideal detector in a scattering (or fluorescence) experiment. In both cases, it is useful to define *photon-counting rates* as the asymptotic limit

$$C_S = \lim_{t\to\infty}\frac{d}{dt}\lim_{t_0\to-\infty}\operatorname{tr}\{N_S U(t,t_0)\rho^{\text{in}}U^\dagger(t,t_0)\}\,, \tag{9}$$

where ρ^{in} is defined by (5) as the "in" asymptote, $U(t,t_0)$ is the time evolution operator of the whole system ($A+B+S+L$) in the Schrödinger picture, generated by the (time-independent second-quantized) total Hamiltonian H, and

$$N_S = a_S^\dagger a_S \tag{10}$$

is the number operator of the S mode. We distinguish between a *scattering* experiment and an *attenuation* experiment:

$$S \notin \{L\} \quad \text{(scattering)}\,, \tag{11a}$$

$$S \in \{L\} \quad \text{(attenuation)}\,. \tag{11b}$$

In the latter case, the attenuation rate of the S mode of the beam is given by

$$A_S = -C_S \quad (S\in\{L\})\,. \tag{12}$$

Quantizing the field in a macroscopically large volume, where the density of scattering modes is infinitely large and coincidence of two photons in the same mode is vanishingly small, one can define a scattering rate into an infinitesimal solid angle $d\Omega$ by

$$\frac{dF_S}{d\Omega} = C_S(1)f_S(\Omega)\,, \tag{13}$$

where $f_S(\Omega)$ is the density of modes per solid angle, and N_S in (9) is replaced by the projection operator $P_S(1)$ for the one-photon occupation-number state in the S mode, $P_S(1) = |1_S\rangle\langle 1_S|$; i.e.,

$$C_S(1) = \lim\frac{d}{dt}\operatorname{tr}\{P_S(1)U(t,t_0)\rho^{\text{in}}U^\dagger(t,t_0)\}\,(S\notin\{L\})\,. \tag{14}$$

The trace in (9) or (14) is over the complete Hilbert space. Owing to the unitarity of U,

$$\frac{d}{dt}\operatorname{tr}\{U\rho^{\text{in}}U^\dagger\} = 0 \tag{15}$$

at all times. Therefore (9), or (14), is unaltered if a c number is added to N_S, or $P_S(1)$.

The total Hamiltonian H in the time-evolution operator

$$U(t,t_0) = \exp[-iH(t-t_0)/\hbar] \tag{16}$$

includes all interactions with the radiation modes, in second-quantized form, as well as other interactions (collisions, etc.). Note, however, that on expanding (9), or (14), in power series of the interactions, the last one to appear in the left of U (or the right of $U^\dagger$) must be V_S, the interaction with the S mode. All other interactions commute with N_S (or P_S).

The displacement operators in (7) can be displaced from their position as acting on the vacuum state ρ_L^{eq} to a position in which they act on N_S (or P_S), by using the property

$$a_L^\pm(t)D(\alpha_L) = D(\alpha_L)[a_L^\pm(t) + \alpha_L^\pm(t)]\,. \tag{17}$$

Here

$$a^\pm(t) = a^\pm e^{\mp i\omega_L t}\,,\quad \alpha^\pm(t) = \alpha^\pm e^{\mp i\omega_L t}\,, \tag{18}$$

where $a^+ = a$, $a^- = a^\dagger$, $\alpha^+ = \alpha$, $\alpha^- = \alpha^*$, and ω_L is the frequency of the L mode. Therefore, transforming to the interaction picture with respect to H_L (the free L-mode Hamiltonian), we can shift $D(\alpha_L)$ from right to left, adding the c number $\alpha_L^\pm(t)$ each time $a_L^\pm$ appears in the interaction, until we reach N_S on the right. Similarly, $D^\dagger(\alpha_L)$ is shifted from left to right until we reach N_S on the left (using the invariance of the trace under cyclic permutations). Transforming back to the Schrödinger picture, the result is

$$C_S = \lim \frac{d}{dt} \mathrm{tr}\{D^\dagger(\alpha_L) N_S D(\alpha_L) X(t,t_0) \rho^{\mathrm{eq}} X^\dagger(t,t_0)\}, \tag{19}$$

where ρ^{eq} replaces ρ^{in}, and $X(t,t_0)$ is the time-evolution operator obeying the Schrödinger equation

$$\frac{d}{dt} X(t,t_0) = -(i/\hbar)[H + V_L^{\mathrm{cl}}(t-t_0)] X(t,t_0), \tag{20}$$

with a classical-field time-dependent interaction,

$$V_L^{\mathrm{cl}}(t) = \langle \alpha_L(t) | V_L | \alpha_L(t) \rangle. \tag{21}$$

The interaction with the L mode, in the electric-dipole approximation, is

$$V_L^{\mathrm{cl}}(t) = -\vec{\mu}_A \cdot \vec{\epsilon}_L \sum_{\pm} \mathcal{E}_L^{\pm}(t) e^{\pm i \vec{k}_L \cdot \vec{R}_A} \equiv \sum_{\pm} V_L^{\mathrm{cl}\pm}. \tag{22}$$

Here $\vec{\mu}_A$ and $\vec{R}_A$ are, respectively, the dipole moment and the center-of-mass position of A, $\vec{\epsilon}_L$ is the polarization of the L mode, and

$$\mathcal{E}_L^{\pm}(t) = \pm i(\hbar\omega/2\Lambda^3)^{1/2} \alpha_L^{\pm}(t) \tag{23}$$

are the electric field expectation values in the familiar "box normalization" in a cube of length Λ. In an ideal setup, where the field is evenly distributed over a macroscopically large volume, the photon flux $c|\alpha_L|^2\Lambda^{-3}$ is independent of Λ. Hence, $\mathcal{E}_L^{\pm}$, too, is independent of Λ. Notice, however, that interactions with second-quantized fields, such as $V_S (S \notin L)$, are inversely proportional to $\Lambda^{3/2}$. As the density of modes f_S in (13) is proportional to Λ^3, C_S $(S \notin L)$ will accommodate V_S just once in X and in $X^\dagger$. C_S does accommodate, however, the emission to all field modes other than S (the F modes) an arbitrary number of times (fluorescence cascades), allowing at most one photon per mode, since the summation over F cancels Λ^{-3}. Also, note that the definition of photon-counting rates can be extended to incorporate coincidence rates of two *distinct* photons.

Consider, again, Eq. (19). In *scattering* experiments N_S [or $P_S(1)$] commutes with $D(\alpha)$ and one simply gets

$$C_S(1) = \lim \frac{d}{dt} \mathrm{tr}\{P_S(1) X(t,t_0) \rho^{\mathrm{eq}} X^\dagger(t,t_0)\} \quad (S \notin \{L\}). \tag{24}$$

In *attenuation* measurements

$$D^\dagger(\alpha_S) N_S D(\alpha_S) = a_S^\dagger a_S + |\alpha_S|^2 + (\alpha_S^* a_S + \alpha_S a_S^\dagger) \quad (S \in \{L\}). \tag{25}$$

The first term represents forward scattering of a second-quantized field in the single S mode, and vanishes as Λ^{-3}. $|\alpha_S|^2$ is a c number, and hence does not contribute to the trace. We are thus left with

$$A_S = -\lim \frac{d}{dt} \mathrm{tr}\{(\alpha_S^* a_S + \alpha_S a_S^\dagger) \times X(t,t_0) \rho^{\mathrm{eq}} X^\dagger(t,t_0)\} \quad (S \in \{L\}). \tag{26a}$$

The appearance of $\alpha_S^* a_S$ requires that the classical-field interaction $V_S^{\mathrm{cl}}(t)$ in a power-series expansion of $X(t,t_0)$ be replaced just *once* by a second-quantized V_S^-, which is proportional to $a_S^\dagger$. Its magnitude is compensated by α_S^* (all higher powers of $V_S^{\pm}$ vanishing as inverse powers of Λ). Similarly, $\alpha_S a_S^\dagger$ requires that V_S^+ be included just once in $X^\dagger(t,t_0)$. Exactly the same result is reached if one replaces $\alpha_S^* a_S + \alpha_S a_S^\dagger$ by the S-mode vacuum projection operator $P_S(0) = |0_S\rangle\langle 0_S|$, while replacing the solitary $a_S^\dagger$ by α_S^* (and a_S by α_S), retaining, however, the *order*: $V_S^{\mathrm{cl}-}$ is the last interaction on the left of X (or $V_S^{\mathrm{cl}+}$ the last one on the right of $X^\dagger$). Hence

$$A_S = -\lim \frac{d}{dt} \mathrm{tr}\{P_S(0)[X^{(-)}(t,t_0) \rho^{\mathrm{eq}} X^\dagger(t,t_0) + X(t,t_0) \rho^{\mathrm{eq}} X^{(-)\dagger}(t,t_0)]\} \quad (S \in \{L\}). \tag{26b}$$

With $X^{(-)}$ defined by the restrictions above, it is related to X by

$$X^{(-)}(t,t_0) = -(i/\hbar) \int_{t_0}^{t} dt' U_0(t,t') V_S^{\mathrm{cl}-}(t') X(t',t_0), \tag{27}$$

where U_0 is the interaction-free time-evolution operator. Taking the time derivative in (26b) one gets, after some manipulations,

$$A_S = -(2/\hbar) \lim_{\substack{t_0 \to -\infty \\ t \to \infty}} \{\mathrm{Im}\, \mathcal{E}_S^-(t) p_S^{\mathrm{ext}}(\vec{k}_S, t)\} \quad (S \in \{L\}), \tag{26c}$$

where

$$p_S^{\mathrm{ext}}(\vec{k}_S, t) = \mathrm{tr}\{\vec{\epsilon}_S \cdot \vec{\mu}_A e^{i\vec{k}_S \cdot \vec{R}_A} P_S(0) X(t,t_0) \rho^{\mathrm{eq}} X^\dagger(t,t_0)\} \tag{28}$$

is the polarization of A by the external field, in the dipole approximation. Equation (28) is a vacuum expectation value in the S mode (but includes all F-mode cascades). It incorporates the external field modes, as classical fields, to all powers.

IV. TIME-INDEPENDENT THEORY

A time-independent formalism can be introduced to obtain the asymptotic time limits in (24) or (26). This formalism is similar to the one used in ordinary scattering theory,[58] with two exceptions: (a) We deal directly with the time evolution of the density matrix (and not with the Schrödinger amplitudes), as a most appropriate way of introducing thermal bath effects. (b) We remove the explicit time dependence in the classical-field interactions.

The first goal is secured by using tetradic (Liouville-space) notation,[59–61] in order to convert the binary form $X\rho X^\dagger$ into a single perturbation series. Define the tetradic operator $\mathfrak{X}$ by

$$(X\rho X^\dagger)_{ab}=\sum_{cd} X_{ac}X^*_{bd}\rho_{cd}\equiv\sum_{cd}\mathfrak{X}_{ab;cd}\rho_{cd}\,. \tag{29}$$

Similarly, define the tetradic analog of H, namely, the Liouvillian

$$\mathcal{H}_{ab;cd}=\hbar^{-1}(HI^*-IH^*)_{ab;cd}\equiv\hbar^{-1}(H_{ac}\delta_{bd}-\delta_{ac}H^*_{bd})\,. \tag{30}$$

The tetradic analog of (20) is

$$\frac{d}{dt}\mathfrak{X}(t,t_0)=-i[\mathcal{H}+\mathcal{V}_L(t-t_0)]\,\mathfrak{X}(t,t_0)\,, \tag{31}$$

where $\mathcal{V}_L=\hbar^{-1}(V_LI^*-IV^*_L)$, using the condensed notation of (30). The double perturbation expansion in powers of V_L is then replaced by a single perturbation series in powers of $\mathcal{V}_L$, although at the price of doubling the number of steps (it takes twice as many perturbation steps to go from aa to bb, as from a to b). The tetradic operators are defined on a Hilbert space of dyadics (Liouville space). Using the double-bracket notation,[62] ordinary dynamical variables or density matrices can be described as vectors,

$$\rho_{ab}\equiv\langle\!\langle ab\,|\,\rho\rangle\!\rangle\,, \tag{32}$$

and tetradic operators as matrices,

$$\mathcal{H}_{ab;cd}\equiv\langle\!\langle ab\,|\,\mathcal{H}\,|\,cd\rangle\!\rangle\,, \tag{33}$$

where the metric of this space is specified by defining the scalar product

$$\langle\!\langle A\,|\,B\rangle\!\rangle=\mathrm{tr}\{A^\dagger B\}\,. \tag{34}$$

The various counting rates can now be written as tetradic matrix elements. Thus, e.g., (26b) attains the form

$$A_S=-\lim\frac{d}{dt}\langle\!\langle P_S(0)\,|\,\mathfrak{X}^{(-)}(t,t_0)\,|\,\rho^{\mathrm{eq}}\rangle\!\rangle\,, \tag{35}$$

where in $\mathfrak{X}^{(-)}$, $\mathcal{V}^{\mathrm{cl}-}_S$ is the last interaction on the left. Similarly, (24) is rewritten

$$C_S(1)=\lim\frac{d}{dt}\langle\!\langle P_S(1)\,|\,\mathfrak{X}(t,t_0)\,|\,\rho^{\mathrm{eq}}\rangle\!\rangle\,, \tag{36}$$

where $\mathfrak{X}$ is binary in $a^\pm_S$. Note the disparity between the bra vectors (projection operators) and the ket vectors (density matrices) in (35) and (36).

Our second goal, that of removing the explicit time dependence, is achieved by the Floquet method,[63] adapted to the density-matrix formalism.[3] The method is based on the expansion of the solution in harmonics of the fundamental frequencies of the perturbation:

$$\rho(t)=\sum_{\hat n}\rho^{(\hat n)}(t)e^{-i\hat n\cdot\omega t}$$
$$\times(\hat n=\{\hat n_L\};\quad \hat n_L=0,\pm1,\pm2,\ldots)\,, \tag{37}$$

where

$$\hat n\cdot\omega=\sum_{\{L\}}\hat n_L\omega_L\,. \tag{38}$$

The various components $\rho^{(\hat n)}$ are governed by an infinite set of equations of motion with time-independent coefficients, in which $V^{\mathrm{cl}\pm}_L$ raises (lowers) the harmonics numbers $\hat n_L$ by unity. The matrix elements $\rho^{\hat n}_{ab}$ can be treated as vector components in an extended Hilbert space,

$$\rho^{\hat n}_{ab}=\langle\!\langle ab;\hat n\,|\,\rho\rangle\!\rangle\,. \tag{39}$$

This *double space* is a direct product of the dyadic Liouville space, and the Floquet space of harmonics numbers $|\hat n\rangle\!\rangle$, which is the classical analog of the occupation-number representation. In Floquet space, $\mathcal{H}$ is diagonal, while $\mathcal{V}^{\mathrm{cl}}_L$ turns into a time-independent nondiagonal operator by substituting

$$\alpha^\pm(t)\to\hat\alpha^\pm\,|\,\hat n\rangle\!\rangle=\alpha^\pm\,|\,\hat n\pm1\rangle\!\rangle \tag{40}$$

as (time-independent) raising and lowering operators. The time-dependent exponential harmonic factors are taken care of by subtracting from $\mathcal{H}$ the Floquet-space diagonal operator of frequency harmonics Ω, where

$$\Omega\,|\,\hat n\rangle\!\rangle=\hat n\cdot\omega\,|\,\hat n\rangle\!\rangle\,. \tag{41}$$

The double-space time-evolution operator is then

$$\mathfrak{X}(t,t_0)\to\mathcal{Y}(t,t_0)=\exp[-i\mathcal{L}(t-t_0)]\,, \tag{42}$$

where

$$\mathcal{L}=\mathcal{H}-\Omega+\mathcal{V}^{\mathrm{cl}}_L \tag{43}$$

is time independent.

We are now in a position to take the time limits $t_0\to-\infty$, $t\to\infty$. First, as only steady-state solutions contribute in this limit, we are interested in the "vacuum expectation" values in Floquet space $\langle\!\langle 0\,|\,\mathcal{Y}\,|\,0\rangle\!\rangle$. Second, we can use the identity[60,61]

$$\lim \frac{d}{dt}\mathcal{U}(t-t_0)=-i\mathcal{T}(+i0)\,, \qquad (44)$$

where $\mathcal{T}(z)$ is the double-space analog of the scattering T matrix, obeying the Lippmann-Schwinger equation,

$$\mathcal{T}(z)=\mathcal{V}+\mathcal{V}(z-\mathcal{L}_0)^{-1}\mathcal{T}(z)\,, \qquad (45)$$

where $\mathcal{L}_0=\mathcal{L}-\mathcal{V}$. Here z is a complex number, and its limit on reaching the origin from above the real axis is taken in (44). All photon-counting rates can be expressed as double-space matrix elements of $\mathcal{T}$. Thus, e.g.,

$$C_S(1)=-i\langle\langle P_S(1);\hat{0}\,|\,\mathcal{T}(+i0)\,|\,\rho^{\mathrm{eq}};\hat{0}\rangle\rangle\,. \qquad (46)$$

Closely associated with $\mathcal{T}$ is the Green's operator $\mathcal{G}$, defined by

$$\mathcal{G}(z)=(z-\mathcal{L})^{-1}\,, \qquad (47)$$

in terms of which

$$\mathcal{T}(z)=\mathcal{V}+\mathcal{V}\mathcal{G}(z)\mathcal{V}\,. \qquad (48)$$

Its Fourier transform gives the time-evolution operator,

$$\mathcal{U}(t)=\pm(2\pi i)^{-1}\int_{-\infty}^{\infty}e^{-ixt}\mathcal{G}(x\pm i0)\,dx \quad (t\gtrless 0)\,. \qquad (49)$$

Another closely associated operator is the double-space analog of the Möller wave operator,

$$\mathcal{M}(z)=1+\mathcal{G}(z)\mathcal{V}\,, \qquad (50)$$

in terms of which steady-state solutions of the density matrix can be expressed as

$$\rho^{\mathrm{st}}=\langle\langle\hat{0}\,|\,\mathcal{M}(+i0)\,|\,\hat{0}\rangle\rangle\rho^{\mathrm{eq}}\,. \qquad (51)$$

In a scattering problem involving free molecules (with no thermal bath) and where all fields are in occupation-number states, (46) simply reduces to the Golden Rule, expressed in terms of the ordinary (dyadic) T matrix. The tetradic matrices $\mathcal{T}$ and $\mathcal{M}$ can be used to express scattering rates and steady-state populations in A, averaged over the thermal bath, in the presence of strong coherent radiation.

V. THERMALLY RELAXING SYSTEMS

The definition of $\mathcal{T}$ by (48) is not unique. Any division of $\mathcal{L}$ into $\mathcal{L}_0$ and $\mathcal{V}$ will do, provided only the initial state (density operator) and final state (projection operator) are stationary states of $\mathcal{L}_0$:

$$\mathcal{L}_0\,|\,\rho^{\mathrm{eq}};\hat{0}\rangle\rangle=\mathcal{L}_0\,|\,P_S;\hat{0}\rangle\rangle=0\,. \qquad (52)$$

We may include in $\mathcal{V}$ all interactions of A with the rest of the system. Some of them are "relevant" to the resonance scattering process, such as $\mathcal{V}_S$ or $\mathcal{V}_L^{\mathrm{cl}}$, and others are "irrelevant", such as the interactions with the bath ($\mathcal{V}_B=\mathcal{V}_F+\mathcal{V}_M$). The latter contribute to virtual processes, cascading, etc., which are not directly involved in the interaction of the free atomic system A with the relevant fields (L or S). Furthermore, the two types of interaction may coexist; A can interact with L while it is dynamically correlated to the bath. We shall use below a scheme in which only interactions of the relevant modes with the bare uncorrelated atomic system are incorporated in the relevant interaction. The $\mathcal{T}$ matrix is then explicitly expanded in power series of the relevant interaction. All other interactions (pure or mixed) are introduced as self-energy insertions (relaxation effects).

The distinction between "free" states of the relevant degrees of freedom and states in which they are dynamically correlated to the bath can be formally achieved by using double-space projection operators of the kind introduced by Zwanzig.[59,64] Suppose we divide the complete double space into two parts by the complementary projection operators $\mathcal{P}$ and $\mathcal{Q}=1-\mathcal{P}$. A proper way to choose $\mathcal{P}$ will be discussed later below. Define

$$\begin{aligned}\mathcal{V}^{\mathrm{r}}&=\mathcal{P}(\mathcal{V}_L^{\mathrm{cl}}+\mathcal{V}_S)\mathcal{P}\,,\\ \mathcal{V}^{\mathrm{ir}}&=\mathcal{V}-\mathcal{V}^{\mathrm{r}}=\mathcal{P}\mathcal{V}_B\mathcal{P}+\mathcal{P}\mathcal{V}\mathcal{Q}+\mathcal{Q}\mathcal{V}\mathcal{P}+\mathcal{Q}\mathcal{V}\mathcal{Q}\,,\end{aligned} \qquad (53)$$

as the "relevant" and "irrelevant" parts of the interaction, respectively. In calculating a matrix element of $\mathcal{T}$ in the $\mathcal{P}$ subspace, we can use double-perturbation expansions in terms of $\mathcal{V}^{\mathrm{r}}$ and $\mathcal{V}^{\mathrm{ir}}$, of the kind used in the distorted-wave method. Collecting first terms involving $\mathcal{V}^{\mathrm{ir}}$ into proper self-energy insertions, defined by

$$\Sigma(z)=\mathcal{P}\mathcal{V}_B\mathcal{P}+\mathcal{P}\mathcal{V}\mathcal{Q}(z-\mathcal{Q}\mathcal{L}\mathcal{Q})^{-1}\mathcal{Q}\mathcal{V}\mathcal{P}\equiv\mathcal{P}\sigma(z)\mathcal{P}\,, \qquad (54)$$

we finally get

$$\mathcal{P}\mathcal{T}(z)\mathcal{P}=[\mathcal{M}^{\mathrm{ir}}_{(-)}(z)\mathcal{T}^{\mathrm{r}}(z)+\Sigma(z)]\mathcal{M}^{\mathrm{ir}}_{(+)}(z)\,. \qquad (55)$$

Here

$$\mathcal{T}^{\mathrm{r}}(z)=\mathcal{V}^{\mathrm{r}}+\mathcal{V}^{\mathrm{r}}\mathcal{G}^{\mathrm{r}}(z)\mathcal{V}^{\mathrm{r}}\,, \qquad (56)$$

where

$$\mathcal{G}^{\mathrm{r}}(z)=[z-\mathcal{L}_0^{\mathrm{r}}-\Sigma(z)-\mathcal{V}^{\mathrm{r}}]^{-1}\,, \qquad (57)$$

and $\mathcal{L}_0^{\mathrm{r}}=\mathcal{P}\mathcal{L}_0\mathcal{P}$. The operator $\mathcal{T}^{\mathrm{r}}$ is defined explicitly in terms of the relevant interaction $\mathcal{V}^{\mathrm{r}}$, with bath effects introduced through the contribution of $\Sigma(z)$ to the propagator $\mathcal{G}^{\mathrm{r}}(z)$. The operators

$$\begin{aligned}\mathcal{M}^{\mathrm{ir}}_{(+)}(z)&=1+[z-\mathcal{L}_0^{\mathrm{r}}-\Sigma(z)]^{-1}\Sigma(z)\,,\\ \mathcal{M}^{\mathrm{ir}}_{(-)}(z)&=1+\Sigma(z)[z-\mathcal{L}_0^{\mathrm{r}}-\Sigma(z)]^{-1}\,,\end{aligned} \qquad (58)$$

that precede and follow $\mathcal{T}^{\mathrm{r}}$, respectively, are a kind of Möller operators that describe the rearrangement of the initial and final states by the irrelevant interactions. The extra $\Sigma(z)$ in (55) allows for transitions from the initial to the final state by irrelevant interactions solely.

We are now in a position to define the projection operator. First of all, we should require that the initial state $|\rho^{eq};\hat{0}\rangle\!\rangle$ and the final state $|P_S;\hat{0}\rangle\!\rangle$ lie completely in the subspace spanned by $\mathcal{P}$. As $\mathcal{V}_S$ is not included in $\Sigma(z)$, it immediately follows that

$$\langle\!\langle P_S;\hat{0}|\Sigma(z)=0, \quad \langle\!\langle P_S;\hat{0}|\mathcal{M}^{\rm ir}_{(-)}(z)=\langle\!\langle P_S;\hat{0}| , \qquad (59)$$

allowing us to omit $\mathcal{M}^{\rm ir}_{(-)}$ and the intermediate $\Sigma(z)$ from (55). Next, we require that $\mathcal{P}$ be defined so that $\mathcal{V}_L^{\rm cl}$ cannot induce correlations with the bath if they are not already present. This means that $\mathcal{V}_L^{\rm cl}$ does not contribute to $\mathcal{P}\mathcal{V}\mathcal{Q}$ and $\mathcal{Q}\mathcal{V}\mathcal{P}$, but may contribute to $\mathcal{Q}\mathcal{V}\mathcal{Q}$. (The corresponding contribution of $\mathcal{V}_S$ is vanishingly small.) The *equilibrium* proper self-energy is the limit of $\Sigma(z)$ in the absence of $\mathcal{V}_L^{\rm cl}$,

$$\Sigma^{eq}(z)=\lim_{\alpha_L\to 0}\Sigma(z) . \qquad (60)$$

By matter of *defining* the equilibrium state,

$$\Sigma^{eq}(z)|\rho^{eq};\hat{0}\rangle\!\rangle=0 . \qquad (61)$$

It seems as if $\Sigma(z)$ would not obey this rule owing to the inclusion of the external field. Recall, however, that ρ^{eq} was separated into an uncorrelated product by Eq. (1) as a convenient approximation. The true equilibrium state is a stationary state of the *full* Liouvillian $\mathcal{L}-\mathcal{V}_L^{\rm cl}$ in the absence of the external fields, including $\mathcal{V}_B$. In an expansion of the time evolution in powers of all interactions, ρ^{eq} remains unaffected and hence the system stays confined to the $\mathcal{P}$ subspace, until the first application of $\mathcal{V}_L^{\rm cl}$. But as $\mathcal{V}_L^{\rm cl}$ enters Σ only through $\mathcal{Q}\mathcal{V}\mathcal{Q}$, it cannot modify the equilibrium state. Hence

$$\Sigma(z)|\rho^{eq};\hat{0}\rangle\!\rangle=0, \quad \mathcal{M}^{\rm ir}_{(+)}(z)|\rho^{eq};\hat{0}\rangle\!\rangle=|\rho^{eq};\hat{0}\rangle\!\rangle , \qquad (62)$$

irrespective of the presence of the external fields. The scattering problem is then completely specified by substituting $\mathcal{T}^{\rm r}$ for $\mathcal{T}$ in (46), the new expression beginning with $\mathcal{V}_L^{\rm cl}$ on the right and ending with $\mathcal{V}_S$. Similarly $\mathcal{T}^{{\rm r}(-)}$ substitutes $\mathcal{T}^{(-)}$ in a similar expression for the attenuation rate, with $\mathcal{T}^{{\rm r}(-)}$ ending with $\mathcal{V}_L^{\rm cl-}$ on the left.

A projection operator in double space that meets both requirements made above is the Zwanzig projection operator[59,60,64]

$$\mathcal{P}^{(0)}=|\rho_B^{eq}\rangle\!\rangle\langle\!\langle I_B| , \qquad (63)$$

where I_B is the unit operator in the bath degrees of freedom. Given a tetradic operator $\mathcal{A}$, $\mathcal{P}^{(0)}$ averages it out over the bath:

$$\mathcal{P}^{(0)}\mathcal{A}\rho^{eq}={\rm tr}_B(\mathcal{A}\rho_B^{eq})\rho^{eq}\equiv\langle\mathcal{A}\rangle_B\rho^{eq} , \qquad (64)$$

where the trace is taken over all bath degrees of freedom, leaving $\langle\mathcal{A}\rangle_B$ defined on the relevant degrees of freedom $(A+L+S)$. Double-space vectors in the subspace projected by $\mathcal{P}^{(0)}$ can be labeled $|ab;n_Sn'_S;\hat{n}\rangle\!\rangle$, where $|ab\rangle\!\rangle$ represents the operator $|a\rangle\langle b|$ (in the space of eigenstates of H_A), and $|n_Sn'_S\rangle\!\rangle$ represents $|n_S\rangle\langle n'_S|$ in the space of occupation-number states of S. These are eigenvectors of $\mathcal{L}_0^{\rm r}$:

$$\mathcal{L}_0^{\rm r}|ab;n_Sn'_S;\hat{n}\rangle\!\rangle =[\omega_{ab}+(n_S-n'_S)\omega_S-\hat{n}\cdot\omega]|ab;n_Sn'_S;\hat{n}\rangle\!\rangle , \qquad (65)$$

where $\hbar\omega_{ab}$ is the energy difference between a and b.

The proper self-energy $\Sigma(z)$ defined in terms of $\mathcal{P}^{(0)}$ incorporates all relaxation phenomena as *virtual* radiative processes (including radiative damping, collision broadening, etc.). It does not incorporate fluorescence cascades[50] as true (intermediate and final) states. In order to incorporate cascading in the definition of $\Sigma(z)$, let us define the sequence of operators

$$\xi_B^{(1)}=\sum_F a_F^\dagger\rho_B^{eq}a_F , \qquad (66)$$

$$\xi_B^{(2)}=\sum_F\sum_{F'\neq F} a_{F'}^\dagger a_F^\dagger\rho_B^{eq}a_Fa_{F'} ,$$

$$\vdots$$

describing states of one-photon cascades, etc., coexisting with the rest of the system in thermal equilibrium. The extended definition of $\mathcal{P}$ would be

$$\mathcal{P}=\sum_{m=0}^{\infty}\mathcal{P}^{(m)}, \quad \mathcal{P}^{(m)}=|\xi_B^{(m)}\rangle\!\rangle\langle\!\langle I_B| \quad (m=1,2,\ldots) . \qquad (67)$$

As the coincidence of two photons in the same F mode is vanishingly small, in the limit of large volume, each time $\Sigma(z)$ reappears in the calculation it will be completely ignorant of the number of cascade photons already present. Using (67) for $\mathcal{P}$ in radiative damping we therefore get

$$\Sigma(z)=\Sigma^{(0)}(z)+\Sigma^{(1)}(z)+\cdots . \qquad (68)$$

Here, in terms of explicit matrix elements in F space of the operator σ introduced in (54),

$$\Sigma^{(0)}(z)=\langle\!\langle 0_F0_F|\sigma(z)|0_F0_F\rangle\!\rangle \qquad (69)$$

incorporates virtual processes (including radiative damping),

$$\Sigma^{(1)}(z)=\sum_F\langle\!\langle 1_F1_F|\sigma(z)|0_F0_F\rangle\!\rangle \qquad (70)$$

represents a one-photon cascade, etc. Note that $\Sigma(z)$ incorporates all intramolecular transitions induced by the bath (elastic as well as inelastic), since it is defined on the complete Hilbert space of A.

Having thus fully specified the projection operator, we have reduced the problem to the relevant subspace of Eq. (65). Using $\mathcal{T}^{\mathrm{r}}$ and $\mathcal{G}^{\mathrm{r}}$, defined on this basis, we can write down the expressions for scattering and attenuation: So, for one-photon scattering,

$$C_S(1) = -i \sum_{ab} \langle\!\langle bb; 1_S 1_S; \hat{0} | \mathcal{T}^{\mathrm{r}}(+i0) | aa; 0_S 0_S; \hat{0} \rangle\!\rangle \rho_a^{\mathrm{eq}} \quad (S \in \{L\}), \quad (71)$$

where $\mathcal{T}^{\mathrm{r}}$ is quadratic in $\mathcal{V}_S$, but to arbitrary power in $\mathcal{V}_L^{\mathrm{cl}}$. Similarly,

$$A_S = -\tfrac{1}{2}\,\mathrm{Im} \sum_{abcd} \beta_{ab}^{(1S)*} \sum_{L} [\langle\!\langle ab; \hat{1}_S | \mathcal{G}^{\mathrm{r}}(+i0) | cd; \hat{1}_L \rangle\!\rangle \beta_{cd}^{(1L)} - \langle\!\langle ab; \hat{1}s | \mathcal{G}^{\mathrm{r}}(+i0) | dc; -\hat{1}_L \rangle\!\rangle \beta_{cd}^{(1L)*}] (\rho_d^{\mathrm{eq}} - \rho_c^{\mathrm{eq}}) \quad (S \in \{L\}), \quad (72)$$

where the sum over L is carried over all external field modes, and

$$\beta_{cd}^{(1L)} = -(2/\hbar) \langle c | \vec{\mu}_A \cdot \vec{\epsilon}_L e^{i\vec{k}_L \cdot \vec{R}_A} | d \rangle \mathcal{E}_L^{+} \quad (73)$$

is the coupling coefficient, the absolute value of which is the Rabi nutation frequency of the transition $d \to c$. The interaction $\mathcal{V}^{\mathrm{r}}$ in (72) contains only the classical-field interaction $\mathcal{V}_L^{\mathrm{cl}}$.

VI. THE PROPER SELF-ENERGY

Given a complete basis of vectors $|\alpha\beta; \hat{n}\rangle\!\rangle$ in double space, Liouvillian operators generally obey the symmetry rules

$$\langle\!\langle \alpha\beta; \hat{n} | \mathcal{L} | \gamma\delta; \hat{n}' \rangle\!\rangle = \langle\!\langle \gamma\delta; \hat{n}' | \mathcal{L} | \alpha\beta; \hat{n} \rangle\!\rangle^* = -\langle\!\langle \beta\alpha; -\hat{n} | \mathcal{L} | \delta\gamma; -\hat{n}' \rangle\!\rangle^* . \quad (74)$$

The first equality expresses Hermitian conjugation. The latter is called Liouville conjugation[60,61]; it is closely associated with the microscopic reversibility of the time evolution under time reversal. Considering the proper self-energy as an operator defined on the reduced basis of Eq. (65), one gets as a result of Liouville conjugation

$$\langle\!\langle ab; n_S n'_S; \hat{n} | \Sigma(z) | cd; n_S n'_S; \hat{n} \rangle\!\rangle = -\langle\!\langle ba; n'_S n_S; -\hat{n} | \Sigma(-z^*) | dc; n'_S n_S; -\hat{n} \rangle\!\rangle^* . \quad (75)$$

Equation (75) allows for the division of $\Sigma(z)$ into an antisymmetric part (Δ) and a symmetric part (Γ) under Liouville conjugation,

$$\Sigma(z) = \Delta(z) - i\Gamma(z) . \quad (76)$$

While Δ is interpreted as a frequency-shift matrix, acting as a perturbation of $\mathcal{L}_0^{\mathrm{r}}$, Γ is interpreted as a relaxation matrix, having the opposite character under time reversal.

As defined in (54), the proper self-energy depends on the external fields through the inclusion of $\mathcal{V}_L^{\mathrm{cl}}$ in $\mathcal{Q}\mathcal{L}\mathcal{Q}$, in addition to $\mathcal{V}_B$. Let $\mathcal{P}$ be interpreted as representing states of the "bare" relevant system ($A + L + S$), uncorrelated with the bath (the latter being in a state of thermal equilibrium), and $\mathcal{Q}\mathcal{V}_B\mathcal{P}$ be interpreted as inducing such dynamic correlations as virtual excitations of the bath. Σ^{eq} is a measure of the effect of such virtual excitations in equilibrium. The occurrence of $\mathcal{V}_L^{\mathrm{cl}}$ with the bath excitations in $\mathcal{Q}\mathcal{V}\mathcal{Q}$ modifies these virtual excitation rates.

In order to understand under what conditions such modifications become necessary, one should study first the meaning of the various time scales associated with $\Sigma(z)$.

The magnitude of elements of $\Gamma(i0)$ is interpreted as an inverse *relaxation* time. Following the terminology of Bloch and followers,[47,48] one usually associates a T_1 relaxation time with elements of Γ connecting level "populations",

$$T_1 \sim |\langle\!\langle aa | \Gamma | bb \rangle\!\rangle|^{-1} , \quad (77)$$

and a T_2 relaxation time with elements connecting two-level "coherences",

$$T_2 \sim |\langle\!\langle ab | \Gamma | cd \rangle\!\rangle|^{-1} \quad (a \neq b, c \neq d) . \quad (78)$$

The z dependence of $\Gamma(z)$ serves to introduce another time parameter, τ, called the *correlation* (or *memory*) time, as the characteristic decay time of the memory kernel,[64,65]

$$\Phi(t) = (2\pi i)^{-1} \int_{-\infty}^{\infty} \Gamma(x + i0) e^{-ixt} dx \quad (t > 0) , \quad (79)$$

e.g., by defining

$$\tau = \left| \int_0^\infty t\Phi(t)\, dt \Big/ \int_0^\infty \Phi(t)\, dt \right| . \quad (80)$$

To be more specific, (80) is a matrix relation. However, we shall refer below to τ as an order-of-magnitude parameter, generally meaning an upper bound to the various elements of (80).

A third type of characteristic time, associated with the coupling strength to the external fields, is the inverse of the Rabi nutation frequency, β^{-1}, where

$$\beta \sim |\beta_{ab}^{(1L)}| \,. \tag{81}$$

The latter serves to introduce a time scale over which the external fields appreciably modify the density matrix. In order to see effects peculiar to strong fields, such as saturated absorption, or multiphoton processes, we ought to have

$$\beta T_i \gtrsim 1 \quad (i=1,2)\,. \tag{82}$$

On the other hand, if we want to retain only couplings of the field to the bare atom, leaving $\Sigma(z)$ dependent on equilibrium properties only, β should be small on the scale of the inverse correlation time,

$$\beta\tau \ll 1\,. \tag{83}$$

Obviously, both (82) and (83) can be met only if

$$\tau \ll T_i \quad (i=1,2)\,. \tag{84}$$

Condition (84), which frequently holds in many dilute (or weakly coupled) systems, such as dilute gases, is known as the short-memory limit.[64,65] It enables us to define a significant range of the coupling strength β over which strong-field effects can be observed without having to modify the equilibrium relaxation rates, replacing $\Sigma(z)$ by $\Sigma^{\text{eq}}(z)$. Major simplifications are obtained in this range: (i) As $\Sigma^{\text{eq}}(z)$ depends only on $\mathcal{V}_B$, its calculation is simpler, (ii) $\Sigma^{\text{eq}}(z)$ is diagonal in Floquet space:

$$\langle\langle ab;\hat{n}' | \Sigma^{\text{eq}}(z) | cd;\hat{n}\rangle\rangle = \delta_{\hat{n}\hat{n}'} \Sigma_{ab;cd}^{\text{eq}(\hat{n})}(z)\,, \tag{85}$$

cutting down many possible couplings. (iii) The symmetry of Σ^{eq} is determined by ρ_B^{eq}. If the bath is isotropic (spherically symmetric), as in fluids, Σ^{eq} is invariant under rotations, and is correspondingly simplified, allowing the use of reduced matrix elements, independent of the degeneracy quantum numbers (see Appendix A). Since only elements such as (85), with $\omega_{ab} - \omega_{cd}$ small, are generally important, therefore, barring accidental near-degeneracy of two states of the same symmetry species, we shall not have matrix elements connecting "populations" with "coherences".

A most important simplification arising from (84), but not necessarily requiring (83), is the Markovian approximation. As τ is much shorter than T_1 and T_2, we can replace $\Sigma(z)$ by its value at the origin, $\Sigma(+i0)$, over a margin of z values (along the real axis) that is wide compared to the magnitude of Σ. Therefore, one can approximately Fourier transform $\mathcal{G}^{\text{r}}(z)$ of Eq. (57), to obtain a time-evolution operator for the reduced $(A+L+S)$ space, with $\Sigma(z)$ as constant parameters,

$$\Sigma(x+i0) \approx \Sigma(+i0) \quad (\tau \ll T_1, T_2)\,. \tag{86}$$

By differentiation with respect to time, one then gets

$$\frac{\partial}{\partial t}\rho^{\text{r}}(t) = -i[\mathcal{L}_0^{\text{r}} + \mathcal{V}^{\text{r}} + \Sigma(i0)]\rho^{\text{r}}(t)\,, \tag{87}$$

where

$$\rho^{\text{r}}(t) = \mathcal{P}\rho(t)\mathcal{P} \tag{88}$$

is the reduced density matrix of the relevant system. In homogeneously broadened systems, where effects of the positional (translational) states of A are negligible, (87) is reduced to the discrete set of internal states of A, where it constitutes the Bloch equation. (For translational effects see Appendix B.) Note, however, that as (83) is not necessary, we obtain a modified Bloch equation, with field-dependent relaxation rates, when very strong fields are present, such that

$$\beta\tau \gtrsim 1\,. \tag{89}$$

The structure of the modified equations is then considerably complicated, as symmetry breaking and nondiagonality in Floquet space introduce many new couplings. As we shall see below, these modifications can be safely neglected in radiative damping, but may become significant in collision broadening, particularly where inelastic (T_1) processes are involved.

VII. RESONANCE SCATTERING

Before discussing specific relaxation mechanisms, let us consider one further simplification, namely, the reduction of the complete set of vectors $|ab\rangle\rangle$ in A space into a subset of level pairs resonantly coupled to the relevant radiation modes. This step is essential, because one is generally concerned with only a small number of levels, and the errors (or corrections) involved in neglecting all the rest should be known.

Consider all vectors $|ab, n_S n_S'; \hat{n}\rangle\rangle$ involving a pair of levels a, b of A that are directly connected by application of $\mathcal{V}_L^{\text{cl}}$ (to any power) or $\mathcal{V}_S$ or both, and that obey

$$|\omega_{ab} + (n_S - n_S')\omega_S - \hat{n}\cdot\omega| \leqslant \delta\,. \tag{90}$$

Here δ is an arbitrarily chosen fixed interval, qualified only by the requirement that

$$\beta, |\Sigma_{ab;cd}| \ll \delta \ll \omega_L \tag{91}$$

(which can be easily met in optical spectra). The $\mathcal{P}$ space is thus divided into a *resonance set* defined by the requirements made above and the complementary off-resonance set. This division is formally summarized by introducing proper projection operators,

$$\mathcal{P}=\mathcal{P}^R+\mathcal{P}^N. \tag{92}$$

The projection of $\mathcal{T}^{\mathrm{r}}$ onto the resonance set by $\mathcal{P}^R$ can be expressed in terms of operators confined to this subspace, using the same methods that led to the separation of "relevant" from "irrelevant" interactions. So,

$$\mathcal{T}^R(z)=\mathcal{P}^R\mathcal{T}^{\mathrm{r}}(z)\mathcal{P}^R=\mathcal{W}(z)+\mathcal{W}(z)\mathcal{G}^R(z)\mathcal{W}(z). \tag{93}$$

Here

$$\mathcal{W}(z)=\mathcal{P}^R\mathcal{V}^{\mathrm{r}}\mathcal{P}^R+\mathcal{P}^R\mathcal{V}^{\mathrm{r}}\mathcal{P}^N[z-\mathcal{P}^N(\mathcal{L}_0^{\mathrm{r}}+\mathcal{V}^{\mathrm{r}})\mathcal{P}^N]^{-1}\mathcal{P}^N\mathcal{V}^{\mathrm{r}}\mathcal{P}^R, \tag{94}$$

where, thanks to (91), we have neglected the proper self-energy $\Sigma(z)$ accompanying $\mathcal{L}_0^{\mathrm{r}}$ in the denominator in (94). Also,

$$\mathcal{G}^R(z)=[z-\mathcal{L}_0^R-\Sigma^{\mathrm{eff}}(z)-\mathcal{W}(z)]^{-1}, \tag{95}$$

where $\mathcal{L}_0^R=\mathcal{P}^R\mathcal{L}_0^{\mathrm{r}}\mathcal{P}^R$ is the matrix of resonance frequencies obeying (90), and

$$\Sigma^{\mathrm{eff}}(z)=\mathcal{P}^R\Sigma(z)\mathcal{P}^R+\mathcal{P}^R\Sigma(z)\mathcal{P}^N\{z-\mathcal{P}^N[\mathcal{L}_0^{\mathrm{r}}+\Sigma(z)]\mathcal{P}^N\}^{-1}\times\mathcal{P}^N\Sigma(z)\mathcal{P}^R. \tag{96}$$

In this manner, the interaction $\mathcal{V}^{\mathrm{r}}$ defined on the complete set $\mathcal{P}$ is replaced by $\mathcal{W}(z)$ on $\mathcal{P}^R$ and $\Sigma(z)$ is replaced by $\Sigma^{\mathrm{eff}}(z)$. As $\mathcal{W}(z)$ is practically independent of the self-energy, the corrections to the single-photon coupling $\mathcal{P}^R\mathcal{V}^{\mathrm{r}}\mathcal{P}^R$ can be considered as representing *simultaneous* transitions of two or more photons, with no intermediate-state time-delay effects.

Consider, for example, the second-order term

$$\mathcal{W}^{(2)}=\mathcal{P}^R\mathcal{V}^{\mathrm{r}}\mathcal{P}^N(z-\mathcal{P}^N\mathcal{L}_0^{\mathrm{r}}\mathcal{P}^N)^{-1}\mathcal{P}^N\mathcal{V}^{\mathrm{r}}\mathcal{P}^R. \tag{97}$$

Its matrix element between the "population" vector $|aa\rangle\!\rangle$ and the two-photon coherence $|ac\rangle\!\rangle$ (involving a summation over a complete set of intermediate levels b),

$$\langle\!\langle ca;\hat{2}_L|\mathcal{W}^{(2)}|aa;\hat{0}_L\rangle\!\rangle=\hbar^{-2}\sum_b(V_L^{\mathrm{cl}+})_{cb}(\omega_L-\omega_{ba})^{-1}(V_L^{\mathrm{cl}+})_{ba}\equiv\tfrac{1}{2}\beta_{ca}^{(\hat{2}_L)}(\omega_L), \tag{98a}$$

is the coupling coefficient for simultaneous two-photon absorption. Similarly, the second-order element

$$\langle\!\langle ca;1_S0_S;\hat{1}_L|\mathcal{W}^{(2)}|aa;0_S0_S;\hat{0}_L\rangle\!\rangle=\hbar^{-2}\sum_b[(V_S^{+})_{cb}(\omega_L-\omega_{ba})^{-1}(V_L^{\mathrm{cl}+})_{ba}+(V_L^{\mathrm{cl}+})_{cb}(-\omega_S-\omega_{ba})^{-1}(V_S^{+})_{ba}]\equiv\tfrac{1}{2}\beta_{ca}^{(1_S,\hat{1}_L)} \tag{98b}$$

is the coupling coefficient for ordinary (nonresonant) Raman scattering. $\mathcal{W}^{(2)}$ may also have diagonal elements between coherences, by undergoing nonresonant virtual transitions. Thus

$$\langle\!\langle ab;\hat{n}_L|\mathcal{W}^{(2)}|ab;\hat{n}_L\rangle\!\rangle=\frac{1}{2}\sum_{\pm}[\beta_{aa}(\pm\omega_L)-\beta_{bb}(\pm\omega_L)] \tag{99}$$

is the Bloch-Siegert shift[66,67] of the $\hat{n}_L$-photon coherence, the β coefficients being defined by (98a) with the exception that $V_L^{\mathrm{cl}-}$ replaces one of the two interaction-matrix elements. The approximation

$$\mathcal{W}\approx\mathcal{W}^{(1)}=\mathcal{P}^R\mathcal{V}^{\mathrm{r}}\mathcal{P}^R \tag{100}$$

is commonly known as the *rotating-wave approximation*.

Nondiagonal high-order couplings, such as (98), that involve a change in $\hat{n}_L$ or n_S, can be added to the "relevant" interaction (100) as representing resonance couplings of a higher order, together constituting an *extended* RWA. Elements such as (99) (Bloch-Siegert shifts), that are diagonal in the relevant photon numbers, can be added as perturbations to the resonance-frequency matrix $\mathcal{L}_0^R$. These perturbations will not be dealt with further below.

The proper self-energy has also undergone modifications by projecting onto the resonance set, as is evident by (96). In addition to the direct relaxation couplings $\mathcal{P}^R\Sigma\mathcal{P}^R$, indirect couplings can occur through intermediate states not belonging to the resonance set. Such, for example, is the element

$$\Sigma_{cc;aa}^{\mathrm{eff}}=-i\left\{\Gamma_{cc;aa}+\sum_{bb'}\Gamma_{cc;b'b'}\times(iz-\Gamma)^{-1}_{b'b';bb}\Gamma_{bb;aa}\right\}\quad(c\neq a) \tag{101}$$

(Δ having no elements in the space of "populations" $|aa\rangle\!\rangle$). An element $c\neq a$ expresses the enhancement of the direct T_1 relaxation from a to c [$\Gamma_{cc;aa}(i0)$ being negative] by indirect transitions through intermediate levels b, b', etc., which are not interrupted by resonance interaction with the radiation.

Elements of (101) with $c=a$ represent an increase of the lifetime of level a [$\Gamma_{aa;aa}(i0)$ being positive] by cross exchange with neighboring energy levels. Such an exchange is possible if the transition from a to b is (at least partially) reversible. If b is a long-lived metastable state, a member of a dense set of levels (as in internal conversion), or a true continuum state (e.g., when a is a predissociation state, or an autoionizing state), the exchange is irreversible and the corrections to Γ will vanish. It is important to realize that the projection $\mathcal{P}$ is defined on the *complete* set of states of the relevant degrees of freedom, and hence the sum rule

$$\sum_b \Gamma_{bb;aa} = 0 , \qquad (102)$$

expressing conservation of population, is obeyed. Irreversible transitions of the kind described above, where the b states cannot be reached by the radiation processes, will lead to a depletion of populations in the resonance set, leading to vanishing steady-state solutions.

It is nevertheless possible to observe the *transient* behavior of the resonance set in such cases, by resorting to the dynamical equations. The z dependence of the principal-part contributions to $\mathcal{W}(z)$ is very slow, owing to (91), allowing their replacement by $\mathcal{W}(i0)$ in Fourier transforming to derive the time dependence. (The δ-function contributions are very rapidly oscillating in time and can be neglected on a "coarse-grained" time scale.) If, in addition, $\Sigma^{\text{eff}}(z)$ is also a slowly varying function of z, one can write down a reduced Bloch equation (in the limit of homogeneous broadening only), defined on the resonance set only, with $\mathcal{V}^r$ replaced by $\mathcal{W}(i0)$ and $\Sigma(i0)$ by $\Sigma^{\text{eff}}(i0)$:

$$\frac{\partial}{\partial t}\rho^R(t) = -i[\mathcal{L}_0^R + \mathcal{W}(i0) + \Sigma^{\text{eff}}(i0)]\rho^R(t) + i\Sigma^{\text{eff}}(i0)\rho^{R,\text{eq}} . \qquad (103)$$

Here

$$\rho^R(t) = \mathcal{P}^R \rho(t) \mathcal{P}^R , \qquad (104)$$

with $\mathcal{L}_0^R$ containing only the slowly oscillating (near-resonance) eigenvalues of $\mathcal{L}_0^r$. The extra term involving ρ^{eq} should be added, since the equilibrium condition (62) generally does not apply to the incomplete subspace $\mathcal{P}^R$.

In resonance subsets where escape by relaxation is (at least partially) reversible, nonvanishing steady-state solutions exist, and one can use the reduced operators $\mathcal{T}^R$ and $\mathcal{G}^R$ to obtain the resonance attenuation and scattering rates. The coupling coefficients in (72), for example, should be replaced by higher-order coupling coefficients if simultaneous two-photon transitions are involved in the cd or ab resonances, provided that at least one of the photons in the ab resonance is an S-mode photon.

VIII. LEVEL EXCITATIONS

A convenient aid to the calculation of attenuation rates and of steady-state populations of excited states is the matrix of level-to-level excitation rates,

$$W_{ba} = -i\langle\langle bb;\hat{0}|\mathcal{T}^R(+i0)|aa;\hat{0}\rangle\rangle . \qquad (105)$$

These are not transition rates in the true sense of taking the asymptotic time limits, since individual-level populations are not stationary states of $\Sigma(z)$, and therefore undergo relaxation following the resonance excitation [described by the operator $\mathfrak{M}^{ir}_{(-)}$ in (55)].

Suppose now that the final state $|bb;\hat{0}\rangle\rangle$ can be reached from the $\hat{n}_S$-photon resonance coherence $|db;\hat{n}_S\rangle\rangle$, with a coupling coefficient $\beta_{db}^{(\hat{n}_S)*}$. However, the same coherence can lead to $|dd;\hat{0}\rangle\rangle$, with the opposite-sign coefficient $-\beta_{db}^{(\hat{n}_S)*}$. Similarly, $|aa;\hat{0}\rangle\rangle$ and $|cc;\hat{0}\rangle\rangle$ both connect to $|ca;\hat{n}_L\rangle\rangle$ with $\pm\beta_{ca}^{(\hat{n}_L)}$. Considering that to each $|ca;\hat{n}_L\rangle\rangle$ there is a Liouville-conjugate $|ac;-\hat{n}_L\rangle\rangle$, and taking advantage of the symmetry of $\mathcal{G}^R$ under Liouville conjugation, we can write

$$W_{ab} = \sum_{SL}\sum_{ijkl}(\delta_{aj}-\delta_{ai})\hat{W}^{SL}_{ij;kl}(\delta_{bl}-\delta_{bk}) , \qquad (106)$$

where

$$\hat{W}^{SL}_{db;ca} = \tfrac{1}{2}\,\mathrm{Im}\,\beta_{db}^{(\hat{n}_S)*} \times [\langle\langle db;\hat{n}_S|\mathcal{G}^R(+i0)|ca;\hat{n}_L\rangle\rangle\beta_{ca}^{(\hat{n}_L)} - \langle\langle db;\hat{n}_S|\mathcal{G}^R(+i0)|ac;-\hat{n}_L\rangle\rangle\beta_{ca}^{(\hat{n}_L)*}] . \qquad (107)$$

Equation (107) expresses the contribution of the pair of resonance coherences ac and db to the excitation rate from a (or c) to b (or d).

The attenuation rate, expressed in terms of (107), is

$$A_S = -\sum_L\sum_{abcd}\hat{W}^{SL}_{db;ca}(\rho_a^{\text{eq}}-\rho_c^{\text{eq}}) = \sum_L\sum_{abcd}\hat{W}^{SL}_{bd;ca}(\rho_a^{\text{eq}}-\rho_c^{\text{eq}}) , \qquad (108)$$

where, by the resonance conditions, $\omega_{ca}>0$, $\omega_{db}>0$. In the two-level system ($\omega_{ab}>0$), this simply reduces to the well-known expression

$$A_S = -W_{aa}(\rho_a^{\text{eq}}-\rho_b^{\text{eq}}) = W_{ba}(\rho_a^{\text{eq}}-\rho_b^{\text{eq}}) \quad \text{(2 levels)} . \qquad (109)$$

Equation (72) is a particular application of (108) to one-photon resonances in the RWA.

The excitation rates are also useful in the calculation of steady-state populations. These populations are related to the equilibrium populations in a complete closed basis by

$$\rho^{st} = \mathcal{M}^{r}(+i0)\rho^{eq}, \tag{110a}$$

where

$$\mathcal{M}^{r}(z) = 1 + \mathcal{G}^{r}(z)\mathcal{V}^{r} = 1 + \mathcal{G}_0^{r}(z)\mathcal{T}^{r}(z), \tag{111a}$$

and

$$\mathcal{G}_0^{r}(z) = [z - \mathcal{L}_0^{r} - \Sigma(z)]^{-1} \tag{112a}$$

is the zero-interaction limit of $\mathcal{G}^{r}(z)$. This expression can be reduced to the resonance set if the set acts like a closed subset under the combined effect of resonance interaction and relaxation [i.e., if the sum rule (102) holds on the subset, with Γ^{eff} replacing Γ]:

$$\rho^{R,st} = \mathcal{M}^{R}(+i0)\rho^{R,eq}, \tag{110b}$$

where

$$\mathcal{M}^{R}(z) = 1 + \mathcal{G}^{R}(z)\mathcal{W}(z) = 1 + \mathcal{G}_0^{R}(z)\mathcal{T}^{R}(z) \tag{111b}$$

and

$$\mathcal{G}_0^{R}(z) = [z - \mathcal{L}_0^{R} - \Sigma^{eff}(z)]^{-1}. \tag{112b}$$

In this case the radiation simply redistributes the populations in the reduced set $\rho^R = \mathcal{P}^R\rho\mathcal{P}^R$, keeping the overall population in the set constant. Neglecting the rather unlikely possibility of having a matrix element of Σ connecting a "population" $|aa\rangle\!\rangle$ with a coherence $|ab\rangle\!\rangle$, we can rewrite (110b) in matrix notation (treating the populations as column vectors),

$$\rho^{R,st} = [I + \Gamma^{-1}W]\rho^{R,eq}, \tag{113}$$

where I is the unit matrix, and

$$\Gamma_{ab} = \langle\!\langle aa;\hat{0}\,|\,\Gamma^{eff}(+i0)\,|\,bb;\hat{0}\rangle\!\rangle \tag{114}$$

is the level-relaxation (T_1) matrix.

The excitation-rate matrix combines populations only. However, intermediate states in the Born expansion of $\mathcal{T}^R$ include both populations and coherences. Let us define the *single-passage* rate matrix R as the matrix combining populations via coherences only,

$$R_{ba} = -i\langle\!\langle bb;\hat{0}_L\,|\,\mathcal{T}^{R}_{coh}(+i0)\,|\,aa;\hat{0}_L\rangle\!\rangle, \tag{115}$$

where populations are excluded as intermediate states in $\mathcal{T}^{R}_{coh}$. In terms of R,

$$W = R[I - \Gamma^{-1}R]^{-1} = (R^{-1} - \Gamma^{-1})^{-1} \tag{116}$$

and

$$\rho^{R,st} = (I - \Gamma^{-1}R)^{-1}\rho^{R,eq}. \tag{117}$$

The introduction of the single-passage rates helps to simplify the calculations.[53] For example, when only one-photon transitions are involved, the dimensionality of the problem can be reduced stepwise by a renormalization scheme that introduces one-photon coherences, two-photon coherences, etc., in the form of a finite continued fraction. Also, it takes a population vector to cross from $\hat{n} > 0$ coherences to $\hat{n} < 0$ ones. Therefore

$$R = R^{(+)} + R^{(-)} = 2\,\mathrm{Re}R^{(+)}, \tag{118}$$

where in $R^{(\pm)}$ all intermediate coherences have positive (negative) $\sum \hat{n}_L$, the last equality in (118) following from Liouville-conjugation symmetry.

The introduction of R enables us to write a non-Markovian generalized rate equation involving only level populations (assuming Σ^{eff} is Markovian),

$$\frac{\partial}{\partial t}r(t) = -\Gamma[r(t) - \rho^{eq}] + \int_{-\infty}^{t} \tilde{R}(t - t')r(t')\,dt', \tag{119}$$

where

$$r_a(t) = \langle a\,|\,\rho_A(t)\,|\,a\rangle, \tag{120}$$

and the memory kernel is the Fourier transform of $R(z)$,

$$\tilde{R}(t) = (2\pi i)^{-1}\int_{-\infty}^{\infty} e^{-ixt}R(x + i0)\,dx \quad (t > 0), \tag{121}$$

$R(z)$ being the extension of $R = R(i0)$ to arbitrary z above the real axis. Notice that $\tilde{R}(t)$ usually depends only on coherence (T_2) propagators, and its time scale of variation is determined by the T_2 relaxation rates. Therefore, in the limit of strong T_2 relaxation (as when strong elastic collisions dominate the self-energy),

$$T_2 \ll T_1, \tag{122}$$

Eq. (119) reduces to the simple rate equation

$$\frac{\partial}{\partial t}r(t) = -\Gamma[r(t) - \rho^{eq}] + Rr(t), \tag{123}$$

and the level excitation can be treated as an incoherent rate process.[68]

IX. RADIATIVE DAMPING

Radiative damping in the presence of strong coherent fields has been studied from various points of view by several authors.[8,50] We shall therefore dwell only briefly on its properties, from the point of view presented here.

Consider the proper self-energy resulting from virtual radiative processes in the absence of collisions, and in the weak-field limit. The damping of the $\hat{n}_L$-photon resonance coherence $|ab\rangle\!\rangle$ is given by

$$\Sigma^{eq(\hat{n}_L)}_{ab;ab}(z) \equiv \langle\!\langle ab;\hat{n}_L\,|\,\Sigma^{eq}(z)\,|\,ab;\hat{n}_L\rangle\!\rangle. \tag{124}$$

The only contribution to $\mathcal{Q}\mathcal{V}\mathcal{P}$ in (54) comes here from spontaneous emission to all F modes. We consider the vacuum as the initial state in the optical limit implied by (3). Hence

$$\mathfrak{V}_F|ab;0_F0_F;\hat{n}_L\rangle\!\rangle=\hbar^{-1}\sum_c\left[\langle c1_F|V_F|a0_F\rangle|cb;1_F0_F;\hat{n}_L\rangle\!\rangle-\langle c1_F|V_F|b0_F\rangle^*|ac;0_F1_F;\hat{n}_L\rangle\!\rangle\right]. \tag{125}$$

Summing over all virtual atomic states, and over all F modes,

$$\Sigma^{\mathrm{eq}(\hat{n}_L)}_{ab;ab}(z)=\hbar^{-2}\sum_F\sum_C\{|\langle c1_F|V_F|a0\rangle|^2(z-\omega_F+\omega_{bc}+\hat{n}_L\omega_L)^{-1}+|\langle c1_F|V_F|b0_F\rangle|^2(z-\omega_F-\omega_{ac}+\hat{n}_L\omega_L)^{-1}\}. \tag{126}$$

In the limit $z\to+i0$, and assuming near-resonance conditions $\hat{n}_L\omega_L\approx\omega_{ab}$, we simply get

$$\Sigma^{\mathrm{eq}(\hat{n}_L)}_{ab;ab}(+i0)\approx-\tfrac{1}{2}i(\gamma^{\mathrm{rad}}_a+\gamma^{\mathrm{rad}}_b), \tag{127}$$

where

$$\gamma^{\mathrm{rad}}_a=(2\pi/\hbar^2)\sum_F\sum_C|\langle c1_F|V|a0_F\rangle|^2\delta(\omega_F-\omega_{ac})$$

$$\equiv\sum_c\zeta^{\mathrm{rad}}_{ca} \tag{128}$$

is the spontaneous decay rate of level a. Equation (127) is obtained by neglecting the contribution of the Cauchy principal parts to (126), assuming that the coupling coefficients are very slowly varying functions of ω_F.

The memory kernel $\Phi(t)$ obtained by Fourier transforming $\Sigma^{\mathrm{eq}}(z)$, according to (79), is singular at short times ($t\to0$) under the approximations used here (of one-photon electric dipole emission and ω_{ac} an homogeneously broadened optical frequency, neglecting velocity effects).[8] This effectively corresponds to a *zero* correlation time for spontaneous radiative decay,

$$\tau_{\mathrm{rad}}\approx0. \tag{129}$$

Therefore, radiative damping is Markovian for all practical purposes. Furthermore, radiative decay rates should not be appreciably affected by the presence of strong fields, or by the presence of other relaxation mechanisms which are to be added independently to $\Sigma(z)$.

One-photon cascades contribute to off-diagonal elements of $\Sigma(z)$, such as

$$\Sigma^{(1)}_{bb;aa}(z)=\sum_F\langle\!\langle bb;1_F1_F;\hat{0}_L|\sigma(z)|aa;0_F0_F;\hat{0}_L\rangle\!\rangle$$

$$\approx i\zeta^{\mathrm{rad}}_{ba}\quad(z\to+i0), \tag{130}$$

where ζ_{ba} is the decay rate from a to b. Notice that the sum rule (102) is observed when a, b, etc., form a closed set under radiative decay. Cascading contributes also to cross relaxation between neighboring coherences. For example,

$$\Sigma^{(1)}_{cd;ab}(z)=\sum_F\langle\!\langle cd;1_F1_F;\hat{1}_L|\sigma(z)|ab;0_F0_F;\hat{1}_L\rangle\!\rangle$$

$$\approx\tfrac{1}{2}i(\zeta_{ca}g^*+\zeta_{ab}g^{-1})$$

$$(z\to i0,\ \omega_{ab}\approx\omega_{cd}\approx\hat{n}_L\omega_L), \tag{131}$$

where, ignoring space degeneracy, $g\approx\mu_{ab}/\mu_{cd}$ is the ratio of coupling coefficients.

X. COLLISION BROADENING

Collision broadening of linear-response one-photon spectra in dilute gaseous systems has been the subject of numerous publications.[69-71] Some work has been done on two-photon processes, simultaneous or resonant.[72-78] The theory is immediately extended to multiphoton resonance spectra in the domain of not-too-strong radiation, where (83) holds, the only complication arising from space degeneracy. In collision broadening, τ is the duration time of a collision (~10^{-12} sec at room temperature), whereas in dilute gases T_1 and T_2 are mean times between collisions (typically 10^{-8}–10^{-9} sec at atmospheric pressures). Therefore, the domain where field effects can be ignored is quite wide.

At higher field intensities, when (89) replaces (83), the collision-broadening rates should be modified by the presence of the fields. This is particularly important in T_1 processes governed by weak large-gap inelastic collisions where the presence of the radiation can help bridge the energy gap.[79-82] A comprehensive theory of such processes is still unavailable.

We shall deal here only with the theory of foreign-gas broadening, where the bath molecules are treated as distinct from A. The theory can be extended to incorporate resonance transfer by inelastic collisions between identical molecules, just as in the linear-response theories.[55,60]

In the binary-collision approximation, the operator $\sigma(z)$, from which $\Sigma(z)$ is calculated, is simply $N_B\langle\mathcal{T}_C(z)\rangle_B$, where $\mathcal{T}_C$ is the tetradic $\mathcal{T}$

matrix for the collision pair and N_B is the number of bath molecules. (An extra factor Λ^{-3}, the inverse volume, comes from the "box" normalization of the translational states, making $\Sigma(z)$ proportional to the gas density.) Using an expression relating the tetradic $\mathcal{T}$ matrix to the ordinary (dyadic) T matrix,[60] we get (ignoring space degeneracy)

$$\langle\langle cd;\hat{n}_L|\Sigma^{eq}(z)|ab;\hat{n}_L\rangle\rangle$$
$$=N_B\hbar^{-1}\sum_{\gamma\delta}\rho_\gamma^B\Big[\langle c\gamma|T(E_b+E_\gamma+\hat{n}_L\hbar\omega_L+\hbar z)|a\gamma\rangle\delta_{db}\delta_{\gamma\delta}-\delta_{ac}\delta_{\gamma\delta}\langle d\gamma|T(E_a+E_\gamma-\hat{n}_L\hbar\omega_L-\hbar z^*)|b\gamma\rangle^*$$
$$+(2\pi i)^{-1}\int_{-\infty}^{\infty}dx\,\mathfrak{D}^{(\hat{n}_L)}_{c\delta;d\delta}(x;z)\langle c\delta|T(x+\hat{n}_L\hbar\omega_L+\hbar z)|a\gamma\rangle\langle d\delta|T(x+i0)|b\gamma\rangle^*\mathfrak{D}^{(\hat{n}_L)}_{a\gamma;b\gamma}(x;z)\Big]. \tag{132}$$

Here ρ_γ^B is the equilibrium density matrix of the bath molecule, $|\gamma\rangle$, $|\delta\rangle$, etc., forming a complete basis;

$$\mathfrak{D}^{(\hat{n}_L)}_{a\gamma;b\delta}(x;z)=(\hat{n}_L\hbar\,\omega_L-E_a-E_\gamma+\hbar z+x)^{-1}$$
$$-(-E_b-E_\delta+x-i0)^{-1}\,; \tag{133}$$

T is the ordinary binary-collision scattering matrix, obeying the Lippmann-Schwinger equation,

$$T(\hbar z)=V_{AB}+V_{AB}(\hbar z-H_A-H_B)^{-1}T(\hbar z)\,, \tag{134}$$

with the collision-pair Hamiltonian $H_A+H_B+V_{AB}$.

Equation (132) is generally valid, in the binary-collision approximation, when $|a\rangle$, $|b\rangle$, etc., form a complete set of states of *all* degrees of freedom of A, including translational states. The limit of homogeneous broadening, where velocity effects can be neglected, is obtained by transferring the translational degrees of freedom to the role of bath degrees of freedom, incorporated in the summation over γ and δ in (132), leaving a, b, etc., as initial states only. This limit is particularly suitable for heavy A-type molecules perturbed by light B-type molecules with a short-range interaction. Otherwise, velocity effects (such as velocity-changing collisions) will enter $\Sigma(z)$ even in the limit where Doppler broadening is negligible.[83,84]

A frequently used approximation, valid when $\hat{n}_L\omega_L\approx\omega_{ab}\approx\omega_{cd}$, and the collision rates are much smaller than the inverse duration of collision τ_{coll}^{-1}, is the impact approximation.[62,85,86] Equation (132), in the limit $z\to i0$, can then be approximately expressed by on-the-energy-shell elements of T only. Again, ignoring degeneracy,

$$\langle\langle cd;\hat{n}_L|\Sigma^{eq}(i0)|ab;\hat{n}_L\rangle\rangle\approx N_B\hbar^{-1}\sum_{\gamma\delta}\rho_\gamma^B\{[\langle a\gamma|T(E_a+E_\gamma+i0)|a\gamma\rangle-\langle b\delta|T(E_b+E_\delta+i0)|b\delta\rangle^*]\delta_{ca}\delta_{db}\delta_{\delta\gamma}$$
$$+2\pi i\delta(E_a+E_\gamma-E_c-E_\delta)\langle c\delta|T(E_a+E_\gamma+i0)|a\gamma\rangle\,\langle d\delta|T(E_b+E_\delta+i0)|b\gamma\rangle^*\}. \tag{135}$$

The impact approximation is intimately related to the Markovian approximation. The latter, however, deals with the z dependence, while the former is concerned with the energy variables.

Using the "optical theorem" obeyed by on-the-energy-shell elements of the T matrix, we get for population-damping (T_1) rates (in the impact approximation)

$$\langle\langle cc;\hat{0}_L|\Sigma^{eq}(+i0)|aa;\hat{0}_L\rangle\rangle$$
$$=-i[\gamma_a^{\text{inel}}\delta_{ca}-\zeta_{ca}^{\text{inel}}(1-\delta_{ca})]\,, \tag{136}$$

where

$$\zeta_{ca}^{\text{inel}}=\sum_{\gamma\delta}2\pi N_B\hbar^{-1}\rho_\gamma^B|\langle c\delta|T(E_a+E_\gamma+i0)a\gamma\rangle|^2$$
$$\times\delta(E_a+E_\gamma-E_c-E_\delta) \tag{137}$$

is the rate of inelastic collisions from a to c, and

$$\gamma_a^{\text{inel}}=\sum_{c\neq a}\zeta_{ca}^{\text{inel}} \tag{138}$$

is the inverse collisional lifetime of level a. The proper self-energy for an $\hat{n}_L$-photon coherence ($\hat{n}_L\neq 0$) includes a frequency-shift contribution Δ, in addition to $-i\Gamma$. These shifts are usually quite small and will not be discussed here. Diagonal elements of the relaxation matrix are given (in the impact approximation) by

$$\langle\langle ab;\hat{n}_L|\Gamma^{eq}(+i0)|ab;\hat{n}_L\rangle\rangle=\tfrac{1}{2}(\gamma_a^{\text{inel}}+\gamma_b^{\text{inel}})+\gamma_{ab}^{\text{el}}\,, \tag{139}$$

where

$$\gamma_{ab}^{\mathrm{el}} = \pi N_B \hbar^{-1} \sum_{\gamma\delta} \rho_\gamma^B \left| \langle a\delta | T(E_a + E_\gamma + i0) | a\gamma \rangle - \langle b\delta | T(E_b + E_\gamma + i0) | b\gamma \rangle \right|^2 \delta(E_\gamma - E_\delta) \qquad (140)$$

is the proper-T_2 contribution of elastic collisions owing to interference (dephasing) of forward scattering amplitudes in the two levels a and b. The elastic proper-T_2 contribution is particularly important in atomic spectra, where the interaction potentials in the ground and excited states are very different, and inelastic collisions are very rare. Condition (122) then usually holds. In molecular spectra the relative contribution of inelastic collisions is usually not small. The expressions for the collision rates can be appreciably affected by the presence of very strong fields obeying (89), particularly when inelastic collision rates (137) involving a large energy gap

$$|E_a - E_c| \tau_{\mathrm{coll}} \gg 1 \qquad (141)$$

are concerned. The two-body interaction V_{AB} should then be augmented by V_L^{cl} in the calculation of the collision rates.

Strong fields can also affect elastic collisions by modifying the potential curves.[87] However, the magnitude of such an effect in dephasing collisions is not known.

Finally, we should recall that in the strong-field domain $\Sigma(z)$ becomes nondiagonal in the Floquet numbers $\hat{n}_L$, and the spectral structure is considerably complicated.

APPENDIX A: SPACE DEGENERACY

Most works on the response to strong fields avoid for obvious reasons the complications arising from space degeneracy (unless it is an essential part of the effect studied, as in the Hanle effect[50,88,89]). For a general introduction to rotational-symmetry considerations in the density-matrix formalism, the reader is referred to the review article by Omont.[90] We shall be satisfied here with a few fleeting observations.

The A-molecule basis $\{|a\rangle\}$ is completely specified by a set of principal quantum numbers (α), a total angular momentum (j_a), and the component of the angular momentum along a space-fixed axis (m_a). The Liouville-space set

$$|\alpha j_a m_a, \beta j_b m_b\rangle\!\rangle \quad (m_a = -j_a, \ldots, j_a;\, m_b = -j_b, \ldots, j_b) \qquad (\mathrm{A1})$$

forms a degenerate manifold, in which linear combinations can be formed to create a basis for the irreducible representations of the rotation group,[91]

$$|\alpha j_a, \beta j_b; JM\rangle\!\rangle = \sum_{m_a, m_b} (-1)^{j_b - m_b} C(j_a j_b J; m_a - m_b M) \times |\alpha j_a m_a, \beta j_b m_b\rangle\!\rangle\,, \qquad (\mathrm{A2})$$

with the help of the Clebsch-Gordan coefficients.

In the approximation of uncorrelated bath, and assuming that the bath is isotropic (e.g., collisions in a dilute gas), $\Sigma(z)$ is invariant under rotations and therefore is diagonal in J, M, and independent of M. Thus in the attenuation-rate problem,

$$\langle\!\langle \alpha' j_a', \beta' j_b'; J'M'; \hat{n} | \Sigma^{\mathrm{eq}}(z) | \alpha j_a, \beta j_b; JM; \hat{n} \rangle\!\rangle = \delta_{MM'} \delta_{JJ'} \langle\!\langle \alpha' j_a', \beta' j_b' | \Sigma^{(\hat{n}; J)}(z) | \alpha j_a, \beta j_b \rangle\!\rangle\,. \qquad (\mathrm{A3})$$

So, Σ^{eq} removes the degeneracy in J (but not in M) by introducing J-dependent relaxation coefficients.

The interaction with the external field, in the electric-dipole approximation, includes the first-rank tensor operator[92] $\mu^{(1)}$ which can alter J by ±1. M can generally change by 0, ±1, depending on the polarizations $\vec{\epsilon}_L$ of the external-field modes. However, things are considerably simplified in the particular case where all the modes have the *same* (linear) polarization direction. Choosing this direction as the quantization axis for the angular momentum, we have $\Delta M = 0$. The degeneracy is then completely removed by using $M = 0$ throughout the Born expansion of the transition rates, with J alternating by ±1 jumps, with a null value on both ends of the expansion. The intermediate possible values of J are bounded by the vector coupling condition,

$$0 \leqslant J \leqslant j_a + j_b\,, \qquad (\mathrm{A4})$$

given the basis (A2). Therefore, in a finite-level set, where j_a and j_b have the upper bound $j_{\max}$, J is bounded by $2j_{\max}$.

The situation is even further simplified if all field modes propagate in parallel and have the same *circular*, rather than linear, polarizations. For then (using the propagation direction as the quantization axis)

$$M = \pm J = \sum_L \hat{n}_L \qquad (\mathrm{A5})$$

at all intermediate steps in the Born expansion, thus tying up the allowed values of J to the Floquet numbers $\hat{n}$.

APPENDIX B: VELOCITY EFFECTS

The effect of strong fields on Doppler-broadened gas spectra, as an example of an inhomogeneously broadened system, has been studied extensively under the name of saturation, or Lamb-dip, spectroscopy.[27-36] We present it here using our general formalism, and discuss the limit under which inhomogeneous broadening can be eliminated.

The separation of the "relevant" degrees of freedom A from the bath B is a matter of optimal choice, guided by a hierarchy of time scales, on the one hand, and by the requirement of simplicity, on the other hand. System A should be so chosen as to make the relaxation time (T_1 or T_2) much longer than the correlation time (τ) for the interaction with B.

In ordinary gaseous systems, at low densities, the most natural choice of A is the isolated atom (or molecule), if cooperative phenomena are to be neglected. Correlations exist only during the relatively short duration of binary collisions. By the isolated molecule we mean all degrees of freedom (internal and translational). A reduction of the degrees of freedom constituting A is plausible only if there exists a further hierarchy of time scales within the set of one-molecule excitations.

The dependence of resonance frequencies on the translational states, through the Doppler effect, accounts for the inhomogeneous broadening. Let

$$\hbar \sum_L \hat{n}_L \vec{\mathrm{k}}_L \equiv \hbar \vec{\mathrm{K}}_{\hat{n}} \tag{B1}$$

be the momentum transfer associated with the coherence $|ab;\hat{n}\rangle\!\rangle$, where a, b, are internal molecular states. The momentum $\hbar\vec{\mathrm{p}}$, associated with the center-of-mass motion of the molecule A, spans a Euclidean (R_3) manifold of such coherences in double space,

$$|ab(\vec{\mathrm{p}});\hat{n}\rangle\!\rangle \equiv |ab;\vec{\mathrm{p}}+\vec{\mathrm{K}}_{\hat{n}},\vec{\mathrm{p}};\hat{n}\rangle\!\rangle \quad (\vec{\mathrm{p}}\in R_3). \tag{B2}$$

With this manifold is associated a continuum of resonance frequencies,

$$\mathfrak{L}_0^{\mathrm{r}}|ab(\vec{\mathrm{p}});\hat{n}\rangle\!\rangle = \Big[\omega_{ab} - \sum_L \hat{n}_L\omega_L + \nu_{\hat{n}}(\vec{\mathrm{p}})\Big]\,|ab(\vec{\mathrm{p}});\hat{n}\rangle\!\rangle. \tag{B3}$$

Here

$$\nu_{\hat{n}}(\vec{\mathrm{p}}) = m^{-1}\hbar\vec{\mathrm{p}}\cdot\vec{\mathrm{K}}_{\hat{n}} \tag{B4}$$

is the Doppler shift associated with $\vec{\mathrm{p}}$, with m being the molecular mass.

The continuous manifold can be conveniently turned into a discrete one by "box" normalization in a finite volume Λ^3, introducing the denumerable basis

$$|ab[\vec{\mathrm{p}}\,];\hat{n}\rangle\!\rangle = (2\pi/\Lambda)^{3/2}\,|ab(\vec{\mathrm{p}});\hat{n}\rangle\!\rangle. \tag{B5}$$

In the range of field strengths where $\Sigma(z)$ is independent of the external field, the self-energy is diagonal in $\hat{n}$, forming a matrix in the manifold of (B5) with elements

$$\langle\!\langle cd[\vec{\mathrm{q}}\,];\hat{n}|\Sigma^{\mathrm{eq}}(z)|ab[\vec{\mathrm{p}}\,];\hat{n}\rangle\!\rangle. \tag{B6}$$

Elements $\vec{\mathrm{p}}=\vec{\mathrm{q}}$ represent self-damping of individual $\vec{\mathrm{p}}$ components of the manifold, while $\vec{\mathrm{p}}\neq\vec{\mathrm{q}}$ elements (velocity-changing collisions) represent cross relaxation between the various components. Velocity-changing collisions thus play here a role analogous to that of inelastic collisions in an homogeneously broadened multilevel system.

Inhomogeneous velocity effects can be eliminated, and the manifold (B5) replaced by the single vector $|ab;\hat{n}\rangle\!\rangle$ (which corresponds to the confinement of A to internal degrees of freedom only) if the following two conditions are met: (a) The Doppler width is small compared to the magnitude of the self-energy (e.g., at sufficiently high gas densities). (b) The cross sections for velocity changing are *much larger* than those involved in dephasing by elastic collisions, or in inelastic collisions. One can then replace the matrix (B6), defined on the manifold (B5), by the single element

$$\Sigma^{(\hat{n})}_{cd;ab}(z) = \sum_{\vec{\mathrm{p}},\vec{\mathrm{q}}} \rho^A_{\vec{\mathrm{p}}}\langle\!\langle cd[\vec{\mathrm{q}}\,];\hat{n}|\Sigma^{\mathrm{eq}}(z)|ab[\vec{\mathrm{p}}\,];\hat{n}\rangle\!\rangle, \tag{B7}$$

treating the translational motion as part of the "bath".

Another limiting situation in which A can be reduced is the case of the "Brownian-particle model",[60] applicable when the A-type molecule is a very heavy one, and is perturbed by a gas of light molecules with a short-range interaction. In this case, (B6) becomes diagonal in, and independent of, the momentum $\hbar\vec{\mathrm{p}}$. If in spite of the heavy mass the Doppler width is not negligible, saturation dips will occur, but they will be independent of the velocity. The shape of the spectrum will then be obtained by simply convoluting the Gaussian-shaped Doppler profile with the homogeneously broadened fixed-velocity line profile.

The temporal behavior of the density matrix of the Doppler-broadened molecule, in the approximation of Markovian self-energies (and in the limit $\Lambda\rightarrow\infty$) is governed by a generalized linear Boltzmann equation (recalling our assumption of negligible initial correlations). Expanding the A-reduced density matrix in the basis (B2),

$$\rho^A(t) \rightarrow \sum_{\hat{n}}\sum_{ab}\int d\vec{\mathrm{p}}\,\rho^{(\hat{n})}_{ab}(\vec{\mathrm{p}};t)\,|ab(\vec{\mathrm{p}});\hat{n}\rangle\!\rangle, \tag{B8}$$

we have

$$\frac{\partial}{\partial t}\rho_{ab}^{(\hat{n})}(\vec{\mathrm{p}},t)=\Big[\omega_{ab}-\sum_{L}\hat{n}_L\omega_L+\nu_{\hat{n}}(\vec{\mathrm{p}})\Big]\rho_{ab}^{(\hat{n})}(\vec{\mathrm{p}},t)$$
$$+\sum_{cd}\Big\{\sum_{L}\sum_{\pm}\big[\delta_{bd}(V_L^{\pm})_{ac}\,\rho_{cd}^{(\hat{n}_L\mp 1_L)}(\vec{\mathrm{p}},t)-\delta_{ac}(V^{\pm})^{*}_{bd}\rho_{cd}^{(\hat{n}_L\mp 1_L)}(\vec{\mathrm{p}}-\vec{\mathrm{k}}_L;t)\big]$$
$$+\int d\vec{\mathrm{q}}\,\langle\!\langle ab(\vec{\mathrm{p}});\hat{n}\,|\,\Sigma^{\mathrm{eq}}(+i0)\,|\,cd(\vec{\mathrm{q}});\hat{n}\rangle\!\rangle\rho_{cd}^{(\hat{n})}(\vec{\mathrm{q}};t)\Big\}, \tag{B9}$$

where we have used the short-hand notation

$$\hat{n}+1_L\equiv(\hat{n}_1,\ldots,\hat{n}_L+1,\ldots) \tag{B10}$$

for the multimode external field.

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