Resonance Absorption and Scattering of Strong Coherent Radiation in Thermally-Relaxing Systems

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The derivation and uses of a master equation describing the response of a thermally-relaxing molecule in the presence of arbitrarily-strong coherent radiation are discussed, stressing the effects of strong fields, and introducing explicit expressions for the effects of the fields on binary-collision relaxation rates, and on radiative transition rates in resonance absorption and scattering of radiation.

The resonance interaction of coherent radiation with an atomic (or molecular) system, represented by a discrete set of internal states, and undergoing thermal relaxation by coupling to a heat reservoir (radiative damping, collisions in gases, coupling to lattice vibrations, etc.) is traditionally analyzed by the use of a master equation\(^1,2\) (known as the Bloch, or Bloch-Redfield equation). The equation describes the motion of the reduced density matrix for the atomic (or molecular) system. The coherent nature of the interaction with the radiation is entered through the incorporation of non-diagonal "coherence" elements of the density matrix, driven by the applied field (customarily introduced as a classical field). Written in matrix form, the master equation is (letting \(\hbar = 1\))

\[
\frac{\partial}{\partial t} \rho(t) = -i[H^A + V^{AL}(t)],\rho(t)] - \Gamma(\rho(t) - \rho^{eq})
\]

\(1\)

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where $\rho$ is the reduced density matrix, $H^A$ and $V^{AL}$ are, respectively, the free-molecule Hamiltonian and its (time-dependent) interaction with the applied field, and $\Gamma$ is a supermatrix describing the relaxation of the deviation of $\rho$ from the equilibrium state $\rho^{eq}$. Following the terminology of Bloch, it is customary to distinguish between elements of $\Gamma$ pertaining to diagonal elements of $\rho$ (populations) and those pertaining to off-diagonal elements (coherences) denoting them as $T_1$ and $T_2$ relaxation processes, respectively.

Though the optical uses of the master equation were originally suited to discrete internal states, it soon became necessary, with the advent of saturation spectroscopy, to extend it to translational degrees of freedom of the molecules, with their continuum spectrum. Furthermore, as the incident radiation is detuned off resonance, probing the wings of resonance lines, it may not be adequate to use a Markovian master equation, without a "memory" of previous events. The Markovian term $\Gamma(\rho-\rho^{eq})$ should then be replaced by a convolution integral with a memory kernel $\tilde{\Gamma}(t)$. In the Markovian approximation, this integral is replaced by

$$\int^{t}_{-\infty} \tilde{\Gamma}(t-t')(\rho(t') - \rho^{eq}) \, dt'$$

$$\approx (\int^{t}_{-\infty} \tilde{\Gamma}(t') dt')(\rho(t) - \rho^{eq}) \equiv \Gamma(\rho(t) - \rho^{eq}) \tag{2}$$

in the limit where $\rho(t)$ varies slowly on a time scale comparable to the memory time. Finally, since more powerful laser sources are now available, one should question whether the master equation can be used without modifications in the strong-coupling domain. The master equations are known to account satisfactorily for certain features of strongly-saturated spectra (such as the dynamic Stark shifting of line positions). However, the supermatrix $\Gamma$ is left untouched in these treatments. As the radiative coupling becomes more intense, it becomes more likely that radiative transitions will occur during collisions, and thus modify $\Gamma$. It was recently shown by Burnett et al. that field-induced corrections to $\Gamma$ are important even under weak fields in far-wing detunings. These corrections account for the smooth transition
from the line-center "impact" domain to the line-wing "quasistatic" domain. They are also necessary for the maintenance of a positive balance of scattered-light intensity in the resonance redistribution of coherent radiation.

Microscopic theories for the relaxation supermatrix elements are available with great rigor and detail in the case of collision broadening in dilute gases. These theories are essentially derived in the domain of the "linear-response" approximation. The radiative process is treated there as a single elementary event, not to be mixed with the collisional interruptions.

An attempt to approach the strong-coupling domain invokes certain questions: (a) How can one still derive a master equation? (b) What form will the relaxation supermatrix attain under the influence of the applied field? How will it affect its various properties, such as the conservation rule

$$\rho_{\text{eq}} = 0$$

in a closed system? (c) Under what conditions are such corrections necessary? Under what conditions will the unmodified $\Gamma$ still be adequate even in strong fields? Further questions the theory is likely to touch are: (d) Can the equations be extended to include resonance scattering phenomena as well as the response to incident field modes? (e) Is it possible to develop non-perturbative methods for solving the equations, stressing the multiphotonic nature of the transitions even with a limited set of internal states?

This multitude of questions can be resolved by forming a proper means of reducing the equations of motion of the density matrix in the strong-coupling domain. Two parallel techniques, originally evolved in the linear-response domain, can be employed for that matter, namely, the temperature Green's function (or finite-temperature Feynman-diagram) technique, and the Liouville-space tetradic-operator technique. Although the former technique has certain advantages, such as economy in the calculation of specific perturbation terms (e.g., by using the rule of topologically-equivalent diagrams), the Liouville-space method is advantageous in many other ways: (i) It directly relates $\Gamma$ to binary-collision scattering amplitudes and is therefore more
convenient to use with strong collisions, where perturbative methods are inadequate. (ii) It can be generalized to open stationary systems, whereas the Feynman-diagram technique is strictly confined to systems under canonical equilibrium. (iii) As demonstrated by the works of Burnett et al., the separate treatment of molecular interactions in the statistical correlations in the equilibrium density matrix as separated from their effect on the dynamical time evolution, makes the transition to the line wings more transparent.

The extended use of these techniques beyond the domain of linear response is made possible by realizing the following: (1) The radiative processes should be treated as a scattering event in which the relevant participating partners are the absorbing molecule and the pertinent field modes (the incident modes in self-attenuation spectra, and the incident modes plus the detected scattered mode in resonance-scattering spectra). All other (molecular and radiative) degrees of freedom are relegated to the secondary role of a "thermal bath." The reduced equations should refer to all the relevant degrees of freedom (the "A" system), and not just the molecular states, by "averaging out" the irrelevant degrees of freedom (the "B" system). (2) The initial asymptotic state of the radiative event is not a pure stationary state but a mixed equilibrium state, represented by an equilibrium density matrix $\rho^\text{eq}$ (properly modified to incorporate the externally-applied beam of light).

The Liouville-space approach is especially suited for dealing with impure initial states by directly addressing the equations of motion of the density matrix. Density matrices can be envisaged as elements in a Hilbert space (double space, or Liouville space) in which the building elements are quantum-mechanical operators. Given a basis $|a\rangle,|b\rangle,...$, in the ordinary wavevector Hilbert space, the operators $|a\rangle\langle b|,...$, form the building blocks in Liouville space, represented by Baranger's double-vector notation $|ab\rangle\rangle$, etc. Ordinary operators can be expressed as a vector expanded in this basis, e.g.,

$$|X\rangle = \sum_{ab} \langle a|X|b\rangle |ab\rangle\rangle ,$$

where $\langle a|X|b\rangle$ is an ordinary (dyadic) matrix element. The metric of this space is defined by
Equations of motion are generated by Liouvillian superoperators, formed from commutators of ordinary Hamiltonian operators:

$$H \times \equiv [H, X]$$

Superoperators are represented by tetradic matrices, with elements $\langle\langle ab|H|cd\rangle\rangle$ in double space.

The reduction of the equations of motion is achieved by applying to the density matrix the Zwanzig projection operator $^{13,16}$

$$P = |I^B\rangle\langle\langle \rho_o^B|$$

where $\rho_o^B$ is the equilibrium density matrix for the B system (in the limit where its interaction with the A system vanishes), and $I^B$ is the unit operator for the B system. Application of (7) to the full density matrix (for all molecular and radiative degrees of freedom) results in

$$P \rho(t) = \rho_A(t) \rho_o^B$$

where $\rho_A(t)$ is the sought-after reduced density matrix. Its generalized equation of motion is $^5$

$$\frac{d}{dt} \rho_A(t) = -i(H_A^A + V_{ AL}) \rho_A(t) - \int_{-\infty}^{t} \tilde{\Gamma}(t-t'; V_{AL}) \rho_A(t') dt'$$

where $H_A^A$ is the Liouvillian for the freely-evolving molecule plus relevant field modes (the "dressed" molecule), and the memory kernel $\tilde{\Gamma}$ is a well-defined function of the interaction $V_{AL}$ (in superoperator notation) between the molecule and the relevant field modes.

In order to obtain an explicit expression of this field dependence, it is convenient to use the one-sided Fourier transform $\Gamma(z)$ (or Laplace transform $\Gamma(is)$) of $\tilde{\Gamma}(t)$, as is customarily used in finding steady-state solutions for the equations of motion. One can then write

$$\Gamma(z; V_{AL}) = \Gamma(0)(z) + \delta \Gamma(z; V_{AL})$$

where $\Gamma(0)(z)$ is the linear-response supermatrix (obtained in the limit $V_{AL} \rightarrow 0$). $\Gamma(z; V_{AL})$ is a supermatrix (or tetradic matrix) in the basis $|ab\rangle$, etc., of the A system. In the case of classical-like applied
field modes, this basis is replaced by a basis of vectors $|\alpha; \hat{n}\rangle$, where $\hat{n} = 0, \pm 1, \ldots$, are the Floquet numbers of the applied field modes describing the $\hat{n}$-th harmonic response to the applied-field frequency, $\rho^{(\hat{n})}$, and $a, b$ refer to the remaining (quantized) degrees of freedom of $A$; i.e.,

$$|\rho^{(\hat{n})}\rangle = \sum_{ab; \hat{n}} \rho_{ab}^{(\hat{n})} |ab; \hat{n}\rangle$$

(11)

The free evolution of these vectors is described by

$$H^A|ab; \hat{n}\rangle = (\omega_{ab} - \hat{n} \omega_L)|ab; \hat{n}\rangle$$

(12)

where $\omega_{ab}$ is the energy difference between $a$ and $b$, and $\omega_L$ is the applied-field frequency. (In case several field modes are applied, $\hat{n} \omega_L$ is replaced by a sum over the modes.) In resonance scattering $\omega_{ab}$ incorporates the scattered mode.

The linear-response superoperator $\Gamma^{(0)}$ is diagonal in the Floquet $\hat{n}$ numbers. In the approximation of broadening by binary collisions with a foreign gas, its tetradic elements are given by$^{13, 14}$

$$\langle\langle ab; \hat{n} | \Gamma^{(0)}(z) | cd; \hat{n}'\rangle\rangle = \delta_{\hat{n} \hat{n}'} N_B \langle\langle ab; \hat{n} | \text{tr}_B \{T(z) \rho_B \} | cd; \hat{n}'\rangle\rangle$$

(13)

where $N_B$ is the number of perturbing molecules, $T$ is the tetradic analog of the Lipmann-Schwinger binary-collision $T$ matrix (in terms of which it can be explicitly expressed), and the trace is taken over one-perturber states. Extension to resonance broadening by identical molecules (in the approximation where no two coherently-excited molecules collide) is straightforward.$^{14}$

The field-modified $T$ matrix is obtained under these approximations upon replacing $T$ by a renormalized $T^T$ matrix, obeying the equation

$$T^T(z; V^{AL}) = T(z)[1 + G_o(z) V^{AL} G_o(z) T^T(z; V^{AL})]$$

(14)

where

$$G_o(z) = (z - H^A - H^B)^{-1}$$

(15)

is the resolvent operator for the non-interacting collision pair ("dressed" molecule plus perturber). The correction $\delta \Gamma$ is not diagonal in the Floquet numbers, since $V^{AL}$ is not (as it raises or lowers $\hat{n}$ by
one unit). It also does not obey the conservation rule (3), providing a coincident radiative and collisional reshuffling of populations.

To the collision-damping contributions one should add, when necessary, the effects of radiative damping. These include diagonal elements (in double space) representing self decay by virtual emission of photons, and off-diagonal elements representing decay by truly emitted ("cascade") photons (into modes other than the one detected in resonance scattering). Owing to the short correlation times associated with radiation damping, these contributions are not modified by coincidence of the applied fields.

Steady-state populations and transition rates can be expressed as a double-perturbation series in powers of \( V^{AL} \) and \( \Gamma(10; V^{AL}) (z + 10 \) implying the limit as \( z \) approaches the origin in the complex plane from above), using as initial condition

\[
\rho^A(t) \rightarrow \rho_{eq}^A
\]

with \( \rho_{eq}^A \) the equilibrium distribution of the A system (obtained by taking the trace over B). The steady-state transition rate from a to b is given by

\[
W_{ba} = -i \lim_{z \to 10} \langle\langle b|b; 0|(-i\delta\Gamma) + (V^{AL}-i\delta\Gamma)(z-H^{A}_V-V^{AL}+i\Gamma)^{-1}(V^{AL}-i\delta\Gamma)|a; 0\rangle\rangle
\]

where \( \Gamma \) in the resolvent is the fully-renormalized relaxation super-matrix in the strong-coupling limit. The sole \(-i\delta\Gamma\) term and the one on the right end, necessary additions in the line wings, result from the modification of the initial condition (16) by statistical correlations. The left-end \(-i\delta\Gamma\) term is needed in resonance transitions because of mixing of the final state with others during collisions.

With (16) as initial condition, expression (17) can be used in resonance absorption (and resonance scattering) with the last radiative coupling on the left, both in \( V^{AL} \) and in \(-i\delta\Gamma\), being that part of \( V^{AL} \) causing annihilation (creation) of a photon in the desired mode.

The Markovian approximation applies under the near-resonance condition
\[ \Delta \omega = |\omega_{ab} - \hat{n}_L| \ll \tau_c^{-1} \]

where \( \tau_c \) is the "correlation" time (the duration of a collision in binary collisions). Under this condition, it can be shown that the correction \( \delta \Gamma \) to \( \Gamma^{(0)} \) is negligible as long as

\[ \Omega \tau_c \ll 1 \]

where \( \Omega = |\mu E| \) is the Rabi frequency measuring the strength of the radiative coupling (\( \mu \) being the dipole moment matrix element and \( E \) the electric-field amplitude). This condition should be modified in the line wings, replacing \( \Omega \) by

\[ \Omega' = (\Omega^2 + \Delta \omega^2)^{1/2} \]

so that even relatively-weak fields can cause appreciable corrections at large detunings.\(^7\)

A calculation of the transition rates \( W_{ba} \) would generally require a summation over a complete set of intermediate \( |ab;\hat{n}\rangle \) vectors. However, when dealing with near-resonance absorption or scattering of radiation, the calculation is preferably limited to a subset (the "resonance set") in double space that (a) have small (near-resonant) eigenvalues of \( \hat{H}^A \) (the rotating-wave approximation) and (b) are connected to each other by \( \nu^{AL} \). We may therefore have to modify the rate expressions to accommodate for the following possibilities\(^5,\text{17} \): (i) One resonance state is reached from another by multiple applications of \( \nu^{AL} \) involving non-resonant intermediate states (simultaneous multiphoton transitions); (ii) Coupling of one resonance state to another by consecutive applications of \( \Gamma \) involving intermediate states outside the resonance state (indirect relaxation effects). In both cases, the appropriate interaction \( \nu \) (be it \( \nu^{AL} \) or \(-i\Gamma\)) can be replaced by a renormalized ("effective") interaction

\[ \nu^{eff} = \nu + \nu_{Q_R}[z - \nu_{Q_R}(\hat{H}^A + \nu)\nu_{Q_R}] \nu_{Q_R} \]

where \( Q_R \) is a projection on the complementary space of all far-from-resonance \( |ab;\hat{n}\rangle \) vectors. In the case \( \nu = \nu^{AL} \) the renormalization introduces such effects as Bloch-Siegert shifts, two-photon simultaneous transitions, etc. In the case \( \nu = -i\Gamma \), eq. (21) represents such effects
as multilevel sequential decay, level repopulation, etc.\textsuperscript{6,18,19} Such indirect relaxation phenomena introduce a long time-delay effect, expressed in the master equation by a memory kernel.\textsuperscript{17} If the time delay is sufficiently long (e.g., as in large molecules), the effect of indirect relaxation may become negligible on the time scale of short-duration pulses. It may not, however, be neglected in true steady-state phenomena.

Steady-state rates involve the Floquet-space "vacuum" $|\hat{n}=0\rangle$ as end-point states. It would therefore seem advantageous to further reduce the equations of motion to elements of $\rho^A(t)$ confined to this vacuum set. In the rotating-wave approximation (ignoring level degeneracy) these elements refer to level populations. As usual, this is achieved by "projecting out" all vectors with Floquet numbers $\hat{n} \neq 0$. Let us define the single-passage rates\textsuperscript{17,20,21}

\[
R_{ba}(z) = -i<\langle bb|\hat{\sigma}|(V^{AL} - i\sigma)Q_o
\]

\[
[\hat{H}^A + V^{AL} - i\Gamma)Q_o]^{-1} Q_o (V - i\sigma)|aa;\hat{\sigma}> > (22)
\]

where $Q_o = 1 - P_o$ implies only $\hat{n} \neq 0$ in intermediate states. Then the projection

\[
\rho^D(t) = P_o \rho^A(t) \quad (23)
\]

onto the Floquet vacuum obeys the master equation

\[
\frac{\partial}{\partial t} \rho^D(t) = -i(\hat{H}^A + P_o \Gamma P_o)\rho^D(t) + \int_{\infty}^{t} \tilde{R}(t-t')\rho^D(t') dt' \quad (24)
\]

where $\tilde{R}(t)$ is the inverse Fourier transform of $R(z)$. In the approximation where translational effects are neglected this is a generalization of the Pauli master equation, with $R$ supplying the radiative coupling (to infinite order in the coupling strength $V^{AL}$). A Markovian Pauli-type master equation is obtained, for example, in the limit where $T_2$ processes are much stronger than $T_1$ processes\textsuperscript{22} (e.g., when phase interruption by elastic collisions dominates over inelastic collisions).

Except for some limiting situations, the complicated time dependence of $\tilde{R}(t)$ makes this reduction quite useless in studying time-resolved behavior. Nevertheless, the steady-state matrix $R(z+10)$ may serve as a useful auxiliary tool in constructing algorithms for summing.
the infinite perturbation series for spectrally-resolved processes, in
the strong-coupling limit. Treating \( M_{ba} \) and \( K_{ba} \) as matrix elements of
ordinary (dyadic) matrices, the two are related (in the approximation
neglecting degeneracy and translational effects) by

\[ W = R + R G W \]  

(25)

where

\[ G_{ab} = i \langle aa'0| (z + iP0 P0) \rangle_{bb00}^{-1} |bb00 \rangle \]  

(26)

is the resolvent matrix for level-population relaxation (T1 processes).

Whereas G is relatively easy to write down when the resonance set
consists of a small number of levels, R may still be difficult to cal-
culate. It nevertheless has the following advantageous properties:
(a) In a multiple-resonance excitation of an N-level system (by one
or more field modes) it does not include explicitly level-population dy-
namics, and is therefore dependent only on the topology of the radiative
connections between the various levels, and not on their relative posi-
tioning on the energy scale.23 For example, in the three-level two-
mode double resonance there are three ways of arranging the levels (see
Fig. 1), each having quite a different population-dynamics resolvent G,
but all having the same single-passage matrix R. (b) For certain topo-
logies, algebraic expressions can be worked out for R under simplifying
conditions (e.g., Markovian approximation).

One such topology is the "simply-connected" single-chain multiple
N-level resonance, a succession of N non-degenerate levels \( i = 1, \ldots, N \);
not necessarily in the order of increasing energy) where only successive
pairs of levels \( i \leftrightarrow i+1 \) are radiatively coupled, by one field mode
each. The rank-N matrix R can then be expressed as an N-step continued
fraction, the kth step of which involves a rank-(N-k+1) matrix.20,21 (The
double resonances of Fig. 1 are examples of such a topology.) Another
algebraically-soluble topology is the "star-shape" topology in which one
distinct level \( i=1 \) is coupled to all the rest \( i = 2, \ldots, N \). Since
there are \( N!/2 \) ways of folding a multiple-resonance chain on the energy
scale, the advantage of using the auxiliary matrix R is obvious. Such
algebraic solutions have been found extremely useful in forming numeri-
cal models for such processes as the double-resonance Raman amplifier.24
Fig. 1. Three forms of the three-level double resonance.

References

1. G. S. Agarwal, Quantum Optics (Springer Tracts in Modern Physics, Vol. 70), Springer Verlag, Berlin, 1974, and references therein.


