# Intermediate state interactions in optical processes


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Abstract - A general formulation is given for the effect of the inter-
mediate state interaction on the second or higher order optical res-
ponse of a system which interacts with its environment in its excited
states. The emission spectrum is expressed in terms of the corre-
lation function of dipole moment between the excited states and the
final state. The projection operator method is conveniently used to
derive a damping-theoretical expression for the spectrum. Dynamic
and stochastic treatments are formulated generally. As an example,
a four-level atom with an Off-diagonal modulation is treated in some
detail. It is emphasized that the intermediate state interaction
has to be treated to keep its dynamical coherence throughout the
whole process. The intuitive picture of intermediate state relaxa-
tion needs caution.


## INTRODUCTION

In a second order or a higher order optical process, the system under obser-
vation goes through a series of intermediate states before it reaches the
final state. The interaction of the system with its environment (reservoir)
when it is in the intermediate states is called an intermediate state inter-
action, which we shall abbreviate as IMSI hereafter. We are concerned with
the question how the quantum coherence is affected by IMSI and how it is
manifested in optical responses.
Raman scattering and luminescence are both second order optical processes.
In the former, the quantum coherence is conserved, whereas it is interrupted
in the latter by IMSI. Thus, a simple three-level atom gives only the Raman
scattering if the natural radiative damping is the only mechanism acting in
the excited state. The luminescence component appears if an IMSI perturbs
the phase coherence in the excited state. This was treated first by Huber[1]
by a simple phase modulation model and since then by many authors [2].
The present author and his collaborators [3] have made an extensive study of
various stochastic models for the purpose of understanding the nature of IMSI
in the second order optical processes.
Here we would like to discuss the problem from a somewhat more general point
of view. The point is that the effect of IMSI must be considered as coherent
through the whole of an optical process rather than as a separate process of
relaxation in the excited states. Thus it is not always possible to assign
for these states the relaxation or transition rates independent of the way
how the system is excited and de-excited. A simple example will be treated
by a stochastic model of a four-level system in which the upper two states
are perturbed by a random off-diagonal modulation. For this example, the
second order response is separated into two terms corresponding to the Raman
scattering and the luminescent radiation. It is found, however, that the
rates appearing in the expression are dependent on the parameters character-
izing the optical process such as the off-resonance of the incident and
emitted radiation.

## THE MODEL

We consider a system, which we call S hereafter, interacting with radiation
and its environment. The model is introduced by the following assumptions
and definitions:
  1. The system has three groups of quantum state, the ground state, the
intermediate (excited) states and the final state. The states and the energy

levels are denoted by A, $B_1$, $B_2$, .., and C. The system Hamiltonian is denoted by $H_S$.

2. The radiation is treated as semiclassical. The frequency of the incident light is denoted by $\omega_1$ and that of the emitted light by $\omega_2$.

3. The interaction of S with the incident light is denoted by $V_1$, which has the dipole matrix elements between A and B's and is proportional to the electric field of the incident light.

4. The interaction of S with the emitted light is denoted by $V_2$, which has the dipole matrix elements between B's and C. The amplitude of the emitted light is taken as unity.

5. We adopt the resonant approximation and regard $V_1$ and $V_2$ as independent of time as long as we are concerned with CW cases. If the incident light is a pulse of a finite duration, $V_1(t)$ represents its envelope function.

6. The system S interacts with the reservoir R only in the intermediate states. The IMSI is represented by the Hamiltonian $H_I$.

7. The natural radiation damping is considered separately from IMSI. It is represented by a phenomenological damping constant $\gamma_b$ for the states B's.

Including the energies of annihilated or emitted photons, the energies of the initial state A, the intermediated states B's and the final state C are denoted by a, $b_1$, $b_2$, .. and c respectively. Thus the Hamiltonian of S is written as

$$H_S = a|a\rangle\langle a| + \Sigma b_j |b_j\rangle\langle b_j| + c|c\rangle\langle c| \tag{1}$$

with

$$a = A + \omega_1, \quad b_j = B_j, \quad \text{and } c = C + \omega_2.$$

When further the IMSI is included, the system has the Hamiltonian

$$H = H_S + H_I \tag{2}$$

The Hamiltonian of the composite system S + R is denoted by $H_{SR}$, namely

$$H_{SR} = H + H_R = H_S + H_I + H_R . \tag{3}$$

when S is in B's. By the assumption 6, we have

$$H_{SR} = H_0 = H_S + H_R \tag{4}$$

when S is in A or C. In the presence of the radiation field, the total system is governed by the Hamiltonian

$$H_{tot} = H_{SR} + V_1 + V_2. \tag{5}$$

We use $V_2$ as the generator to derive the expression for the probability to find S in the final state by emitting radiation.

GENERAL FORMULATION

The density matrix for the total system evolves in time following the equation

$$\dot{\rho}(t) = - iH_{tot}^\times \rho(t) = - i[H_{tot}, \rho(t)] \tag{6}$$

Note that we take the Planck constant as unity. In order to simplify expressions hereafter, we have introduced the notation (Ref. 4 )

$$O^\times f = [O, f]$$

for a hyper-operator $O^\times$ which constructs a commutator [O, f] with an operand operator f. Equation (6) is integrated with the initial condition

$$\rho(0) = |a\rangle\langle a|\rho_R^0 \tag{7}$$

where $\rho_R^0$ is the equilibrium density matrix of the reservoir R satisfying

$$H_R^\times \rho_R^0 = 0 \tag{8}$$

When Laplace-transformed, Eq. (6) is written as

$$(s + iH_{tot}^\times) \rho[s] = \rho(0) \tag{9}$$

where

$$\rho\,[s] = \int_0^\infty dt\, e^{-st}\, \rho\,(t)$$

We expand $\rho\,(t)$ to the second order of $V_2$. The second order term is found to be

$$\rho^2\,(t) = \int_0^t dt' \int_0^{t'} dt'' \, e^{-i(t-t')\,(H_{SR}^x + V_1^x)}\,(-iV_2^x)\, e^{-i(t'-t'')\,(H_{SR}^x + V_1^x)}$$
$$(-iV_2^x)\, e^{-it''\,(H_{SR}^x + V_1^x)}\, \rho\,(0)$$

Its matrix element $\langle c\,|\rho(t)|\,c\rangle$, when taken the trace over the states of R, is the probability $P(c,t)$ that the system S, starting from the initial state a with the reservoir in equilibrium, interacts with incident radiation to arbitrary order, goes through the intermediate states and reaches the final state c emitting a photon $\omega_2$ at time t. This is given by

$$P(c,t) = Tr_R \langle c\,|\,\rho(t)\,|c\rangle$$

$$= \int_0^t dt_2 \int_0^{t_2} dt_1 \, Tr_R \, \langle c|e^{-i(t-t_2)\,(H_{SR}^x + V_1^x)} V_2\, e^{-i(t_2-t_1)\,(H_{SR}^x + V_1^x)}$$
$$\{e^{-it_1\,(H_{SR}^x + V_1^x)}\, \rho(0)\} V_2|c\rangle$$

$$+ \int_0^t dt_2 \int_0^{t_2} dt_1 \, Tr_R \, \langle c|e^{-i(t-t_2)\,(H_{SR}^x + V_1^x)} \{e^{-i(t_2-t_1)\,(H_{SR}^x + V_1^x)} V_2$$
$$e^{-it_1\,(H_{SR}^x + V_1^x)}\, \rho(0)\}\, V_2|c\rangle \qquad (10)$$

By the assumptions 3 and 6, this is simplified to

$$P(c,t) = \int_0^t dt' \int_0^{t'} dt'' \, Tr_R \langle c\,|\, V_2(t')\, \rho(0)\, V_2(t'')\,|c\rangle \; + \; c.c. \qquad (11)$$

where

$$V_2(t) = e^{i(H_{SR} + V_1)t}\, V_2\, e^{-i(H_{SR} + V_1)t}$$

is a Heisenberg operator. Per unit time, the rate of emission (photon counting rate) $W(c,t)$ is

$$W(c,t) = dP(c,t)/dt$$

$$= \int_0^t dt' \, Tr_R \langle c\,|\, V_2(t)\, \rho(0)\, V_2(t')\,|c\rangle + c.c. \qquad (12)$$

This is essentially the correlation function of the dipole moment between B and C which is forced to oscillate by the incident radiation. The above expression can be written as

$$W(c,t) = \int_0^t dt' \, Tr_R \, \langle c|V_2 e^{-i(t-t')\,(H_{SR}+V_1)}\, e^{-it'\,(H_{SR}+V_1)}\, \rho(0)$$
$$e^{it'\,(H_{SR}+V_1)}\, V_2 e^{i(t-t')\,(H_{SR}+V_1)}\,|\,c\rangle + c.c.$$

$$= \int_0^t dt' \, Tr_R \, \langle c|V_2 e^{-i(t-t')\,(H-c+V_1+H_R^x)}$$
$$\{e^{-it'\,(H_{SR}^x + V_1^x)} \rho(0)\} V_2|c\rangle \; + \; c.c. \qquad (13)$$

by noticing that the rightiest propagator on the first line of the above equation is simply equal to $\exp[i(t-t')(c+H_R)]$ because of the assumptions 4 and 6. We introduce the Laplace transforms$^R$ of $P(c,t)$ and $W(c,t)$ by

$$P[c,s] = \int_0^\infty dt\, e^{-st} P(c,t)$$

and

$$W[c,s] = \int_0^\infty dt\, e^{-st} W(c,t) = s\, P[c,s]$$

The CW response is

$$W(c,\infty) = \lim_{t\to\infty} W(c,t) = \lim_{s\to 0} s\, W[c,s]$$

$$= \lim_{s \to 0} \mathrm{Tr}_R \langle c | V_2 \frac{1}{s + i H_R^\times + i(H - c + V_1)} \rho_\infty V_2 | c \rangle + c.c. \qquad (14)$$

where

$$\rho_\infty = \lim_{s \to 0} \frac{s}{s + i(H_{SR}^\times + V_1^\times)} \rho(0) \qquad (15)$$

represents the dynamical equilibrium of the system when the incident radiation has been present from the infinite past.

In order to see how Eq. (14) is related to the Raman scattering we expand the expression (14) to the second order in $V_1$. First, we expand $\rho_\infty$. There is no contribution to (14) from the zeroth order term. The first order and the second order terms are

$$\rho_\infty^1 = \lim_{s \to 0} \frac{1}{s + i H_{SR}^\times} (-i V_1) \frac{s}{s + i H_{SR}^\times} \rho(0)$$

$$= \lim_{s \to 0} \frac{1}{s + i H_{SR}^\times} ( \rho(0) i V_1 ) + \dots \qquad (16)$$

$$\rho_\infty^2 = \lim_{s \to 0} \frac{1}{s + i H_{SR}^\times} (-i V_1^\times) \frac{1}{s + i H_{SR}^\times} (-i V_1^\times) \frac{s}{s + i H_{SR}^\times} \rho(0)$$

$$= \lim_{s \to 0} \frac{1}{s + i H_{SR}^\times} [\{ \frac{1}{s + i(H_R^\times + H^\times)} V_1 \rho(0) \} V_1$$

$$+ V_1 \{ \frac{1}{s + i(H_R^\times + H^\times)} \rho(0) V_1 \}] \qquad (17)$$

where the irrelevant terms are omitted. $\rho_\infty^1$ has matrix elements $\langle a | \rho_\infty^1 | b \rangle$, while $\rho_\infty^2$ has elements only between the intermediate states. We expand the first propagator in Eq. (14) in $V_1$. The zeroth term combines with $\rho_\infty^2$ and the first term with $\rho_\infty^1$. Thus we obtain

$$W(c, \infty) = \lim_{s \to 0} \mathrm{Tr}_R [\langle c | V_2 | b_j \rangle \langle b_j | \frac{1}{s + i H_R^\times + \gamma_b + i(H - c)} | b_i \rangle \langle b_i | V_1 | a \rangle$$

$$\times \frac{1}{s + i H_R^\times + i(a - c)} \langle c | V_2 | b_1 \rangle^* \langle b_1 | \frac{1}{s + i H_R^\times + \gamma_b + i(H - a)} | b_k \rangle^* \langle b_k | V_1 | a \rangle^* \rho_R^0$$

$$+ \langle c | V_2 | b_n \rangle \langle b_n | \frac{1}{s + i H_R^\times + \gamma_b + i(H - c)} | b_1 \rangle \langle b_1 b_m | \frac{1}{s + i H_{SR}^\times + 2\gamma_b} | b_j b_k \rangle$$

$$\times \langle b_j | \frac{1}{s + i H_R^\times + \gamma_b + i(H - a)} | b_i \rangle \langle b_i | V_1 | a \rangle \rho_R^0 \langle a | V_1 | b_k \rangle \langle b_m | V_2 | c \rangle$$

$$+ \langle c | V_2 | b_n \rangle \langle b_n | \frac{1}{s + i H_R^\times + \gamma_b + i(H - c)} | b_1 \rangle \langle b_1 b_m | \frac{1}{s + i H_{SR}^\times + 2\gamma_b} | b_k b_j \rangle$$

$$\times \langle b_k | V_1 | a \rangle \langle b_j | \frac{1}{s + i H_R^\times + \gamma_b + i(H - a)} | b_i \rangle^* \langle b_i | V_1 | a \rangle^* \rho_R^0 \langle b_m | V_2 | c \rangle ]$$

$$\qquad (18)$$

$$+ c.c.$$

Here we have introduced the natural radiation damping by the assumption 7 as

the transverse damping constant $\gamma_b$ and the corresponding longitudinal damping $2\gamma_b$ into the propagators for the intermediate states. The asterisk to matrix elements means the complex conjugates. This is necessary in order to keep the convention that a hyperoperator operates on operands to the right. In order to see how the operators work, Eq. (18) is expressed explicitly in terms of matrix elements. The usual convention is used that every index appearing twice is summed up.

### SIMPLE EXAMPLES

For the simplest standard example of a three-level atom with no IMSI, Eq. (18) gives

$$W(c,\infty) = \lim_{s\to 0} \langle c|V_2|b\rangle \frac{1}{\gamma_b + i(b-c)} \langle b|V_1|a\rangle \frac{1}{s+i(a-c)}$$

$$\langle a|V_1|b\rangle \frac{1}{\gamma_b - i(b-a)} \langle b|V_2|c\rangle$$

$$+ \langle c|V_2|b\rangle \frac{1}{\gamma_b+i(b-c)} \frac{1}{2\gamma_b} \{ \frac{1}{\gamma_b+i(b-a)} \langle b|V_1|a\rangle\langle a|V_1|b\rangle$$

$$+ \langle b|V_1|a\rangle\langle a|V_1|b\rangle \frac{1}{\gamma_b-i(b-a)} \}\langle b|V_1|c\rangle \quad + \text{ c.c. } \quad (19)$$

The first term gives the Raman response

$$W_R = 2\pi\delta(c-a) \frac{\gamma_b^2 + (b-a)(b-c)}{[\gamma_b^2+(b-a)^2][\gamma_b^2+(b-c)^2]} \langle a|V_1|b\rangle \langle b|V_2|c\rangle \quad (20)$$

by the real part of the factor $[s+i(a-c)]^{-1}$. The imaginary part of this yields a negative contribution, which is exactly cancelled by the second and the third terms of (19). Thus the Raman scattering is the only second order emission if there is no IMSI besides the radiation damping. The incoherent scattering appears when the incident radiation becomes stronger, starting from the fourth order of the Rabi frequency (Ref. 5 ). This is a general matter, not only limited to a three-level system.
An IMSI may change this situation. It may introduce an additional damping mechanism breaking the balance of the transverse and the longitudinal damping and thus producing incoherent luminescence-like scattering. The simplest example is a three-level atom with a random level modulation of the intermediate state. Then we may assume that the quantum level of B is adiabatically modulated by a random frequency shift b'(t), namely

$$b(t) = \bar{b} + b'(t) \quad (21)$$

This problem can be treated generally if b'(t) is assumed as Markovian (2). In the limit of the socalled motional narrowing, where the rate $\gamma_m = 1/\tau_m$ of modulation is so fast that the condition

$$\langle b'^2\rangle^{\frac{1}{2}} /\gamma_m \ll 1 \quad (22)$$

is satisfied, the IMSI gives rise to an additional transverse damping

$$\gamma = \langle b'^2\rangle^{\frac{1}{2}}/\gamma_m \quad (23)$$

but does not affect the longitudinal damping. In this case the second order response $W(c,\infty)$ is

$$W(c,\infty) = 2\pi\delta(a-c) \frac{|\langle a|V_1|b\rangle \langle b|V_2|c\rangle|^2}{\gamma^2 + (b-a)^2}$$

$$+ \frac{\gamma'}{\gamma_b(\gamma_b+\gamma')} \frac{\gamma}{\gamma^2+(b-a)^2} \frac{\gamma}{\gamma^2+(b-c)^2} |\langle a|V_1|b\rangle \langle b|V_2|c\rangle|^2 \quad (24)$$

where

$$\gamma = \gamma_b + \gamma'$$

The second term on the right hand side of Eq. (24) consists of two rate factors, the rate of absorption of $\omega_1$ to excite the atom from A to B and the rate of emission of $\omega_2$ deexciting the atom to C.

### A DAMPING THEORETICAL FORMULATION OF IMSI

A general treatment of IMSI can be formulated with the use of the projection operator method (Ref.6 ) as a damping theory. The basic equation (9) is formally solved as

$$\rho[s] = ( s + i H_{tot}^{\times})^{-1} \rho(0) \tag{25}$$

We define the projection P of a density operator f by

$$P\ f = \rho_R^0\ Tr_R\ f \tag{26}$$

where $\rho_R^0$ is the normalized equilibrium density matrix of the reservoir R satisfying the condition (8) and another projection operator Q by

$$Q = 1 - P$$

Now the density matrix $\rho$ is decomposed into two components

$$\rho = P\ \rho + Q\ \rho$$

Then the resolvent $[s + iH_{tot}^{\times}]^{-1}$ in Eq. (25) is decomposed into four components. Let us write their general forms for a resolvent $[s+iL]^{-1}$:

$$P\ (s + iL)^{-1}P = [\ G_0 + N\ G_1^{-1}\ N^{\dagger}]^{-1} \tag{27a}$$

$$P\ (s + iL)^{-1}Q = -i[\ G_0 + N\ G_1^{-1}N^{\dagger}]^{-1}\ N\ G_1^{-1} \tag{27b}$$

$$Q\ (s + iL)^{-1}P = -i\ G_1^{-1}\ N^{\dagger}[\ G_0 + N\ G_1^{-1}\ N^{\dagger}]^{-1} \tag{27c}$$

$$Q\ (s + iL)^{-1}Q = G_1^{-1} - G_1^{-1}\ N^{\dagger}[\ G_0 + N\ G_1^{-1}\ N^{\dagger}]^{-1}\ N\ G_1^{-1} \tag{27d}$$

where

$$G_0 = s\ P + i\ P\ L\ P, \qquad G_1 = s\ Q + i\ Q\ L\ Q \tag{28a}$$

$$N = P\ L\ Q\ , \quad N^{\dagger} = Q\ L\ P \tag{28b}$$

In terms of this projection, the CW response Eq. (14) is the second order expansion in $V_2$ of the expression

$$Tr_R\ \langle c|\{P\ s^2[\ s + i\ H_{tot}^{\times}]^{-1}P\ \rho(0)\}|c\rangle \tag{29}$$

Effectively, Eq. (25) is replaced then by

$$[\ s + i(H_S^{\times} + V_1^{\times} + V_2^{\times}) + \Phi(s, V_1, V_2)\ ]\ \rho[s] = \rho(0) \tag{30}$$

where

$$\Phi(s, V_1, V_2) = P\ H_I^{\times}\ Q\ \frac{1}{s + i(H_R^{\times} + H_S^{\times} + V_1^{\times} + V_2^{\times}) + iQH_I^{\times}Q}\ Q\ H_I^{\times}P \tag{31}$$

Thus $W(c,\infty)$ is given a damping-theoretical expression. If we ignore $H_I^{\times}$ in the denominator of $\Phi$, then the IMSI is treated in the lowest order perturbation as is often done in deriving relaxation equations. This is a useful approximation yielding the relaxational evolution of the density submatrix of the intermediate state. It is important to notice here that $V_1$ and $V_2$ are contained in $\Phi$ in this approximation. If they are ignored in $\Phi$, this means that the IMSI is treated as a process separate from the whole process. It is considered as a process of transitions and level shifting of

the intermediate states per se and then this effect is simply incorporated as an additional ingredient into the optical process. Then the effective evolution equation will be

$$[ s + i(H_S^x + V_1^x + V_2^x) + \Phi(0, 0, 0)] \rho[s] = \rho(0) \tag{32}$$

in the asymptotic limit of $s \to 0$. This may be called the intermediate-state-relaxation approximation, which is often intuitively assumed in treating IMSI. In some cases this may work as an approximation. But, in general, the approximation is not legitimate, because the presence of $V_1$ and $V_2$ in $\Phi$ is essential in coherent evolution of the whole process.
We can use the projection operator method for the expressions (14) and (18) avoiding tedious expansion procedures of the propagators in $\Phi(s, V_1, V_2)$. The expression (14) is a product of two propagators in succession, while (18) consists of three terms each of which is a product of three propagators. Physically, this means that the IMSI is working coherently throughout the whole process of optical scattering from the initial to the final state. The coherence of interaction becomes unimportant only in the limit of a fast and weak IMSI satisfying a narrowing condition similar to (22). In general, the condition may depend on off-resonance parameters and other time constants characterizing the process in question.

## A STOCHASTIC APPROACH

In order to see the points more closely, it is useful to take a stochastic approach, in which the dynamical evolution of the reservoir R is replaced by a stochastic one. The states of R are now denoted by $r$, and the probability for finding R in the state $r$ is denoted by $p_r(t)$. The stochastic evolution is assumed to follow the Markovian equation,

$$\dot{p}_r(t) = - \sum_{r'} \Gamma(r,r') \, p_{r'}(t) \tag{33}$$

Thus the stochastic operator $\Gamma$ plays the role of $iH_R^x$ in the foregoing treatment. The IMSI is represented by the interaction Hamiltonian $H_I(r)$ acting on S in the intermediate states when R is in the state $r$. This is a random interaction as $r$ changes randomly. Then Eq. (6) is replaced by

$$\dot{\rho}(t) = -i( H(r)^x + V_1^x + V_2^x ) \, \rho(t) - \Gamma\rho(t) \tag{34}$$

with

$$H(r) = H_S + H_I(r)$$

where $\rho(t)$ is now considered as a vector in the space of the reservoir states. $\Gamma$ operates on this vector, whereas the hyperoperators operate on the components of the vector each of which is a density matrix of S. In fact it has been shown by the present author (7) that the solution of Eq. (34) is the expectation of the density matrix $\rho(t)$ of S averaged over all possible paths of $r(t)$ of the reservoir state over the time interval $0 \le t' \le t$ with specified initial state $r_0$ and the final state $r$.
Corresponding to (26), we introduce the projection,

$$P = |0)(0| \tag{35}$$

where $|0)$ is the equilibrium state of R given by the column vector

$$|0) = \begin{pmatrix} p_1^0 \\ p_2^0 \\ \cdot \\ \cdot \end{pmatrix}$$

which satisfies the equation

$$\Gamma |0) = 0 \tag{36}$$

and

$$(0| = (1, 1, \ldots )$$

is its dual vector satisfying

$$(0|\Gamma = 0 \quad \text{and} \quad (0|0) = \sum_r p_r^0 = 1 \tag{37}$$

Then we have the basic form corresponding to (29)

$$\langle c|\{(0|s^2[s + \Gamma + iH(r)^x + V_1^x + V^x]^{-1}|a\rangle\langle a|0)\}|c\rangle \qquad (38)$$

since $(0|\mathbb{P} = (0|$ and $\mathbb{P}|0) = |0)$. When this form is expanded in $V_2$ to the second order, we obtain an expression which corresponds to (14).[2] If it is expanded further to the second order of $V_1$, we obtain the second order CW response corresponding to (19). This is given by

$$W(c,\infty) = \lim_{s\to 0} (0|\langle c|V_2|b_j\rangle\langle b_j|\frac{1}{s+\Gamma+\gamma_b+i(H-c)}|b_i\rangle\langle b_i|V_1|a\rangle \frac{1}{s+\Gamma+i(a-c)}$$

$$\times \langle c|V_2|b_1\rangle^*\langle b_1|\frac{1}{s+\Gamma+\gamma_b+i(H-a)}|b_k\rangle^*\langle b_k|V_1|a\rangle^*|0)$$

$$+(0|\langle c|V_2|b_n\rangle\langle b_n|\frac{1}{s+\Gamma+\gamma_b+i(H-c)}|b_1\rangle\langle b_1 b_m|\frac{1}{s+\Gamma+2\gamma_b}|b_j b_k\rangle$$

$$\times\langle b_j|\frac{1}{s+\Gamma+\gamma_b+i(H-a)}|b_i\rangle\langle b_i|V_1|a\rangle|0) \langle a|V_1|b_k\rangle\langle b_m|V_2|c\rangle$$

$$+(0|\langle c|V_2|b_n\rangle\langle b_n|\frac{1}{s+\Gamma+\gamma_b+i(H-c)}|b_1\rangle\langle b_1 b_m|\frac{1}{s+\Gamma+2\gamma_b}|b_k b_j\rangle$$

$$\times\langle b_k|V_1|a\rangle\langle b_j|\frac{1}{s+\Gamma+\gamma_b+i(H-a)}|b_i\rangle^*\langle b_i|V_1|a\rangle^*\langle b_m|V_2|c\rangle|0)$$

$$+ \text{c.c.} \qquad (39)$$

Therefore a stochastic model works as a substitute of a dynamical model by simplifying the dynamics by a stochastic model and thus makes a nonperturbative calculation feasible. It can be used for modeling a specific physical system. Our aim here is rather to obtain an insight to some general features of the general problem.

### A FOUR-LEVEL ATOM WITH OFF-DIAGONAL RANDOM MODULATION

In order to illustrate the general consideration, let us consider a simple four-level model assuming the initial state A, the intermediate states $B_1$ and $B_2$, and the final state C as the system S. A and $B_1$ are connected by the interaction $V_1$, and $B_2$ and C by $V_2$ (see Fig. 1). The IMSI from the reservoir gives rise to an off-diagonal interaction $\Omega$ between $B_1$ and $B_2$ and produces a connection between A and C. This model is particularly interesting because the IMSI plays an essential role for the higher order optical processes. Thus we assume

$$H_I = \begin{pmatrix} 0 & \Omega \\ \Omega & 0 \end{pmatrix} \qquad (40)$$

as the IMSI Hamiltonian for the states $B_1$ and $B_2$. For H(r) in Eq. (35) we have

$$H(\Omega) = \begin{pmatrix} a & 0 & 0 & 0 \\ 0 & b_1 & \Omega & 0 \\ 0 & \Omega & b_2 & 0 \\ 0 & 0 & 0 & c \end{pmatrix} \qquad (41)$$

We introduce another great simplification by assuming $\Omega$ to jump between two values $+\Delta$ and $-\Delta$ randomly with the average jumping rate $\gamma_m = 1/\tau_m$. Correspondingly the reservoir states are only the set of $+1_m$ and $-1_m$. This is called a two-state jump model. For $\Gamma$ in Eq. (33), we assume the simplest form

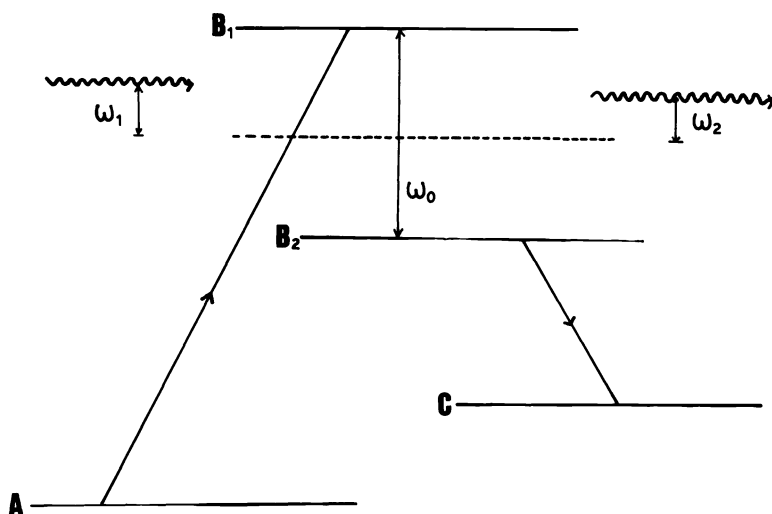$$\Gamma = \gamma_m \begin{pmatrix} 1/2 & -1/2 \\ -1/2 & 1/2 \end{pmatrix} \qquad (42)$$

Fig. 1. A four-level atom with off-diagonal modulation.

for which we have

$$|0) = \begin{pmatrix} 1/2 \\ 1/2 \end{pmatrix} \qquad \text{and} \qquad (0| = (1, \ 1).$$

Other eigenvectors are

$$|1) = \begin{pmatrix} 1/2 \\ -1/2 \end{pmatrix} \qquad \text{and} \qquad (1| = (1, \ -1).$$

which satisfy

$$\Gamma \ |1) = \gamma_m \ |1), \qquad (1| \ . \Gamma = \gamma_m (1| \ .$$

The projection **P**, Eq. (35), is now

$$\mathbf{P} = |0)(0| = \begin{pmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{pmatrix}$$

and so we have

$$\mathbf{Q} = 1 - \mathbf{P} = |1)(1| = \begin{pmatrix} 1/2 & -1/2 \\ -1/2 & 1/2 \end{pmatrix}$$

The expression (39) can be calculated for this model with the use of Eqs.(27) and (28) for the propagators appearing in the expression. These are much simplified because of the two-state jump model assumed here. We have

$$(0|H_I|1) = (1|H_I|0) = \Delta \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{43}$$

$$(0|H_I^\times|1) = (1|H_I^\times|0) = \Delta \begin{pmatrix} 0 & 0 & 1 & -1 \\ 0 & 0 & -1 & 1 \\ 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 \end{pmatrix} \tag{44}$$

because

$$(0|\Omega|0) = (1|\Omega|1) = 0 \quad \text{and} \quad (0|\Omega|1) = (1|\Omega|0) = \Delta \tag{45}$$

Note that the matrix (43) is for the space of $b_1$ and $b_2$, whereas (44) is for the space of four components, $\langle b_1|\rho|b_1\rangle$, $\langle b_2|\rho|b_2\rangle$, $\langle b_1|\rho|b_2\rangle$ and $\langle b_2|\rho|b_1\rangle$ of the excited state density matrix. By the fact that $(1|\Omega|1) = 0$, Eq. (45) G, Eq. (28a), no longer contains $H_I$. Namely, the lowest order perturbation scheme is exact for a two-state jump model. These nice features allow us to carry out an analytical calculation of this model. It is elementary but is tedious. So we give here only the results.
The result previously obtained by Takagawara (8) was a lengthy formula which did not give us much insight into the problem. So we recently reexamined the calculation and found that the final result is nicely rearranged into a compact form (Ref 9).
We set for convenience (see Fig. 1)

$$b_1 - b_2 = \omega_0, \quad (b_1 + b_2)/2 = \bar{b}, \quad a = \bar{b} + \omega_1, \quad c = \bar{b} + \omega_2 \tag{46}$$

and so

$$a - b_1 = \omega_1 - \omega_0/2, \quad c - b_2 = \omega_2 + \omega_0/2 \tag{47}$$

Then the spectral intensity $W(c,\infty)$, Eq. (39), of the scattered light is shown to consist of two terms, namely

$$W(c,\infty) = W_R + W_L \tag{48}$$

where we have

$$W_R = |\langle a|V_1|b_1\rangle\langle b_2|V_2|c\rangle|^2 \ \frac{2\,\gamma_m}{\gamma_m^2 + (\omega_1 - \omega_2)^2} \ \frac{\Delta^2}{|h(\omega_1, \omega_0)|^2 \, |h(\omega_2, -\omega_0)|^2}$$

$$\times [\{(\gamma_b + \gamma_m)^2 + \Delta^2 - (\omega_1 + \tfrac{1}{2}\omega_0)(\omega_2 - \tfrac{1}{2}\omega_0)\}^2 + (\gamma_b + \gamma_m)^2(\omega_1 + \omega_2)^2] \tag{49}$$

with

$$h(\omega, \omega_0) = [\gamma_b + i(\omega - \tfrac{1}{2}\omega_0)][\gamma + \gamma_m + i(\omega + \tfrac{1}{2}\omega_0)] + \Delta^2] \tag{50}$$

and

$$W_L = w_{a\to b_1}\ w_{b_2\to c}\ \frac{w_{12}}{2\,\gamma_b + w_{12}}\ /\ \gamma_b \tag{51}$$

with

$$w_{a\to b_1} = |\langle a|V_1|b_1\rangle|^2 \ \frac{\gamma_m\Delta^2}{|h(\omega, \omega_0)|^2}$$

$$= |\langle a|V_1|b_1\rangle|^2 \frac{\gamma_m}{\gamma_b + \gamma_m} \frac{\gamma'(\omega_1, \omega_0)}{[\gamma_b + \gamma'(\omega_1, \omega_0)]^2 + [\omega_1 - \tfrac{1}{2}\omega_0 - \delta(\omega_1, \omega_0)]^2} \tag{52}$$

$$w_{b_2\to c} = |\langle b_2|V_2|c\rangle|^2 \ \frac{\gamma_m\Delta^2}{h(\omega_2, -\omega_0)^2}$$

$$= |\langle b_2|V_2|c\rangle|^2 \frac{\gamma_m}{\gamma_b + \gamma_m} \frac{\gamma'(\omega_2, -\omega_0)}{[\gamma_b + \gamma'(\omega_2, -\omega_0)]^2 + [\omega_2 + \tfrac{1}{2}\omega_0 - \delta(\omega_2, -\omega_0)]^2} \tag{53}$$

$$w_{12} = \frac{4\,\Delta^2(\gamma_m + 2\gamma_b)}{(\gamma_m + 2\gamma_b)^2 + \omega_0^2} \tag{54}$$

with

$$\Upsilon'(\omega,\ \omega_0) - i\,\delta\,(\omega,\ \omega_0) = \frac{\Delta^2}{(\Upsilon_m + \Upsilon_b) + i(\omega + \frac{1}{2}\omega_0)} \tag{55}$$

The first term $W_R$ looks to correspond to the Raman scattering, whereas $W_L$ to the luminescence. In this model, there is no second order emission if the off-diagonal modulation is not present because, then the states A and C are not connected. By the off-diagonal modulation, $B_1$ and $B_2$ are mixed and the channel from A to C is opened.

In the static limit of $\gamma_m = 0$, the luminescence term is zero and $W_R$ is reduced to

$$W_R = 2\pi\ \delta(\omega_1 - \omega_2)\ \frac{\Delta^2}{[(\omega_1 + \sqrt{\Delta^2 + \omega_0^2/4})^2 + \gamma_b^2][(\omega_1 - \sqrt{\Delta^2 + \omega_0^2/4})^2 + \gamma_b^2]} \tag{56}$$

This is a pure Raman scattering through the intermediate states $B_1$ and $B_2$ which are mixed together by the off-diagonal perturbation and have the dipole matrix elements between both A and C. For a finite value of $\Upsilon_m$, the luminescence appears and the Raman line is broadened to a Loretzian form with the half width equal to $\Upsilon_m$. This broadening is caused by the nonstatic IMSI, through which the reservoir exchanges energy with the radiation. As the modulation rate becomes faster, the luminescence increases in intensity, and the Raman line is broadened further. Because of resonance, the Raman intensity may show peaks at frequencies where $\omega_2$ coincides with the energy difference between either of the excited states and the final state. Theses peaks superpose on luminescence and make one wonder if it is legitimate to call $W_R$ as the Raman term at all. However, as far as we see from our analysis, it is natural to interpret these peaks as the result of resonance enhancement of the Raman component rather than the luminescence. When the modulation rate is so fast that the effect of off-diagonal perturbation is averaged out, the optical response will totally disappear. The integrated intensity of the second order optical response thus increases from a finite value corresponding to (56) as $\gamma_m$ increases from zero, attains a maximum and finally vanishes. An analytical expression of the integrated intensity is easily obtained for this model.

Figures 2 and 3 illustrate the spectral distributions of $W_R$ and $W_L$ for a particular set of the parameters. The excited states are separated by $\omega_0 = 0.3$ and are modulated by an off-diagonal with the magnitude equal to 0.5. The off-resonance of the incident light is set at 0.15. The natural radiation damping rate is taken as 0.01. The intensity contours are calculated for different values of the modulation rate $\gamma_m$ of the off-diagonal perturbation. Figure 2 is for the Raman term, and Fig. 3 for the luminescence term. The Raman response shows a sharp peak at the Raman position, $\omega_1 = \omega_2$, for $\gamma_m = 0.01$ and the resonance peaks at $\omega_2 = \pm 0.5$. These peaks decline rather quickly as $\gamma_m$ increases. Already for $\gamma_m = 0.1$, the Raman peak is weaker than the resonance peaks and becomes unnoticeable for $\gamma_m = 0.5$. In Fig. 3, the luminescence peaks at $\omega_2 = \pm 0.5$ are distinct for small values of $\gamma_m$, but merge into a single peak when $\gamma_m$ becomes larger than 0.5 and are motionally narrowed. These numbers are not so significant but the figures indicate the general features.

The luminescence term $W_L$ consists of three factors. The first and second factors correspond to the transition rates from A to $B_1$ and from $B_2$ to C by absorption and emission of light, respectively. The third factor is the branching ratio for the channel $B_1 \to B_2$, $2\gamma_b$ being the decay rate of $B_1$ due to the radiation damping. It is to be noticed, however, the rates $w_{a \to b}$ or $w_{b_1 \to c}$ is not quite the same as the absorption or the emission rate, which is given by the formula

$$w_{a \to b}(abs) = \lim_{s \to 0} Re \int_0^\infty dt\ e^{-st}\ Tr\ V_1(t)\rho(0)\ V_1(0)$$

$$= |\langle a|V_1|b\rangle|^2\ \frac{\gamma_b + \gamma'(\omega_1,\ \omega_0)}{[\gamma_b + \gamma'(\omega_1,\ \omega_0)]^2 + [\omega_1 - \frac{1}{2}\omega_0 - \delta(\omega_1,\ \omega_0)]^2} \tag{57}$$

or

**Four-Level Atom ; Raman Term**

$\omega_1 = 0.15$
$\omega_0 = 0.3$
$\Delta = 0.5$
$\gamma_b = 0.01$

**Four-Level Atom ; Luminescence Term**

$\omega_1 = 0.15$
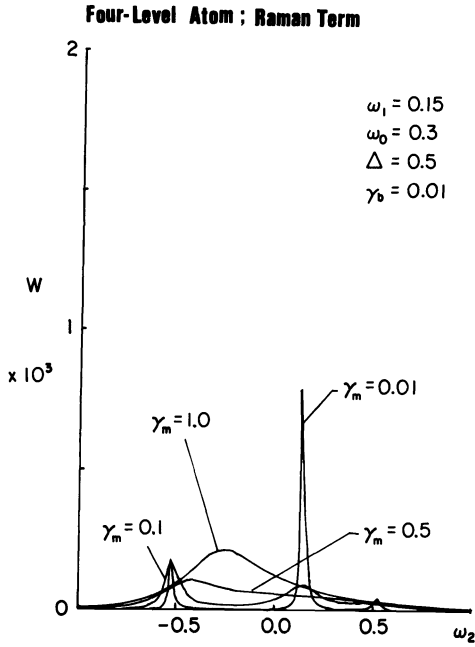$\omega_0 = 0.3$
$\Delta = 0.5$
$\gamma_b = 0.01$

Fig. 2. The Raman-like spectrum of a four-level atom modulated by an off-diagonal IMSI.
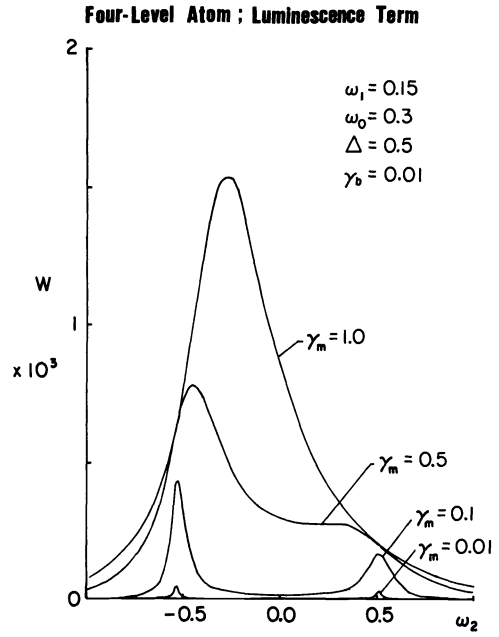
Fig. 3. The luminescence spectrum of a four-level atom modulated by an off-diagonal IMSI.

$$w_{b_2 \to c}(\text{emission}) =$$

$$= |\langle b_2|V_2|c\rangle|^2 \frac{\gamma_b + \gamma'(\omega_2, -\omega_0)}{[\gamma_b + \gamma'(\omega_2, -\omega_0)]^2 + [\omega_2 - \frac{1}{2}\omega_0 - \delta(\omega_2, -\omega_0)]^2} \tag{58}$$

The expressions (52) and (56) are related by

$$w_{a \to b_1} = w_{a \to b_1}(\text{abs}) \frac{\gamma_m}{\gamma_b + \gamma_m} \frac{\gamma'(\omega_1, \omega_0)}{\gamma_b + \gamma'(\omega_1, \omega_0)} \tag{59}$$

and (53) and (58)  by a similar relation.  If the natural damping is ignored (52) and (53) are identical with the corresponding rates of absorption and emission respectively.  We have, at present, no physical intuition to explain this delicate differece of the rates.   Except this , the expression (51) for $W_L$  shows that this in fact represents the luminescence process which is composed of three steps.
The shift $\delta$ and the width $\gamma'$ of the excited state appearing in Eqs. (52) and (53) are generally dependent on the off-resonance $\omega_1 - \omega_0/2$  or $\omega_2 + \omega_0/2$ .  Only in the case of exact resonance, namely when $\omega_1 = \omega_0/2$  or $\omega_2 = -\omega_0/2$, they are equal to those of the state $B_1$ or $B_2$ modulated by the IMSI  independently of the optical process.
On the other hand, the transition rate $w_{1 \to 2}$ in Eq. (54) is intrinsic to the excited states in the sense that it is exactly equal to that which results from the  IMSI.  It should be noted, however, that the intrinsic relaxation of the intermediate states by IMSI is incorporated into the optical process only as an element in the luminescent process.  Other factors in $W_R$  and $W_L$ indicate the importance of dynamical coherence of IMSI in an optical process. This will be  clearer if transient responses are treated along the same line. We have done this to some extent, but more are left for future studies.
The separation of the Raman and the luminescence terms, as was shown for our simple model,  is conjectured to be a general matter.  A few more examples have been treated  parallel to the model here discussed.  We have not, how- ever been able to show this in a general way.  If a nice prescription

found for this purpose, it can be applied to a wider class of physical pro-
blems in which the IMSI plays an essential role.

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