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Floquet–Liouville supermatrix approach. II. Intensity-dependent generalized nonlinear optical susceptibilities

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We present a practical *nonperturbative* method for *exact* treatment of *intensity-dependent* generalized nonlinear optical susceptibilities $\chi(\omega)$ in intense polychromatic fields, valid for arbitrary laser intensities, detunings, and relaxation. By means of the many-mode Floquet theory, the time-dependent Liouville equation can be transformed into an equivalent *time-independent* infinite-dimensional Floquet–Liouville supermatrix (FLSM) eigenvalue problem. It is then shown that the nonlinear optical susceptibilities $\chi(\omega)$ can be completely determined simply from the supereigenvalues and eigenfunctions of the Floquet–Liouvillian $\hat{L}_F$. In addition to this exact FLSM approach, we have also presented higher-order perturbative results, based on the extension of the Salwen's nearly degenerate perturbation theory, appropriate for somewhat weaker fields and near-resonant multiphoton processes, but beyond the conventional perturbative or rotating wave approximation (RWA). In the case of two-level systems, for example, the implementation of Salwen's method in the time-independent $\hat{L}_F$ allows the reduction of the infinite-dimensional FLSM into a 4×4 dimensional effective Hamiltonian, from which essential *analytical* formulas for intensity-dependent $\chi(\omega)$ can be obtained. These methods are applied to a detailed study of intensity-dependent spectral line shapes (such as hole burning and extra resonance peaks at the line center, and the effects of saturation, detuning, and radiative and collisional damping, etc.) and subharmonic structures in nonlinear multiple wave mixings $\chi[(m+1)\omega_1 - m\omega_2]$ for two-level systems in intense linearly polarized bichromatic fields.

I. INTRODUCTION

The determination of nonlinear optical susceptibilities represents a significant area of both experimental and theoretical research in nonlinear optics.[1-3] Calculations of nonlinear susceptibilities in a medium with discrete quantum levels are usually performed by means of perturbative methods.[1-3] The perturbative treatment is adequate when both the pump and the probe fields are weak and the corresponding nonlinear optical susceptibilities are independent of field strengths. However, a number of recent experimental works were carried out under the conditions that both the pump and the probe fields are strong.[4-7] Distinct new features such as subradiative structures, multiphoton absorption peaks, and high-order (up to 27th order[4]) nonlinear wave mixings, etc. have been observed. In most of these nonlinear optical processes, when the fields are intense enough to saturate the transitions, nonlinear susceptibilities become intensity dependent. Nonperturbative response functions are required to explain these intense-field effects. Currently while several nonperturbative methods[8-10] have been proposed,they are all based on the assumption of the validity of the rotating wave approximation (RWA), and consider only exact or near resonant processes. As such the ac-Stark shifts which are known to be significant in strong fields are often ignored. And multiphoton processes where non-RWA channels have important contributions (such as those in off-resonant processes, etc.) cannot be properly treated by these methods.

In this paper, we present an *exact* nonperturbative method for the calculation of intensity-dependent nonlinear optical susceptibilities in polychromatic fields valid for arbitrary laser intensities, detunings, and relaxation. The method is based on the extension of the recently developed Floquet–Liouville supermatrix (FLSM) approach[11] (hereafter called paper I). The FLSM formalism allows the exact transformation of the time-dependent Liouville equation for the density matrix of quantum systems (undergoing arbitrary relaxation) into an equivalent *time-independent non-Hermitian* Floquet–Liouvillian $\hat{L}_F$ eigenvalue problem. This yields a numerically stable and computational efficient approach for the unified treatment of nonresonant and resonant, one- and multiple-photon, steady-state, and transient phenomena in nonlinear optical processes, much beyond the conventional perturbative and RWA approaches. The FLSM theory is reviewed in Sec. II mainly to define necessary notations and to outline the essential results for the reduced density matrix elements. In Sec. III, we present an exact formulation of the intensity-dependent nonlinear optical susceptibilities for two-level systems in polychromatic fields valid for arbitrary field strengths. Further, in Sec. IV, we present a higher-order nearly degenerate perturbative analysis of the Floquet–Liouvillian $\hat{L}_F$. This yields useful analytical expressions for field-dependent nonlinear optical susceptibilities, appropriate for somewhat weaker fields and near-resonant processes but beyond the RWA limit. A detailed study of the effects of intensity, detuning, and relaxation (radiative decay and collisional damping) upon nonlinear response functions and high-order wave mixings is presented in Sec. V for the specific case of two-level systems in bichromatic fields using the analytical formulas derived in Sec. IV. Finally in Sec. VI we extend the exact FLSM numerical method for a detailed exploration of the multiphoton subradiative structures in high-order wave mixing processes in very intense fields. This is followed by a conclusion in Sec. VII. Atomic units are used throughout unless otherwise specified.

II. FLOQUET–LIOUVILLE SUPERMATRIX (FLSM) TREATMENT OF THE NONLINEAR RESPONSE OF N-LEVEL QUANTUM SYSTEMS IN POLYCHROMATIC FIELDS

In this section we review the basic elements of the exact FLSM treatment[11] of the nonlinear response of a set of nondegenerate N-level quantum systems, driven by M linearly polarized monochromatic laser fields. Extensions to the case of circular or elliptic polarization as well as to degenerate systems are straightforward. The time development of the system is governed by the Liouville equation[2,10]

$$i\partial_t \rho(t) = [H(t),\rho(t)] + i[R,\rho(t)]\,, \tag{1}$$

where ρ is the density matrix of the system, reduced by an averaging over all irrelevant degrees of freedom acting as a thermal bath, and $H(t)$ is the Hermitian Hamiltonian defined by

$$H(t) = H_0 + V(t)\,. \tag{2}$$

H_0 is the unperturbed Hamiltonian of the N-level system with eigenvalues $\{E_\alpha\}$ and eigenfunctions $\{|\alpha\rangle\}$, i.e.,

$$H_0|\alpha\rangle = E_\alpha|\alpha\rangle, \quad \alpha = 0,1,2,...,N-1\,. \tag{3}$$

$V(t)$ is the electric dipole interaction between the system and the M-mode classical fields $\mathbf{E}(t)$,

$$V(t) = -\boldsymbol{\mu}\cdot\mathbf{E}(t)\,, \tag{4}$$

where

$$\mathbf{E}(t) = \sum_{i=1}^{M} \boldsymbol{\epsilon}_i \cos(\omega_i t + \phi_i)\,, \tag{5}$$

$\boldsymbol{\mu}$ is the electric dipole moment operator of the system, and $\boldsymbol{\epsilon}_i$, ω_i, and ϕ_i specifying, respectively, the amplitude, frequency, and the initial phase of the ith field. In the Markov approximation, the relaxation term $[R,\rho(t)]$ has the following form and consists of T_1 (population damping) and T_2 (coherent damping) mechanisms which are due to the coupling of the system to the thermal bath by radiative decays and collisions, etc. More explicitly,[10,11]

$$[R,\rho]_{\alpha\alpha} = -\Gamma_{\alpha\alpha}\rho_{\alpha\alpha} + \sum_{\beta(\neq\alpha)} \gamma_{\beta\alpha}\rho_{\beta\beta} \quad (T_1 \text{ process})\,, \tag{6a}$$

$$[R,\rho]_{\alpha\beta} = -\Gamma_{\alpha\beta}\rho_{\alpha\beta}, \quad \alpha\neq\beta \quad (T_2 \text{ process})\,. \tag{6b}$$

The quantities $\gamma_{\beta\alpha}$ give the inelastic rates for making a transition from the state $|\beta\rangle$ to $|\alpha\rangle$. The off-diagonal decay rate $\Gamma_{\alpha\beta}$ $(=\Gamma_{\beta\alpha})$ is given by

$$\Gamma_{\alpha\beta} = 1/2(\Gamma_{\alpha\alpha} + \Gamma_{\beta\beta}) + \Gamma'_{\alpha\beta}\,, \tag{7}$$

where $\Gamma'_{\alpha\beta}$ arises from phase-changing collisions. For closed systems (namely, $\mathrm{Tr}\,\rho = 1$, $\mathrm{Tr}[R,\rho] = 0$), assumed in the following sections, we have further the relation

$$\Gamma_{\alpha\alpha} = \sum_\beta \gamma_{\alpha\beta}\,. \tag{8}$$

In the tetradic or Liouville space,[12] spanned by the basis $\{|\alpha\beta\rangle \equiv |\alpha\rangle\langle\beta|;\alpha \text{ and } \beta = 0,1,2,...,N-1\}$, Eq. (1) can be recast into an inhomogeneous superoperator equation, namely,

$$i\partial_t \hat{\rho}(t) = \hat{L}(t)\hat{\rho}(t) + i\hat{\mathbf{f}}\,. \tag{9}$$

Here $\hat{\rho}(t)$ is the supervector defined by

$$\hat{\rho}(t) = \sum_{\alpha,\beta} \hat{\rho}_{\alpha\beta}|\alpha\rangle\langle\beta|\,, \tag{10}$$

$\hat{L}$ is the (nonsingular) superoperator or Liouvillian detailed elsewhere,[11] and $\hat{\mathbf{f}}$ is the source supervector given by

$$\hat{\mathbf{f}}_{\mu\nu} = \gamma_0\delta_{\mu 0}\delta_{\nu 0}\,, \tag{11}$$

where $\gamma_0 \equiv \Sigma_{\beta\neq 0}\gamma_{\beta 0}$, assuming $|0\rangle$ is the ground level. Equation (9) can be solved most expediently by invoking the many-mode Floquet theory (MMFT),[13,14] analogous to solving the Schrödinger equation with Hamiltonian having the same time dependence as that in Eq. (1). The MMFT renders the time-dependent superoperator equation (9) into an equivalent *time-independent* infinite-dimensional super-eigenvalue equation, namely,

$$\sum_{\sigma\tau}\sum_{\{k\}} \langle\alpha\beta;\{m\}|\hat{L}_F|\sigma\tau;\{k\}\rangle\langle\sigma\tau;\{k\}|\Omega_{\mu\nu;\{n\}}\rangle = \Omega_{\mu\nu;\{n\}}\langle\alpha\beta;\{m\}|\Omega_{\mu\nu;\{n\}}\rangle\,, \tag{12}$$

where $\hat{L}_F$ is the *time-independent* many-mode Floquet–Liouville supermatrix (FLSM) defined in terms of the generalized tetradic–Floquet basis $|\alpha\beta;\ \{m\}\rangle \equiv |\alpha\rangle\langle\beta| \otimes |\{m\}\rangle$, where $\{m\}$ is the set of Fourier indices, $\{m\} = m_1,m_2,...,m_M$.

The structure of the FLSM $\hat{L}_F$, which is non-Hermitian, is illustrated in Fig. 1 for the two-level two-mode case. The

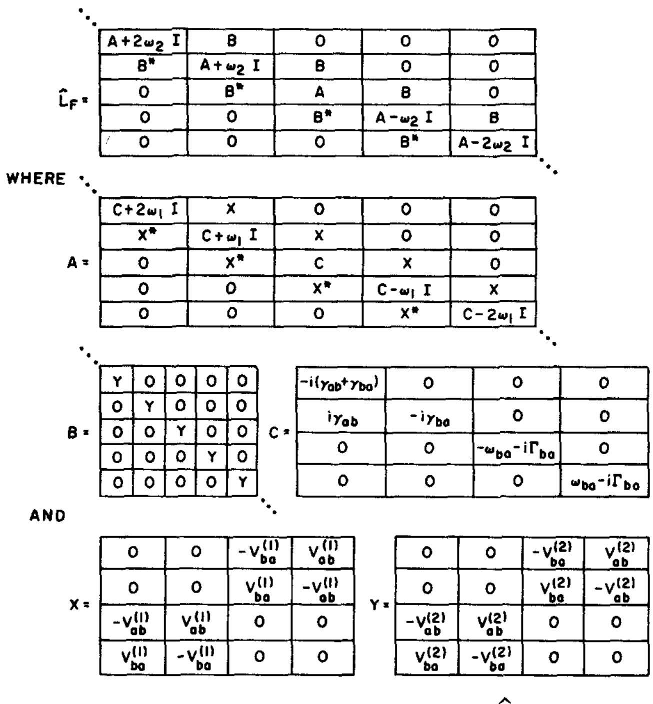

FIG. 1. Structure of the Floquet–Liouville supermatrix $\hat{L}_F$ for the case of two-level systems (with level spacing ω_{ba}) in linearly polarized bichromatic fields. ω_1 and ω_2 are the two radiation frequencies $V_{ab}^{(i)}$ $(i=1,2)$ are the electric dipole couplings, and γ_{ab}, γ_{ba}, and $\Gamma_{ba} = (\gamma_{ab}+\gamma_{ba})/2$ are relaxation parameters.

multiply periodic structure of $\hat{L}_F$ renders the following important periodic relationships for its supereigenvalues $\Omega_{\mu\nu;\{n\}}$ and eigenvectors $|\Omega_{\mu\nu;\{n\}}\rangle$:

$$\text{(i)}\ \ \mathrm{Im}(\Omega_{\mu\nu;\{n\}}) < 0\,, \tag{13}$$

$$\text{(ii)}\ \ \Omega_{\mu\nu;\{n+k\}} = \Omega_{\mu\nu;\{n\}} + \sum_{i=1}^{M} k_i\omega_i\,, \tag{14}$$

and

$$\text{(iii)}\ \ \langle\alpha\beta;\{m+k\}|\Omega_{\mu\nu;\{n+k\}}\rangle = \langle\alpha\beta;\{m\}|\Omega_{\mu\nu;\{n\}}\rangle\,. \tag{15}$$

Further, it has been shown that in the limit of $\gamma_{\alpha\beta} = \Gamma_{\alpha\beta} = 0$ (i.e., no relaxations) the supereigenvalues Ω and eigenvectors $|\Omega\rangle$ of $\hat{L}_F$ are related to the quasienergy eigenvalues λ and eigenvectors $|\lambda\rangle$ of H_F, where H_F is the Floquet Hamiltonian for the nondamping case,[13] by the following relations:

$$\Omega_{\alpha\beta;\{m\}} = \gamma_{\alpha,\{0\}} - \gamma_{\beta,\{0\}} + \sum_{i=1}^{M} m_i\omega_i\,, \tag{16}$$

$$\langle\mu\nu;\{k\}|\Omega_{\alpha\beta;\{0\}}\rangle = \sum_{\{n\}} \langle\mu,\{n\}|\lambda_{\alpha,\{0\}}\rangle\langle\lambda_{\beta,\{0\}}|\nu,\{n-k\}\rangle\,. \tag{17}$$

Thus the supereigenvalues Ω have the physical interpretation as the "difference spectrum" of the quasienergies.

In terms of the eigenvalues and eigenvectors of the superoperator $\hat{L}_F$ the reduced density matrix $\rho(t)$ can be expressed as $\rho(t) = U(t;t_0)\rho(t_0)$, where U is the non-Hermitian super-evolution operator given by, in matrix form,

$$U_{\alpha\beta;\mu\nu}(t;t_0) = \sum_{\{m\}}\Big(\langle\alpha\beta;\{m\}|\exp[-i\hat{L}_F(t-t_0)]|\mu\nu;\{0\}\rangle + \gamma_0\delta_{\mu\nu}\sum_{\sigma\tau}\sum_{\{m\}}\langle\alpha\beta;\{m\}|\Omega_{\sigma\tau;\{k\}}\rangle\langle\Omega^*_{\sigma\tau;\{k\}}|00;\{0\}\rangle$$
$$\cdot\{1-\exp[-i\Omega_{\sigma\tau;\{k\}}\cdot(t-t_0)]\}/i\Omega_{\sigma\tau;\{k\}}\Big)\cdot\exp(i\sum_{j=1}^{M} m_j\omega_j t)\,. \tag{18}$$

Furthermore, since $\mathrm{Im}\,\Omega < 0$ for all Ω, the reduced density matrix has a simple form at large times $t\to\infty$,

$$\rho_{\alpha\beta}(t)\to\gamma_0\sum_{\{m\}}\Big(\sum_{\sigma\tau}\sum_{\{k\}}\langle\alpha\beta;\{m\}|\Omega_{\sigma\tau;\{k\}}\rangle\langle\Omega^*_{\sigma\tau;\{k\}}|00,\{0\}\rangle/i\Omega_{\sigma\tau;\{k\}}\Big)\exp\Big(i\sum_{j=1}^{M} m_j\omega_j t\Big)\,, \tag{19}$$

which is *independent* of the initial state $\rho(t_0)$ and is *oscillatory* in the course of time, dictated by the Fourier term $\exp(i\Sigma_{j=1}^{M} m_j\omega_j t)$. Thus in steady state, the off-diagonal density matrix element $\rho_{\alpha\beta}(t)$ exhibits harmonic frequencies of the form $m_1\omega_1 + m_2\omega_2 + \cdots + m_M\omega_M$, where $m_1, m_2,\ldots,m_M$ are arbitrary integers.

III. INTENSITY-DEPENDENT GENERALIZED NONLINEAR OPTICAL SUSCEPTIBILITIES: EXACT FLSM NONPERTURBATIVE TREATMENT

The nonlinear response of an ensemble of systems to the incident polychromatic fields takes the form of a dielectric polarization density $\mathbf{P}(t)$ which acts as a source term in Maxwell's wave equation. The polarization density is related to the expectation value of the dipole moment operator μ and can be calculated from the density matrix $\rho(t)$,

$$\langle P(t)\rangle = N_0\langle\mu\rangle = N_0\,\mathrm{Tr}[\mu\rho(t)]\,, \tag{20}$$

where N_0 is the number density in the ensemble and $\rho(t)$ can be determined by the FLSM method described in Sec. II.

Without loss of generality, we shall now confine our discussion to the two-level systems driven by intense M-mode polychromatic fields. The polarization density now has the form

$$\langle P(t)\rangle = N_0[\mu_{ba}\rho_{ab}(t) + \mu_{ab}\rho_{ba}(t)]\,, \tag{21}$$

where μ_{ab} is the transition dipole matrix element between the unperturbed atomic states $|a\rangle$ and $|b\rangle$ (assumed to be of opposite parity and $E_a < E_b$).

In the steady state, the polarization density can be expanded as a Fourier series in the incident frequencies [as shown by Eq. (19)],

$$\langle P(t)\rangle = \sum_{m_1m_2\cdots m_M} P_{m_1m_2\cdots m_M}(\omega)e^{-i(m_1\omega_1+m_2\omega_2+\cdots+m_M\omega_M)t}\,, \tag{22}$$

where $P_{m_1m_2\cdots m_M}(\omega)$ is the Fourier component at frequency $\omega = m_1\omega_1 + m_2\omega_2 + \cdots + m_M\omega_M$. As an example, consider the two-mode ($M=2$) case with ω_1 being the pump frequency and ω_2 the probe frequency. We have from Eq. (22),

$$\langle P(t)\rangle = P_{1,0}(\omega_1)e^{-i\omega_1 t} + P_{0,1}(\omega_2)e^{-i\omega_2 t} + P_{2,-1}(2\omega_1-\omega_2)e^{-i(2\omega_1-\omega_2)t} + \cdots\,.$$

The physical consequences of these terms are as follows: $P_{1,0}(\omega_1)$ and $P_{0,1}(\omega_2)$ give rise to absorption (or amplification) of the pump and probe waves, respectively, while the *mixing* response $P_{2,-1}(2\omega_1-\omega_2)$ is responsible for generation of an optical wave with frequency $\omega = 2\omega_1 - \omega_2$, and so on. Note that $P_{\{m\}}(\omega)$ is a nonperturbative result. If expanded in terms of a power series of incident fields, $P_{\{m\}}(\omega)$ can be related to the conventional perturbative nonlinear susceptibilities (to infinite order, in principle). For example, in the case of bichromatic fields ($M=2$),

$$P_{1,0}(\omega_1) = \chi^{(1)}(-\omega_1;\omega_1)\epsilon_1(\omega_1) + \chi^{(3)}(-\omega_1;\omega_1,\omega_1,-\omega_1)\epsilon_1^2(\omega_1)\epsilon_1^*(\omega_1)$$
$$+ \chi^{(3)}(-\omega_1;\omega_1,\omega_2,-\omega_2)\epsilon_1(\omega_1)|\epsilon_2(\omega_2)|^2 + \cdots,$$
$$P_{2,-1}(2\omega_1-\omega_2) = \chi^{(3)}(-2\omega_1+\omega_2;\omega_1,\omega_1,-\omega_2)\epsilon_1^2(\omega_1)\epsilon_2^*(\omega_2)$$
$$+ \chi^{(5)}(-2\omega_1+\omega_2;\omega_1,\omega_1,\omega_1,-\omega_1,-\omega_2)\epsilon_1^3(\omega_1)\epsilon_1^*(\omega_1)\epsilon_2^*(\omega_2)$$
$$+ \chi^{(5)}(-2\omega_1+\omega_2;\omega_1,\omega_1,\omega_2,-\omega_2,-\omega_2)\epsilon_1^2(\omega_1)|\epsilon_2(\omega_2)|^2\epsilon_2^*(\omega_2)$$
$$+ \cdots, \text{ etc.,}$$

where

$$\epsilon_i(n_i\omega_i) = \begin{cases} \epsilon_i(\omega_i)^{n_i}, & n_i \geqslant 0 \\ \epsilon_i^*(\omega_i)^{|n_i|}, & n_i < 0 \end{cases}$$

is the Fourier transform of the ith optical field at ω_i and $\chi^{(q)}$ is the conventional (intensity-independent) perturbative qth order optical susceptibility. At weak incident fields, the lowest (nonvanishing) order susceptibility dominates and the conventional perturbative approach for $\chi^{(q)}$ is adequate. For example, if both the pump and probe fields are weak, the generation of a coherent signal at $2\omega_1-\omega_2$ (four-wave mixing) is described by the third-order ($q=3$) nonlinear susceptibility $\chi^{(3)}(-2\omega_1+\omega_2;\omega_1,\omega_1,-\omega_2)$. However, for strong saturating fields, higher-order nonlinear susceptibilities can contribute significantly. This leads to the concept of intensity-*dependent* generalized nonlinear optical susceptibility $\chi(m_1\omega_1+m_2\omega_2+\cdots+m_M\omega_M)$ defined by

$$\chi_{\{m\}}(\omega) = P_{\{m\}}(\omega)/ [\epsilon_1(m_1\omega_1)\epsilon_2(m_2\omega_2)\cdots\epsilon_M(m_M\omega_M)], \quad (23)$$

where $\omega = m_1\omega_1 + m_2\omega_2 + \cdots + m_M\omega_M$. In the limit of weak fields, $\chi_{\{m\}}(\omega)$ reduces to the lowest nonvanishing order (intensity-independent) $\chi^{(q)}$, as it should be.

Using the results of Sec. II for $\rho(t)$, Eq. (19), we arrive at the following nonperturbative expression for generalized nonlinear optical susceptibility (for the two-level M-mode case) in terms of the supereigenvalues and eigenvectors of the Floquet–Liouvillian $\hat{L}_F$:

$$\chi_{\{m\}}(\omega = m_1\omega_1+m_2\omega_2+\cdots+m_M\omega_M)$$
$$= N_0\gamma_{ba}\Big[\sum_{\sigma\tau}\sum_{\{k\}}(\langle ba;\{m\}|\Omega_{\sigma\tau;\{k\}}\rangle\mu_{ab} + \langle ab;\{m\}|\Omega_{\sigma\tau;\{k\}}\rangle\mu_{ba})\langle\Omega^*_{\sigma\tau;\{k\}}|aa;\{0\}\rangle \cdot(i\Omega_{\sigma\tau;\{k\}})^{-1}\Big]/[\epsilon_1(m_1\omega_1)\epsilon_2(m_2\omega_2)\cdots\epsilon(m_M\omega_M)]. \quad (24)$$

IV. INTENSITY-DEPENDENT NONLINEAR OPTICAL SUSCEPTIBILITIES: HIGH-ORDER NEARLY DEGENERATE PERTURBATIVE TREATMENT

The FLSM method described in Sec. III provides a general nonperturbative numerical technique for the unified treatment of resonant and nonresonant, nonlinear multiwave mixing processes (such as CARS, four-wave mixing, etc.) at arbitrary field strengths, detunings, and relaxations. To exploit analytical properties of nonlinear optical processes and to make connection with commonly used perturbative and RWA approaches, we shall consider in this section the extension of Salwen's almost degenerate perturbation theory[15] to the Floquet–Liouvillian $\hat{L}_F$. This method has been previously used by us to the perturbative analysis of two-mode Floquet Hamiltonian H_F for the study of multiphoton dynamics and spectral line shapes of nondamping two-[13(c)] and three-level[16] systems driven by intense bichromatic fields. In the present case, appropriate extension of Salwen's technique to density matrix allows the reduction of the infinite-dimensional Floquet–Liouvillian $\hat{L}_F$ (cf. Fig. 1) into an effective non-Hermitian Salwen–Liouvillian $\hat{L}_S$, from which essential analytical formulas for intensity-dependent nonlinear optical susceptibilities, beyond the conventional perturbative and RWA approaches, can be obtained.

In this section, we shall consider the important class of a system of dipole-allowed two-level atoms (molecules) undergoing $(2|m|+1)$-photon $[\omega_{ba} \simeq (m+1)\omega_1 - m\omega_2]$ near-resonant transitions in the presence of two intense linearly polarized laser fields characterized by the frequencies (ω_1,ω_2), amplitudes (ϵ_1,ϵ_2), and initial phases (ϕ_1,ϕ_2), respectively. The two-level $|a\rangle$ and $|b\rangle$ $(E_a < E_b)$ are assumed to be of opposite parity.

In a proper rotating frame (*not* the RWA) defined by the unitary transformation

$$R(t) = \begin{bmatrix} 1 & 0 \\ 0 & e^{i[(m+1)\omega_1 - m\omega_2]t} \end{bmatrix} \quad (25)$$

the density-matrix superoperator $\hat{\rho}(t)$ satisfies approximately the Salwen–Liouville equation, namely,

$$i\partial_t\hat{\rho}(t) = \hat{L}_S\hat{\rho}(t) + i\hat{\mathbf{f}}_S, \quad (26)$$

where $\mathbf{f}_S$ is the source supervector given by

$$\hat{\mathbf{f}}_S = \begin{pmatrix} \gamma_{ba} \\ 0 \\ 0 \\ 0 \end{pmatrix}. \quad (27)$$

When the resonance condition $\omega_{ba} \simeq (m+1)\omega_1 - m\omega_2$, m arbitrary integer, is satisfied, the unperturbed tetradic–Floquet states $|aa;00\rangle$, $|bb;00\rangle$, $|ab;m+1,-m\rangle$, and $|ba;-(m+1),m\rangle$, form a four-dimensional almost degenerate set and span the Salwen's "model space." In terms of this model space, the effective Salwen–Liouvillian $\hat{L}_S$ has the following matrix form:

$$\hat{L}_S = \begin{bmatrix} -i(\gamma_{ab}+\gamma_{ba}) & 0 & -u_a^* & u_a \\ i\gamma_{ab} & -i\gamma_{ba} & -u_b^* & u_b \\ -u_a'^* & -u_b'^* & -(\Delta+\delta)-i\Gamma_{ba} & 0 \\ u_a' & u_b' & 0 & (\Delta+\delta)-i\Gamma_{ba} \end{bmatrix}, \tag{28}$$

where γ_{ab} and γ_{ba} are feeding rates and $\Gamma_{ba}(\equiv\Gamma_{ab})$ is the coherence damping rate due to spontaneous emission and collisions, etc. (In the pure radiative damping case, $\gamma_{ab}=0$ and $\Gamma_{ba}=1/2\,\gamma_{ba}$, with γ_{ba} the spontaneous decay rate from the upper level $|b\rangle$ to the ground level $|a\rangle$.) In Eq. (28), Δ is the detuning defined by

$$\Delta=\omega_{ba}-[(m+1)\omega_1-m\omega_2], \tag{29}$$

and δ (*bichromatic* Bloch–Siegert resonance shift) and u (resonance width parameters) represent higher-order perturbation corrections for the rest of the supermatrix $\hat{L}_F$ (called the "external" space). Both δ and u are intensity-dependent quantities and can be expressed in terms of the power series expansion of the electric dipole coupling strengths α and β defined by

$$\alpha=-1/2\langle a|\mu\cdot\epsilon_1|b\rangle e^{-i\phi_1} \tag{30a}$$

and

$$\beta=-1/2\langle a|\mu\cdot\epsilon_2|b\rangle e^{-i\phi_2} \tag{30b}$$

to be described in Sec. IV A.

The steady-state solutions $[d\hat{\rho}(t)/dt=0]$ for the density matrix in Eq. (26) can be solved readily to give the coherence matrix elements

$$\bar{\rho}_{ba}=-\gamma_{ba}[(\Delta+\delta+i\Gamma_{ba})(\gamma_{ba}u_a'+\gamma_{ab}u_b') + u_b^*(u_b'^*u_a'-u_b'u_a'^*)]/\bar{D}, \tag{31a}$$

where

$$\bar{D}=\gamma_{ba}[(\Delta+\delta)^2+\Gamma_{ba}^2](\gamma_{ab}+\gamma_{ba}) + 2\,\mathrm{Re}(z)-4\,\mathrm{Im}(u_a'u_b'^*)\cdot\mathrm{Im}(u_au_b^*)$$

with

$$z=[\Gamma_{ba}-i(\Delta+\delta)] \times[(\gamma_{ab}+\gamma_{ba})u_bu_b'+\gamma_{ba}u_au_a'+\gamma_{ab}u_au_b'],$$

$$\bar{\rho}_{ab}=\bar{\rho}_{ba}^* \tag{31b}$$

which are independent of initial conditions and become time independent in the appropriate rotating frame defined in Eq. (25). From Eqs. (23) and (31), we arrive at the following general analytical expression for intensity-dependent nonlinear optical susceptibility:

$$\chi_{m+1,-m}[\omega=(m+1)\omega_1-m\omega_2] = -N_0\mu_{ab}\gamma_{ba}\{[(\Delta+\delta)+i\Gamma_{ba}]\cdot[\gamma_{ba}u_a'+\gamma_{ab}u_b'] + u_b^*[u_b'^*u_a'-u_b'u_a'^*]\}/\{\bar{D}\cdot\epsilon_1[(m+1)\omega_1]\cdot\epsilon_2(-m\omega_2)\}. \tag{32}$$

It is worth noting that Eqs. (31) and (32) possess the following two distinct features and advantages over other approaches: (i) the intensity-dependent nature of ρ and $\chi(\omega)$ is clearly determined by the two physical parameters δ and u only; and (ii) ρ and $\chi(\omega)$ have the same general functional form as shown by Eqs. (31) and (32), respectively, regardless of the order $(2|m|+1)$ of multiphoton processes. δ and u, of course, depend on m and can be determined via the nearly degenerate perturbative treatment of the Salwen–Liouvillian $\hat{L}_S$ as mentioned earlier. In the following subsections, we present some of the essential analytical results.

A. Shift (δ) and width (u) parameters at the optical frequency $\omega=\omega_1$ (or ω_2)

To fourth order in Rabi frequencies $|\alpha|$ and $|\beta|$, we have for the shift parameter,

$$\delta(\omega_1)=\mathrm{Re}\{|\beta|^2[I(\omega_2)+I(-\omega_2)]+|\alpha|^2I(-\omega_1) + |\alpha\beta|^2I^2(\omega_2)[(\omega_1-\omega_2)^{-1} + (2\omega_{ba}-\omega_1-\omega_2)^{-1}] + |\beta|^4I^2(\omega_2)\cdot[2(\omega_{ba}-\omega_2)]^{-1}\}, \tag{33}$$

where the line shape functions I's are introduced here to shorten the notations:

$$I_{ba}(\omega)=1/(\omega-\omega_{ba}-iP), \tag{34a}$$

$$I_{ab}(\omega)=I_{ba}^*(-\omega)=-1/(\omega+\omega_{ba}-iP), \tag{34b}$$

$$I(\omega)=(\omega_{ba}-\omega+iP)^{-1}+(\omega_{ba}-\omega+iA)^{-1}, \tag{34c}$$

$$I_0(\omega)=\omega^{-1}+(\omega-i\gamma_{ab})^{-1}, \tag{34d}$$

and

$$P=\gamma_{ab}+\gamma_{ba}-\Gamma_{ba}, \tag{35a}$$

$$A=\gamma_{ba}-\Gamma_{ba}. \tag{35b}$$

For the width parameters, we have obtained expressions to the fifth order in $|\alpha|$ and $|\beta|$,

$$u_a(\omega_1)=\alpha+\alpha^*\beta^2\{I_{ab}(-\omega_2)I(-\omega_2)+I_{ab}(\omega_2)I(\omega_2)-I_{ba}(-\omega_1)[I(-\omega_2)+I(\omega_2)]\} -\alpha|\alpha|^2I_{ba}(-\omega_1)I(-\omega_1)-\alpha|\beta|^2[I_{ba}(\omega_2)I(\omega_2)+I_{ba}(-\omega_2)I(-\omega_2)] +\alpha|\alpha|^2|\beta|^2I_{ba}(\omega_2)I^2(\omega_2)[I_{ab}(\omega_2-2\omega_1)-I_{ba}(\omega_2)]-\alpha|\beta|^4I_{ba}(\omega_2)I^2(\omega_2)I_{ba}(2\omega_2-\omega_1), \tag{36}$$

and

$$u_b(\omega_1) = u_a(\omega_1; P \leftrightarrow A), \quad (37)$$

$$u_a'(\omega_1) = u_a(\omega_1; \alpha \leftrightarrow \alpha^*, \beta \leftrightarrow \beta^*), \quad (38)$$

$$u_b'(\omega_1) = u_b(\omega_1; \alpha \leftrightarrow \alpha^*, \beta \leftrightarrow \beta). \quad (39)$$

The corresponding expressions for $\delta(\omega_2)$ and $u_i(\omega_2)$ can be obtained simply by exchanging ω_1 and ω_2 and α and β in $\delta(\omega_1)$ and $u_i(\omega_1)$, respectively.

B. Shift and width parameters at $\omega = (m+1)\omega_1 - m\omega_2$, $m \geq 1$

For the shift parameters, the leading terms are always second order in Rabi frequencies $|\alpha|$ ($|\beta|$), and it is generally sufficient to keep correction terms up to the fourth order even in rather intense fields:

$$\delta(\omega) = \mathrm{Re}(|\beta|^2[I(\omega_2) + I(-\omega_2)] + |\alpha|^2[I(\omega_1) + I(-\omega_1)] + |\beta|^4 I^2(\omega_2)\cdot[2(\omega_{ba} - \omega_2)]^{-1}$$
$$+ |\alpha|^4 I^2(\omega_1)\cdot[2(\omega_{ba} - \omega_1)]^{-1} + |\alpha\beta|^2\{I^2(\omega_1)\cdot(\omega_2 - \omega_1)^{-1} + I^2(\omega_2)\cdot(\omega_1 - \omega_2)^{-1}$$
$$+ [I(\omega_1) + I(\omega_2)]^2\cdot[2\omega_{ba} - \omega_1 - \omega_2]^{-1}\}). \quad (40)$$

For the width parameters, the leading terms are proportional to $\alpha^{m+1}(\beta^*)^m$. Thus it is necessary to carry out perturbation expansion in $\hat{L}_s$ at least up to $(2m+1)$ order in Rabi frequencies. For m small (particularly $m = 0$ and 1), however, the power broadenings are usually rather large at high fields and higher-order correction terms beyond the lowest nonvanishing order are essential to account for intensity dependent phenomena. These higher-order terms are usually very difficult and tedious to obtain. Indeed, we are not aware of any general higher-order study beyond the RWA or lowest (nonvanishing) order perturbation. In Eq. (36), we have already presented higher-order correction terms up to the fifth order for the one-photon dominant case, where the leading term is first order in α. For the three-photon dominant $\omega = 2\omega_1 - \omega_2$ process, we have obtained, up to the fifth-order correction,

$$u_a(2\omega_1 - \omega_2) = -\alpha^2\beta^* I(\omega_1)\cdot[I_{ab}(-\omega_1) - I_{ba}(\omega_2)] + |\alpha|^2\beta\{I(\omega_1)\cdot[I_{ab}(\omega_2) - I_{ba}(-\omega_1)]$$
$$+ I(-\omega_2)[I_{ab}(-\omega_1) - I_{ba}(-\omega_1)]\} + \alpha^2|\alpha|^2\beta^* I^2(\omega_1) I_{ba}(\omega_2)\cdot[I_{ab}(-\omega_1) - I_{ba}(\omega_2)]$$
$$+ \alpha^2\beta^*|\beta|^2(I(\omega_1)\cdot[I_{ab}(-\omega_1) - I_{ba}(\omega_2)]$$
$$\cdot\{I_{ba}(2\omega_2 - \omega_1)\cdot[I(\omega_1) + I(\omega_2)] - I(\omega_1) I_{ab}(-\omega_1)\}), \quad (41)$$

where the third-order correction terms were carried out exactly (i.e., all multiphoton pathways are included) while only the leading generalized rotating wave approximation[14] (GRWA) pathways are retained in the fifth order (see the Appendix). For the five-photon dominant $\omega = 3\omega_1 - 2\omega_2$ process, we have performed the fifth-order correction terms exactly:

$$u_a(3\omega_1 - 2\omega_2) = X + Y + Z, \quad (42a)$$

where

$$X = -\alpha^3\beta^{*2} I(\omega_1) I(2\omega_1 - \omega_2)\cdot[I_{ab}(-\omega_1) - I_{ba}(\omega_2)]$$
$$\cdot[I_{ab}(-2\omega_1 + \omega_2) - I_{ba}(-\omega_1 + 2\omega_2)], \quad (42b)$$

$$Y = -\alpha^*|\alpha|^2|\beta|^2(I(-\omega_2) I(\omega_1 - 2\omega_2)\cdot[I_{ab}(-\omega_1) - I_{ba}(-\omega_1)]\cdot[I_{ab}(-2\omega_1 + \omega_2) - I_{ba}(-3\omega_1)]$$
$$+ I(2\omega_1 - \omega_2)\cdot[I_{ab}(\omega_2) - I_{ba}(-\omega_1)]\cdot\{I(-\omega_2)\cdot[I_{ab}(-2\omega_1 + \omega_2) - I_{ba}(\omega_2 - 2\omega_1)]$$
$$+ I(\omega_1)\cdot[I_{ab}(-\omega_1 + 2\omega_2) - I_{ba}(\omega_2 - 2\omega_1)]\}), \quad (42c)$$

and

$$Z = -\alpha|\alpha|^2|\beta|^2(I(\omega_1 - 2\omega_2)\cdot[I_{ab}(-\omega_1) - I_{ba}(-\omega_1)]$$
$$\cdot\{I(-\omega_2)\cdot[I_{ab}(-3\omega_1) - I_{ba}(\omega_2 - 2\omega_1)] + I(\omega_1)$$
$$\cdot[I_{ab}(-2\omega_1 + \omega_2) - I_{ba}(\omega_2 - 2\omega_1)]\}$$
$$+ I(\omega_1) I(2\omega_1 - \omega_2)\cdot\{[I_{ab}(-\omega_1) - I_{ba}(\omega_2)]\cdot[I_{ab}(-\omega_1 + 2\omega_2) - I_{ba}(\omega_2 - 2\omega_1)]$$
$$+ [I_{ab}(\omega_2) - I_{ba}(-\omega_1)]\cdot[I_{ab}(\omega_2 - 2\omega_1) - I_{ba}(2\omega_2 - \omega_1)]\}$$
$$+ I(-\omega_2) I(2\omega_1 - \omega_2)\cdot[I_{ab}(\omega_2 - 2\omega_1) - I_{ba}(\omega_2 - 2\omega_1)]\cdot[I_{ab}(-\omega_1) - I_{ba}(\omega_2)]$$
$$+ I(\omega_1) I(3\omega_1)\cdot[I_{ab}(\omega_2) - I_{ba}(\omega_2)]\cdot[I_{ab}(2\omega_2 - \omega_1) - I_{ba}(2\omega_2 - \omega_1)]). \quad (42d)$$

For higher-photon processes $\omega = (m+1)\omega_1 - m\omega_2$ ($m \geq 3$), exact performance of the correction terms become very tedious even for the leading $(2m+1)$th order terms [proportional to $\alpha^{m+1}(\beta^*)^m$] and the expressions are very clumsy as the number of multiphoton pathways are enormously large. However, the dominant term in the leading $(2m+1)$th order can be easily obtained within the Salwen–Liouvillian if one considers only the GRWA pathways. In this way, we obtain the following general formula for the leading correction terms:

$$u_a(\omega) = -\alpha^{m+1}(\beta^*)^m \cdot \prod_{k=1}^{m} I[k\omega_1 - (k-1)\omega_2] \cdot \prod_{k=1}^{m} \{I_{ab}[(k-1)\omega_2 - k\omega_1] - I_{ba}[k\omega_2 - (k-1)\omega_1]\}. \quad (43)$$

Equation (43) is a simple but useful general result valid for $m \geqslant 1$. For high photon processes ($m \geqslant 3$), Eq. (43) is usually adequate up to moderate strong laser intensities. The Appendix provides a brief discussion of multiphoton pathways in terms of Feynman diagrams.

C. Analytical solutions for special limiting cases

1. Weak field limits

In the limit of weak pump and probe fields, the intensity-dependent generalized nonlinear optical susceptibility expression, Eq. (32), can be reduced to the more familiar intensity-independent perturbative-RWA results. This is accomplished by (i) ignoring the shifting correction terms δ; and (ii) keeping only the lowest nonvanishing order GRWA terms and dropping all non-GRWA and higher-order correction terms in the width parameters u's discussed in Secs. IV A and IV B. In this way, we obtain

$$\chi_{1,0}(\omega_1) \to \chi^{(1)}(-\omega_1;\omega_1) = \frac{N_0 \mu_{ab}^2 (\gamma_{ba} - \gamma_{ab})}{2(\omega_{ba} - \omega_1 - i\Gamma_{ba})(\gamma_{ab} + \gamma_{ba})}, \quad (44)$$

$$\chi_{0,1}(\omega_2) \to \chi^{(1)}(-\omega_2;\omega_2) = \frac{N_0 \mu_{ab}^2 (\gamma_{ba} - \gamma_{ab})}{2(\omega_{ba} - \omega_2 - i\Gamma_{ba})(\gamma_{ab} + \gamma_{ba})}, \quad (45)$$

and

$$\begin{aligned}
&\chi_{m+1,-m}[\omega = (m+1)\omega_1 - m\omega_2] \\
&\quad \to \chi^{(2m+1)}[-(m+1)\omega_1 + m\omega_2;\omega_1,\omega_1,\ldots,-\omega_2,-\omega_2,\ldots] \\
&= \frac{N_0 \mu_{ab}^{2(m+1)}}{2^{2m+1}[\omega_{ba} - (m+1)\omega_1 + m\omega_2 - i\Gamma_{ba}] \cdot (\gamma_{ab} + \gamma_{ba})} \\
&\quad \cdot \prod_{k=1}^{m} \{[\omega_{ba} - k\omega_1 + (k-1)\omega_2 + i(\gamma_{ab} + \gamma_{ba} - \Gamma_{ba})]^{-1} + [\omega_{ba} - k\omega_1 + (k-1)\omega_2 + i(\gamma_{ba} - \Gamma_{ba})]^{-1}\} \\
&\quad \cdot \Big(\gamma_{ba} \prod_{k=1}^{m} \{[\omega_{ba} + (k-1)\omega_1 - k\omega_2 + i(\gamma_{ab} + \gamma_{ba} - \Gamma_{ba})]^{-1} \\
&\quad - [\omega_{ba} - k\omega_1 + (k-1)\omega_2 - i(\gamma_{ab} + \gamma_{ba} - \Gamma_{ba})]^{-1}\} \\
&\quad - \gamma_{ab} \prod_{k=1}^{m} \{[\omega_{ba} + (k-1)\omega_1 - k\omega_2 + i(\gamma_{ba} - \Gamma_{ba})]^{-1} - [\omega_{ba} - k\omega_1 + (k-1)\omega_2 - i(\gamma_{ba} - \Gamma_{ba})]^{-1}\}\Big). \quad (46)
\end{aligned}$$

2. Laser field phases $\phi_1 = \phi_2 = 0$

In this case, we have the following simplification:

$$u_a' = u_a, \quad (u_a')^* = u_a^*, \quad (47)$$
$$u_b' = u_b, \quad (u_b')^* = u_b^*.$$

The expressions for $\bar{\rho}_{ba}$, Eq. (31), and X_{m+1-m}, Eq. (32), are correspondingly simplified.

3. Small relaxation limit

When the fields are strong or the relaxation rates are relatively small, and if the detuning Δ is not zero, it is often an excellent approximation to ignore the imaginary part of correction terms. This results in the following simplification:

$$u_a \cong -u_b \cong u_a'^* \cong -u_b'^* = -u$$

and

$$u_a' \cong -u_b' \cong (u_a)^* \cong -(u_b)^* = -u'.$$

Thus $\bar{\rho}_{ba}$ simplifies to

$$\bar{\rho}_{ba} = \frac{(\gamma_{ba} - \gamma_{ab})u'(\Delta + \delta + i\Gamma_{ba})}{[(\Delta + \delta)^2 + \Gamma_{ba}^2](\gamma_{ab} + \gamma_{ba}) + 4uu'\Gamma_{ba}}. \quad (48)$$

If, in addition, the laser phases ϕ_1 and ϕ_2 are zero, we have from Eq. (47) that $u = u'$ (real quantity), and

$$\bar{\rho}_{ba} = \frac{(\gamma_{ba} - \gamma_{ab})u(\Delta + \delta + i\Gamma_{ba})}{[(\Delta + \delta)^2 + \Gamma_{ba}^2](\gamma_{ab} + \gamma_{ba}) + 4u^2\Gamma_{ba}}. \quad (49)$$

For practical applications, we have found the simplified expressions, Eqs. (48) and (49), have a rather wide range of applicability. The intensity-dependent phenomena are entirely accounted for by the two physical parameters δ and u in Eq. (49), for example. The intensity-dependent nonlinear optical susceptibility, Eq. (32), now reduces to the following simple form (for real fields, $\phi_1 = \phi_2 = 0$):

$$\chi_{m+1,-m}[\omega = (m+1)\omega_1 - m\omega_2] = \left\{\frac{N_0 \mu_{ab}(\gamma_{ba} - \gamma_{ab})u(\Delta + \delta + i\Gamma_{ba})}{[(\Delta + \delta)^2 + \Gamma_{ba}^2](\gamma_{ba} + \gamma_{ab}) + 4u^2\Gamma_{ba}}\right\} \times [\epsilon_1(\omega_1)]^{-(m+1)}[\epsilon_2(\omega_2)]^{-m}. \quad (50)$$

V. INTENSITY-DEPENDENT SPECTRAL LINE SHAPES AND NONLINEAR RESPONSES OF TWO-LEVEL SYSTEMS IN INTENSE BICHROMATIC FIELDS: ANALYTICAL RESULTS

In this section we present a detailed study of the intensity-dependent nonlinear optical susceptibilities of a dipole-allowed (closed) two-level system driven by two linearly polarized monochromatic fields of frequencies ω_1 and ω_2. The two levels are of opposite parity and $E_a < E_b$. The physical parameters (in arbitrary units) used are: $\omega_{ba} = E_b - E_a = 100$, μ_0 (transition dipole moment) $= 1$, $\phi_1 = \phi_2$ (laser initial phases) $= 0$, γ_{ba} (spontaneous decay rate from $|b\rangle$ to $|a\rangle = 0.1$, and N_0 (number density) $= 1$. Both the effects of radiative and collisional relaxations in nonlinear responses at the optical frequencies $\omega \approx (m+1)\omega_1 - m\omega_2$ will be examined. We shall assume ω_1 is the (stronger) pumping field and ω_2 is the (weaker) probe field, although both are treated in a symmetrical way in our approach. In the following, we study the effects of intensity, detuning, and relaxation on the spectral line shapes and present the results for the important processes at $\omega = \omega_2$ and $2\omega_1 - \omega_2$ using analytical formulas developed in Sec. IV.

A. Intensity-dependent nonlinear optical susceptibilities at the probe frequency $\omega = \omega_2$

The effects of the pump field intensity and radiative and collisional dampings on the line shapes of $\chi(\omega_2)$ are shown as functions of $\omega_2 - \omega_2$, in Figs. 2 and 3. In Figs. 2(a)–2(d), the pump frequency ω_1 is fixed at a large detuning $\Delta_1 \equiv \omega_{ba} - \omega_1 = 5.0$, and the pump field strength $|\alpha|$ is varied from low to medium high values ($|\alpha|/\gamma_{ba} = 1.0, 5.0, 7.5$, and 10.0), while the probe field strength is fixed at a low value ($|\beta| = 0.1\ \gamma_{ba}$). As the pump field strength $|\alpha|$ increases, both the dispersive [Re $\chi(\omega_2)$] and the absorptive [Im $\chi(\omega_2)$] line shapes are broadened and shifted. On the other hand, in the limit of weak pump field, $\chi(\omega_2)$ approach the perturbative results (dotted curves) which are independent of intensity. Figures 2(a) and 2(b) show the results for pure radiative damping ($\gamma_{ab} = 0.0$ and $\Gamma_{ab} = 1/2\gamma_{ba}$) case, whereas Figs. 2(c) and 2(d) show the additional effects due

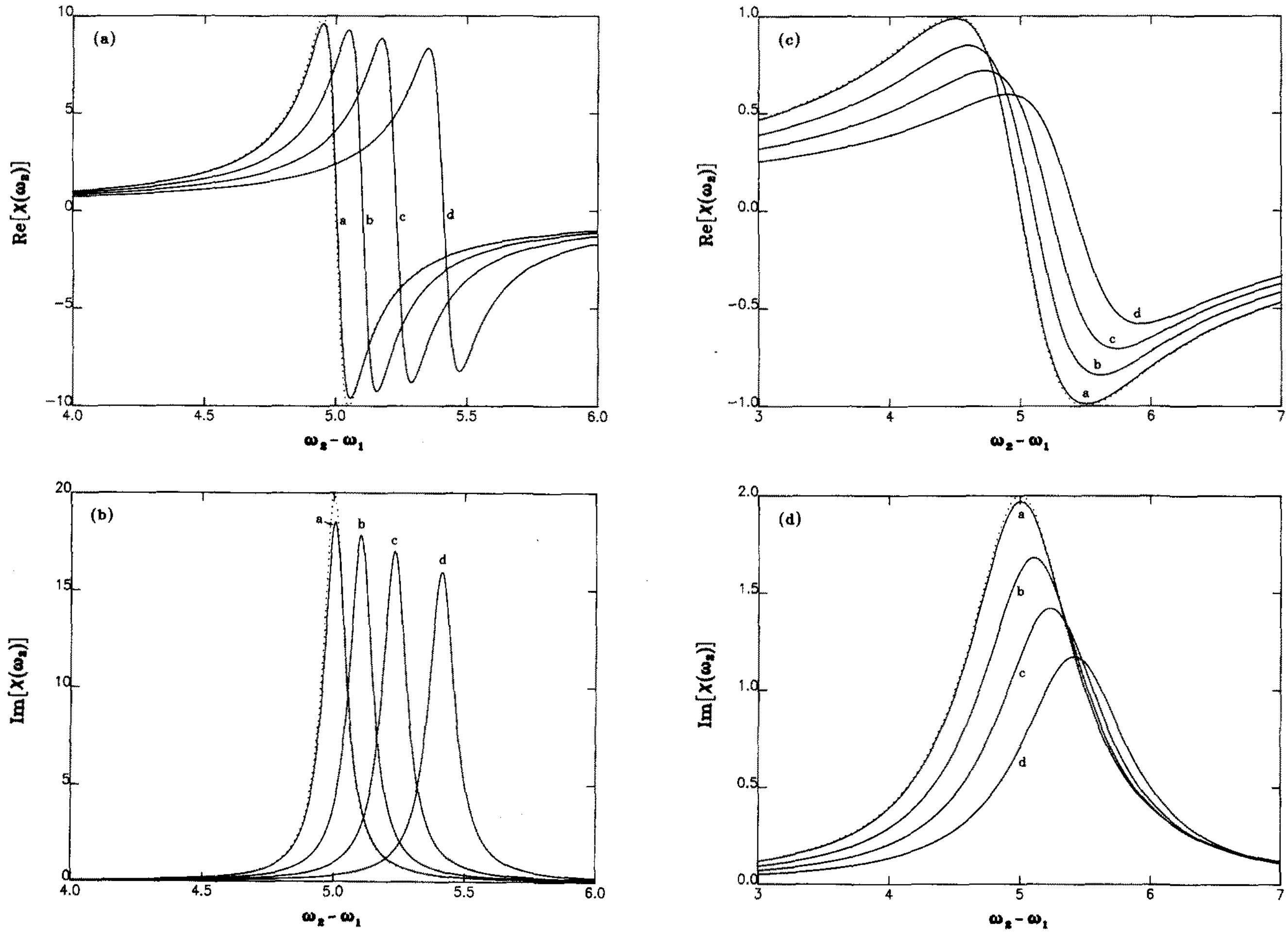

FIG. 2. Intensity-dependent nonlinear optical susceptibilities $\chi(\omega = \omega_2)$ as a function of $\omega_2 - \omega_1$. The pump frequency ω_1 is fixed at a large detuning $\Delta_1 = \omega_{ba} - \omega_1 = 5.0$, while the probe field strength is fixed at $|\beta| = 0.1\gamma_{ba}$, and the pump field strength $|\alpha|$ is varied. The dispersive responses, Re $\chi(\omega_2)$, are shown in (a) and (c) while the absorptive responses are shown in (b) and (d). The physical parameters used are: $\omega_{ba} = 100$, $\omega_1 = 95$, $\phi_1 = \phi_2 = 0$, $\gamma_{ba} = 0.1$, $\gamma_{ab} = 0$ (arbitrary units). The curves labeled a, b, c, and d in each figure correspond, respectively, to $|\alpha|/\gamma_{ba} = 1, 5, 7.5$, and 10. The dotted curve in each figure shows the first-order perturbative result which is intensity independent. (a) and (b) show the results for the case of pure radiative decay (i.e., collisionless) so that $\Gamma_{ba} = 1/2\ \gamma_{ba}$. (c) and (d) include also the effects of collisional relaxation, with $\Gamma_{ba} = 5\gamma_{ba}$.

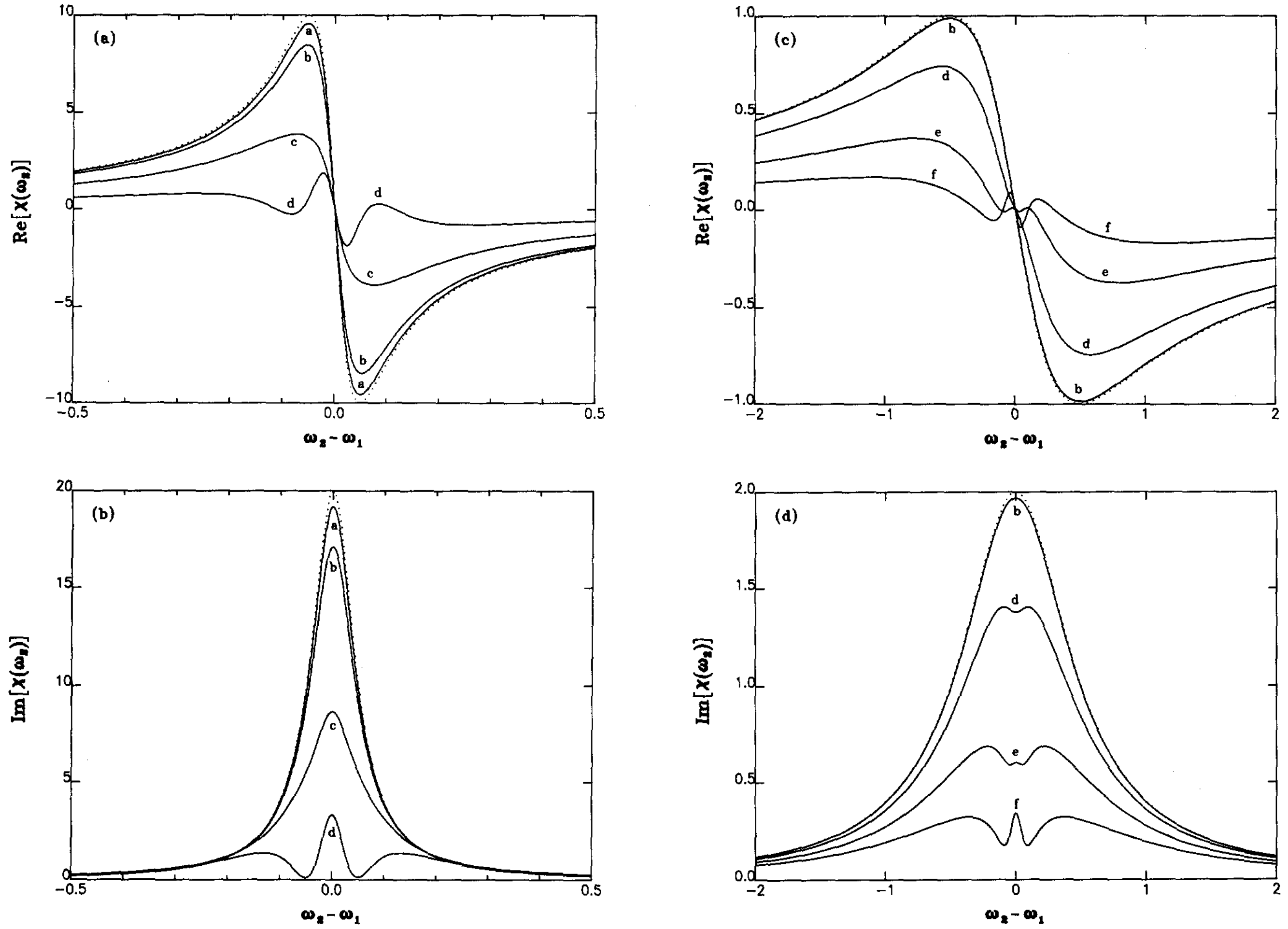

FIG. 3. Intensity-dependent nonlinear optical susceptibilities $\chi(\omega = \omega_2)$, as a function of $\omega_2 - \omega_1$, when the pump frequency ω_1 is tuned at resonance with ω_{ba}. Curve notations similar to those in Fig. 2. Physical parameters used are: $\omega_{ba} = \omega_1 = 100$, $\gamma_{ba} = 0.1$, $\gamma_{ab} = 0.0$, $\beta = 0.01\gamma_{ba}$. The curves labeled a, b, c, d, e, and f correspond, respectively, to $|\alpha|/\gamma_{ba} = 0.05, 0.1, 0.25, 0.5, 1.0$, and 1.5. Other parameters are the same as in Fig. 2. (a) and (b) show the results for this pure radiative damping case, while (c) and (d) include the effects of collisional relaxation.

to collisional dampings ($\Gamma_{ab} = 5\,\gamma_{ba}$). It is seen that collisions substantially broaden the line shapes and lower down the magnitude of the susceptibilities.

Figures 3(a)–3(d) show the similar effects for $\chi(\omega_2)$ except the pump frequency ω_1 is now tuned at resonance with the level spacing ($\omega_{ba} = \omega_1 = 100.0$). Again, in the limit of weak pump field, $\chi(\omega_2)$ approach the perturbative results (dotted curves) which are intensity independent.

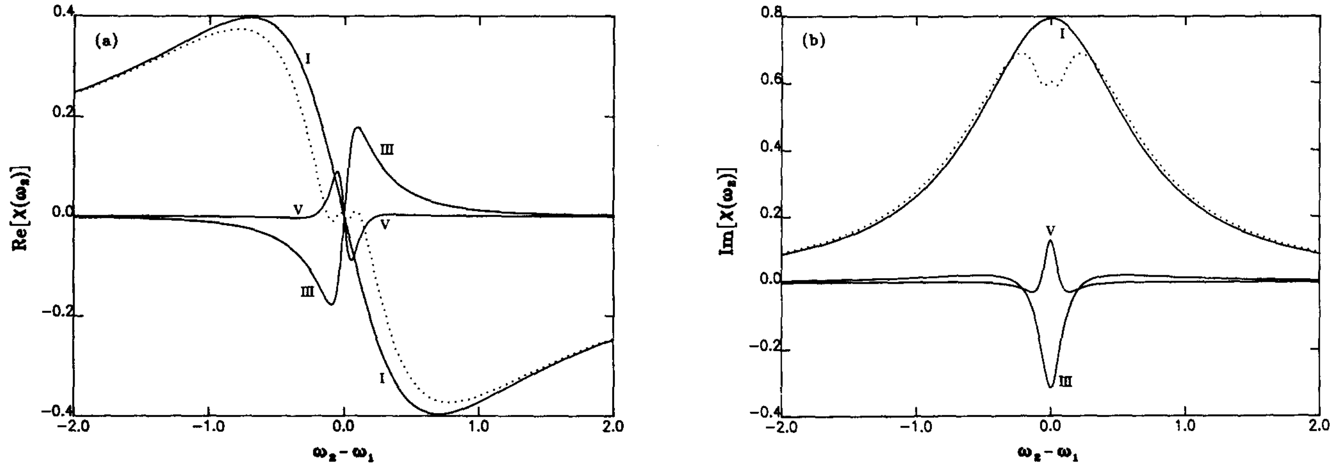

FIG. 4. Analysis of the line shape shown in the curve labeled e in Figs. 3(c) and 3(d). The dispersive and the absorptive responses are shown in (a) and (b), respectively. The first (I), the third (III), and the fifth (V) order contributions to $\chi(\omega_2)$ are shown in each figure, whereas the total $\chi(\omega_2)$ are indicated by dotted curves.

However, as the pump field strength $|\alpha|$ increases, more dramatic changes in line shapes can be seen in both the pure radiative damping case [Figs. 3(a) and 3(b)] and the additional collisional damping case [Figs. 3(c) and 3(d)]. In particular, we found an extra absorption peak appears at the line center ($\omega_1 = \omega_2 = \omega_{ba}$) at strong pump fields even in the case of collisionless relaxation [curve d in Fig. 3(b)]. In the case of both radiative and collisional dampings, the absorptive response [Im $\chi(\omega_2)$] first shows a dip (as also observed in experiment[17]) and then an extra peak begins to arise from the center of the dip when the intensity of the pump field further increases [see Fig. 3(d)].

To understand the origin of these extra peaks (which have not been reported before), we make the following analysis of the line shape shown in the curve labeled e in Fig. 3(d). In Figs. 4(a) and 4(b), we depict the first-, third-, and fifth-order (in Rabi frequencies $|\alpha|$ and $|\beta|$) contributions of the nonlinear susceptibilities $\chi(\omega_2)$. [The total $\chi(\omega_2)$'s are shown in dotted lines.] As can be seen, while the first-order $\chi(\omega_2)$ provides the backbone curve, the third-order $\chi(\omega_2)$ is responsible for the spectral hole in homogeneously broadened lines (as also been pointed out by others[18]), and the newly observed extra peak is found to be arised from the fifth-order contribution [Fig. 4(b)]. Clearly, when the pump field intensity is further increased, higher-order contributions will eventually set in, leading to multipeak structures. The dispersive line shape [Fig. 4(a)] can be similarly analyzed.

B. Intensity-dependent nonlinear optical susceptibilities at $\omega = 2\omega_1 - \omega_2$

Figures 5(a)–5(d) show the intensity-dependent four-wave mixing nonlinear responses $\chi(\omega = 2\omega_1 - \omega_2)$, as functions of $\omega_2 - \omega_1$, subjected to pure radiative [Figs. 5(a) and 5(b)] and additional collisional dampings [Figs. 5(c) and 5(d)]. The pumping frequency ω_1 is fixed at resonance with the level spacing ($\omega_1 = \omega_{ba} = 100.0$), and the probe field strength is fixed at a low value ($|\beta| = 0.01\,\gamma_{ba}$), while the pump field strength $|\alpha|$ varies from weak to medium strong. The general behavior of the line shape functions of $\chi(2\omega_1 - \omega_2)$ are qualitatively similar to those of $\chi(\omega_2)$, except the direction of the ac Stark shift and the sign of the absorptive response are reversed.

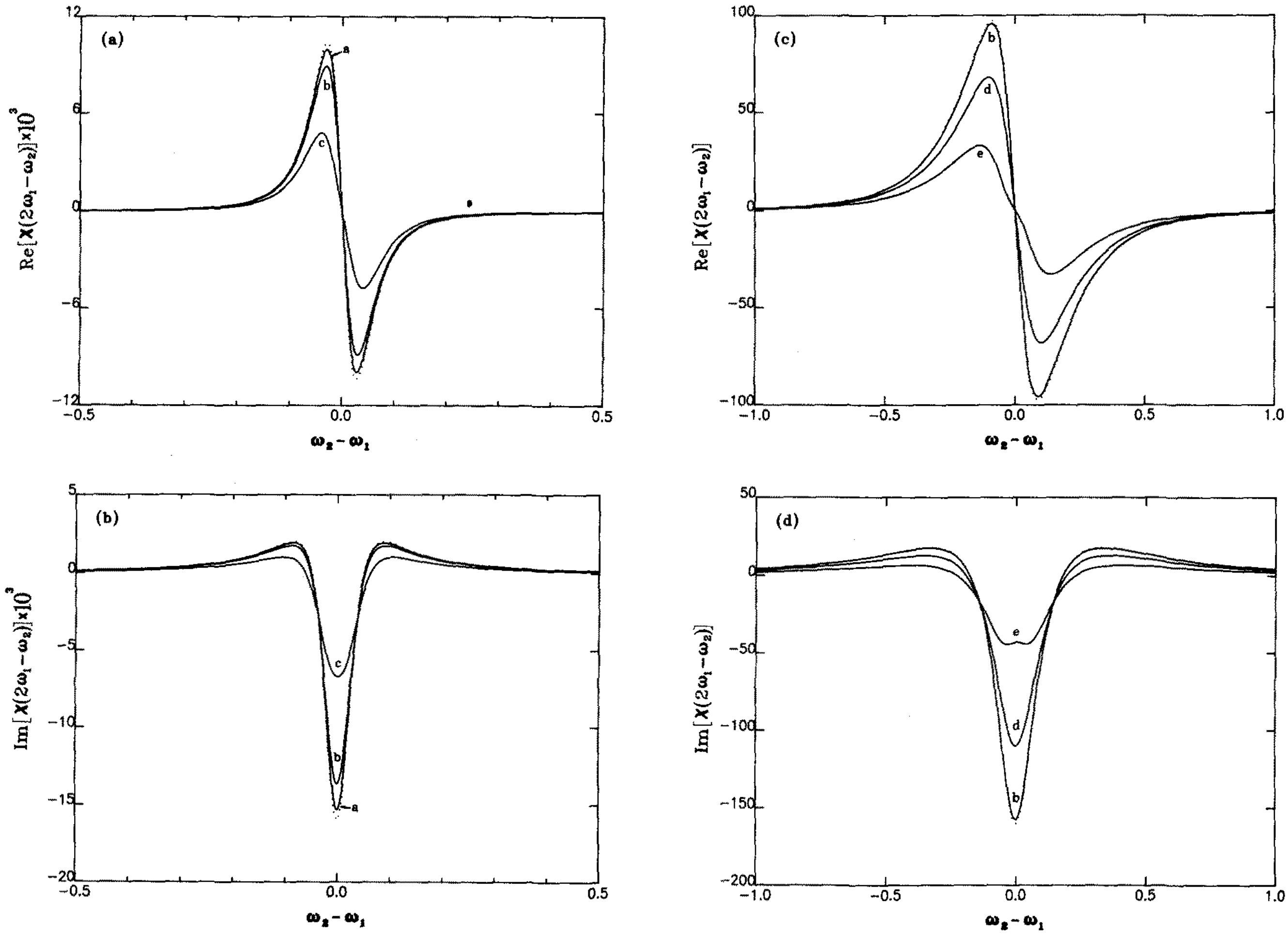

FIG. 5. Intensity-dependent nonlinear optical susceptibilities corresponding to the four-wave mixing process, $\omega = 2\omega_1 - \omega_2$, as a function of $\omega_2 - \omega_1$. The pump frequency ω_1 is fixed at the resonance frequency ($\omega_1 = \omega_{ba}$). Parameters used are the same as in Fig. 4, except that $|\alpha|/\gamma_{ba} = 0.05, 0.1, 0.25, 0.5$, and 1.0 corresponds, respectively, to the curve labeled a, b, c, d, and e in each figure. The dotted curves are third-order perturbative results which are intensity independent.

Similar results can be obtained for higher-order mixing processes at $\omega = (m+1)\omega_1 - m\omega_2$, $m \geqslant 2$ at higher laser intensities. Contrary to the lower-order processes where transitions are relatively easily saturated and higher-order corrections beyond the lowest nonvanishing terms are significant, we found that the GRWA formula, Eq. (46), in general provides a good approximation for higher-order processes up to medium strong intensities.

VI. NONLINEAR OPTICAL SUSCEPTIBILITIES AND MULTIPLE-WAVE MIXINGS AT VERY INTENSE FIELDS: EXACT FLSM NUMERICAL RESULTS FOR TWO-LEVEL TWO-MODE CASE

At very intense laser fields, the GRWA or even the high-order Salwen–Liouvillian analytical approach (Sec. IV) are generally not sufficient to explore the rich multiphoton subradiative structures to be discussed below. Here the field is referred to as very strong if the corresponding Rabi frequency is much larger than the relaxation rates (for example, $|\alpha| \gg \gamma_{ba}$, etc.). In this case, the Floquet–Liouville supermatrix (FLSM) approach (Sec. III) provides an efficient and powerful method for the nonperturbative treatment of various intensity-dependent nonlinear optical phenomena. In this section, we use this approach to study the nonlinear wave mixings of two-level systems in very intense bichromatic fields (i.e., both the "pump" and the "probe" field strengths are strong). The physical parameters used are: $\omega_{ba} = 100.0$, $|\alpha| = 20\,\gamma_{ba}$ $|\beta| = 10\,\gamma_{ba}$, $\gamma_{ba} = 0.1$ (arbitrary units). For pure radiative relaxation, $\gamma_{ab} = 0$ and $\Gamma_{ab} = 1/2\gamma_{ba}$, while for collisional relaxation we choose $\Gamma_{ab} = 2\,\gamma_{ba}$.

In this case study, we assume ω_1 is associated with the stronger field and that it is fixed at resonance with the level transition (i.e., $\omega_{ba} = \omega_1 = 100.0$). (Again, we point out that in the FLSM approach, both the "pump" and the "probe" fields are treated entirely on an equal footing. In fact, when both fields are strong, there is no need to distinguish which field is the pump field and which field is the probe field.) In Fig. 6, we present the real part of the supereigenvalues, $\mathrm{Re}[\Omega_{\mu\nu;k_1k_2}]$, as a function of $\omega_2 - \omega_1$, for the case of purely radiative relaxation. The tetradic–Floquet indices $|\mu\nu;k_1k_2\rangle$, where $\mu,\nu = a$ or b and k_1 and k_2 arbitrary integers, are shown on the right-hand side. These eigenvalues are obtained by diagonalizing a truncated Floquet–Liouvillian $\hat{L}_F$ (Fig. 1) which contains up to 11 photon (i.e., $6\omega_1 - 5\omega_2$ and $6\omega_2 - 5\omega_1$) blocks. Each avoided crossing between the supereigenvalues $|ab;1,0\rangle$ and $|ba;-1,0\rangle$ corresponds to a multiphoton (subharmonic) resonance transition. For example, the positions of the avoided crossings from the right-hand side to the line center correspond, respectively, to the subharmonics $(2\omega_1 - \omega_2)$, $(3\omega_1 - 2\omega_2)$, $(4\omega_1 - 3\omega_2)$, and so on, while those from the left-hand side to the center correspond, respectively, to $(2\omega_2 - \omega_1)$, $(3\omega_2 - 2\omega_1)$, $(4\omega_2 - 3\omega_1)$,..., subharmonic multiphoton resonant transitions. The central part of the diagram con-

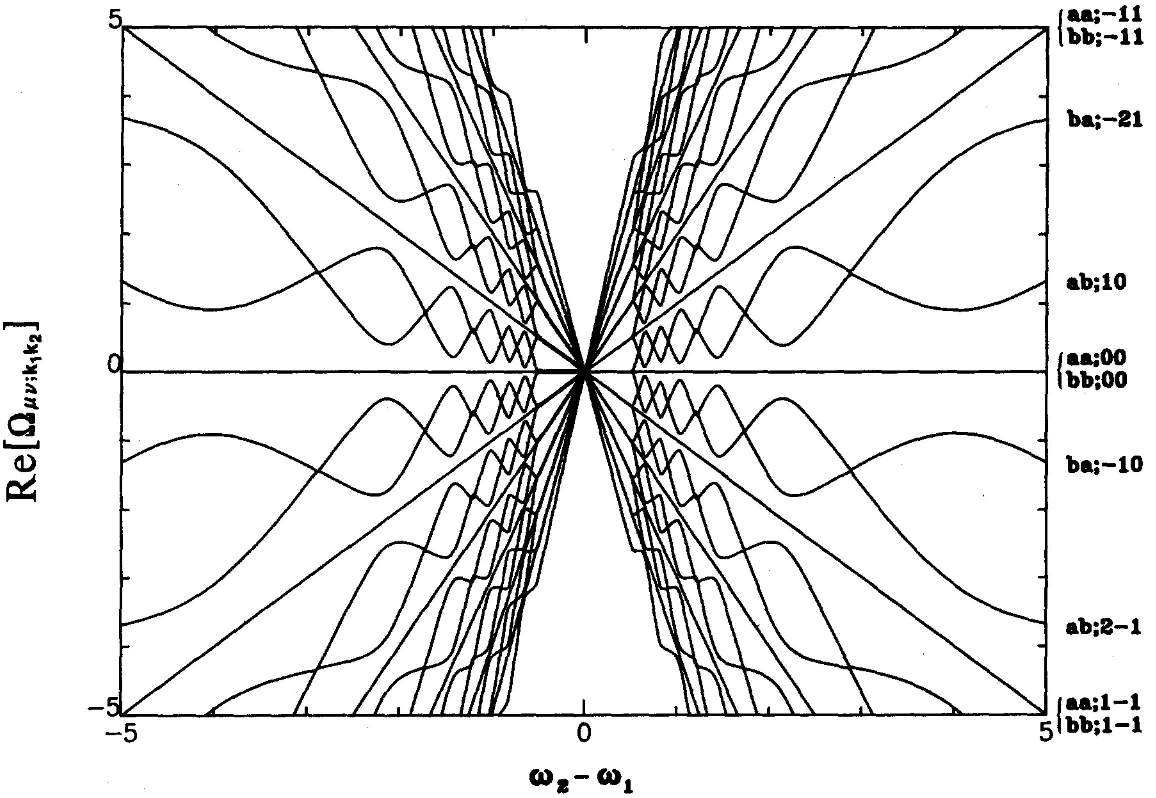

FIG. 6. Supereigenvalues (real parts), $\mathrm{Re}(\Omega)$, are shown, as a function of $\omega_2 - \omega_1$, for the case of a closed two-level system driven by two intense linearly polarized monochromatic fields of frequencies ω_1 and ω_2. Parameters used are $\omega_{ba} = \omega_1 = 100$, $\gamma_{ba} = 0.1$, $\gamma_{ab} = 0.0$, $\Gamma_{ba} = 1/2\gamma_{ba}$, $|\beta| = 10\gamma_{ba}$, $|\alpha| = 20\gamma_{ba}$ and $\phi_1 = \phi_2 = 0.0$. The tetradic–Floquet indices $|\mu\nu;k_1k_2\rangle$ are shown on the right-hand side. Note that $\Omega_{aa;k_1k_2}$ and $\Omega_{bb;k_1k_2}$ are almost degenerate and cannot be distinguished in the figure.

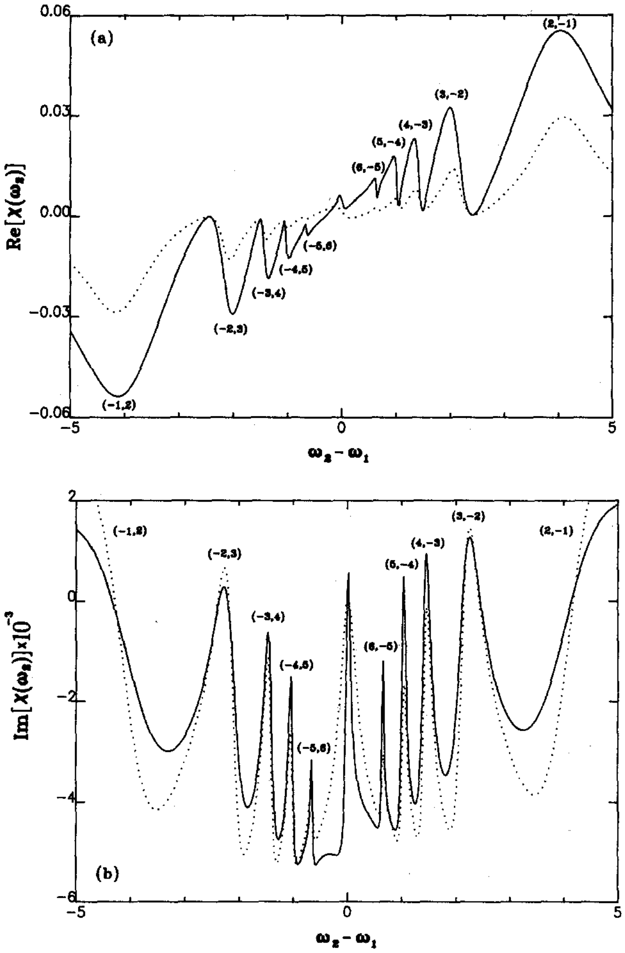

FIG. 7. Generalized nonlinear optical susceptibilities $\chi(\omega = \omega_2)$ at intense bichromatic fields are shown as a function of $\omega_2 - \omega_1$. The dispersive responses are shown in (a) and the absorptive responses in (b). The solid curves are the results for the pure radiative damping case ($\Gamma_{ba} = 1/2\gamma_{ba}$), and the dotted curves include the effects of collisional relaxation ($\Gamma_{ba} = 2\gamma_{ba}$). Other parameters are the same as in Fig. 6. The multiphoton subradiative structures are labeled as (n_1, n_2) corresponding to the $n_1\omega_1 + n_2\omega_2$ processes, where n_1 and n_2 are (positive or negative) integers.

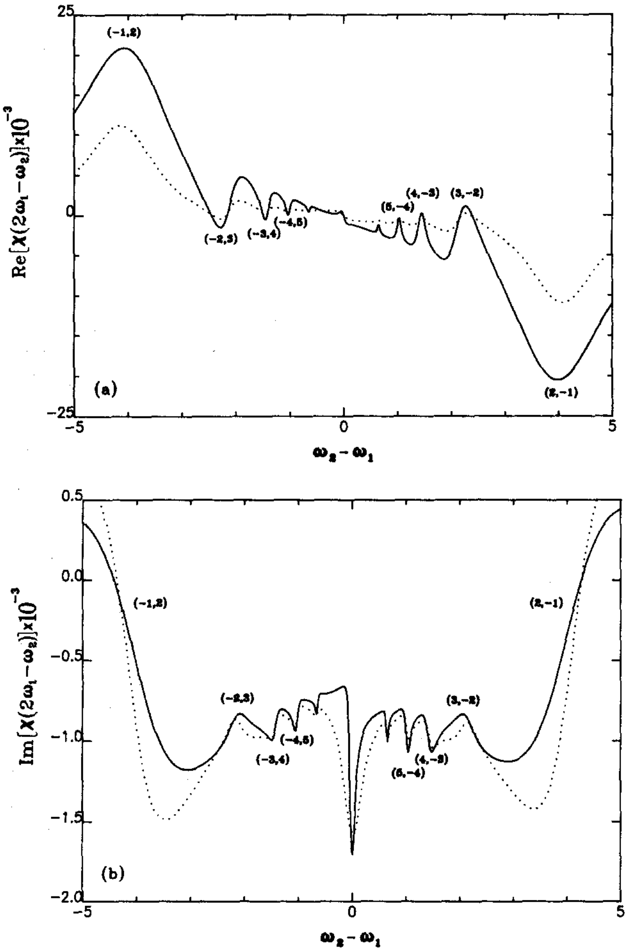

FIG. 8. Generalized nonlinear optical susceptibilities $\chi(\omega = 2\omega_1 - \omega_2)$. Parameters are the same as in Fig. 7.

tains infinite higher-order processes which are not shown. Also the one-photon processes occur far away from both sides and are not shown. Several features of the supereigenvalue plot worth mentioning: (i) The supereigenvalue pattern is not exactly symmerical with respect to the line center. (ii) There is one-to-one correspondence between the avoided crossing pattern and the multiphoton resonance absorption line shape (such as power broadening, ac Stark shift, etc.), similar to the well-known quasienergy plot[14] for the nondamping case.

In Figs. 7–9, we present the generalized nonlinear optical susceptibilities, as a function of $\omega_2 - \omega_1$, at the optical frequencies $\omega = \omega_2$ (Fig. 7), $2\omega_1 - \omega_2$ (Fig. 8), $3\omega_1 - 2\omega_2$ (Fig. 9), respectively. The results for the purely radiative damping cases are shown in solid curves, while the effects of additional collisional damping are shown in dotted curves. A number of salient features can be observed in these graphs: (i) Various subradiative peaks (or holes) appear in both the dispersive [Re $\chi(\omega)$] and the absorptive [Im $\chi(\omega)$] responses in intense fields. Each subharmonic peak is labeled with the indices (n_1, n_2) corresponding to the $n_1\omega_1 + n_2\omega_2$ resonant process, which can also be identified from the appropriate supereigenvalue avoided crossing location. (ii) For each $\chi(\omega)$, the line shape is not exactly symmetrical (or antisymmetrical) with respect to the line center. This, of course, is related to the nonsymmetrical nature of the supereigenvalue pattern. The asymmetry can be attributed to the effects of antirotating terms. Indeed, in the limit of GRWA, we found that the resonance spectral line shapes possess exact symmetrical (or antisymmetrical) patterns. (iii) In strong fields, most subharmonic peaks have distorted Lorentzian line shapes as also been observed in some experiments.[19] (iv) In both the collisionless and collisional damping cases, we always observe a central resonant absorption peak (or hole) [Figs. 7(b)–9(b)] at zero detunings (i.e., $\omega_1 = \omega_2 = \omega_{ba}$). A similar central peak in four-wave mixing has been reported by Agarwal and Nayak.[20] However, higher-order mixings are not reported in their work. Figure 9(b) shows that the central resonant peaks get narrower and smaller in amplitude as the order of multiphoton mixing process increases. (v) *Negative* absorption spectra [Im $\chi(\omega)$] can occur virtually in all nonlinear wave mixings, particularly for lower-order mixings. For example, while the absorptive responses of $\chi(\omega_2)$, Fig. 7(b), and

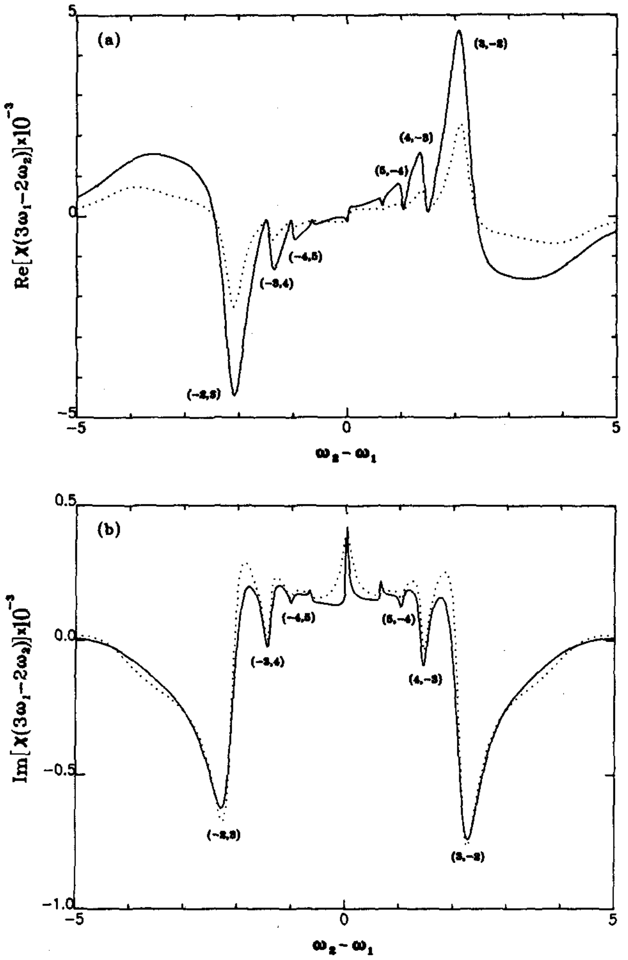

FIG. 9. Generalized nonlinear optical susceptibilities $\chi(\omega = 3\omega_1 - 2\omega_2)$. Parameters are the same as in Fig. 7.

$\chi(2\omega_1 - \omega_2)$, Fig. 8(b), are mostly negative, only a small portion of Im $\chi(4\omega_1 - 3\omega_2)$,not shown, is negative. The negative absorption can be attributed mainly to the saturation effects in intense fields and the absorption spectra turn to the emission spectra.

VII. CONCLUSION

In summary, we have presented in this paper a practical nonperturbative Floquet–Liouville supermatrix method for general treatment of intensity-dependent nonlinear optical susceptibilities in polychromatic fields, valid for arbitrary laser intensities, detunings, and relaxation. The nonlinear responses are shown to be completely determined by the supereigenvalues and eigenvectors of the Floquet–Liouvillian. In addition, we have also derived several general expressions for intensity-dependent nonlinear optical susceptibilities beyond the conventional perturbative and RWA approaches. Extension of the method to the study of other nonlinear optical processes is in progress.

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APPENDIX

In this Appendix, we provide some explanation of the multiphoton pathways occurring in the generalized rotating wave approximation (GRWA) and in the higher order Salwen–Liouvillian approach discussed in Sec. IV.

It is instructive to introduce at this point the double sided Feynman diagrams to illustrate the multiphoton pathways for various correction terms. Figures 10(a) and 10(b) show the Feynman diagrams for the $\omega_{ba} \approx (2\omega_1 - \omega_2)$ and $\omega_{ba} \approx (3\omega_1 - 2\omega_2)$ multiphoton processes, respectively, in the GRWA framework, for the correction term u_a in Eq. (43). Each Feynman diagram in Fig. 10(a) [Fig.10(b)]

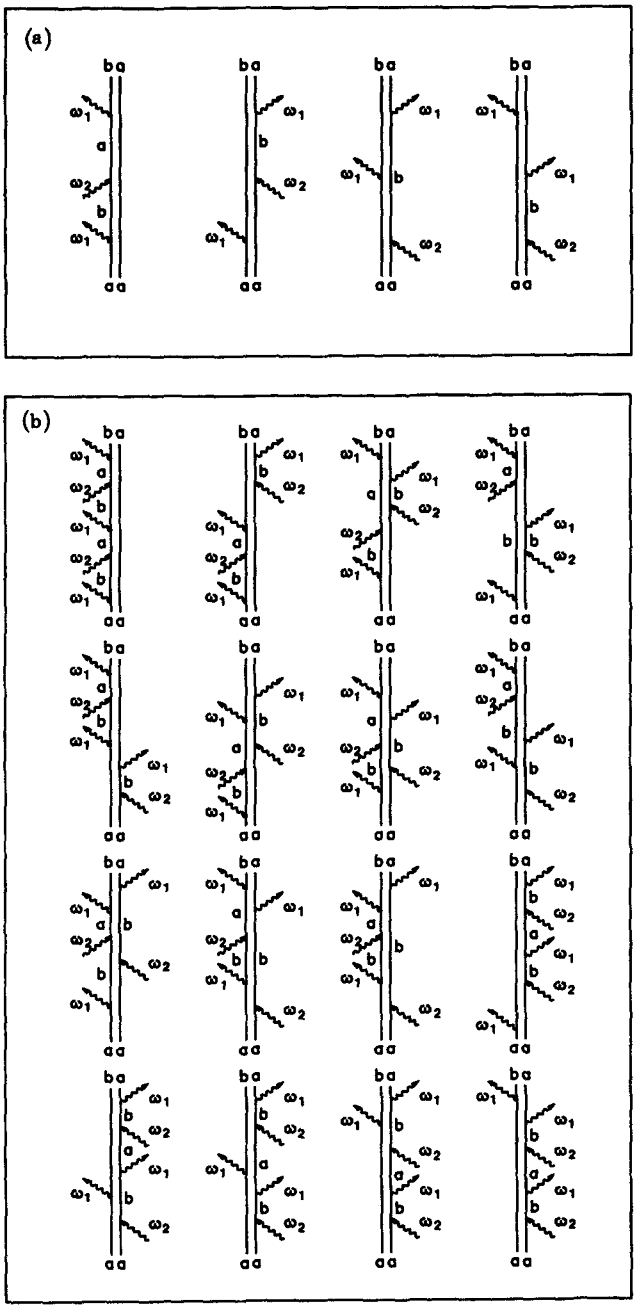

FIG. 10. Feynman diagrams for the GRWA pathways [Eq. (43)] corresponding to (a) $2\omega_1 - \omega_2$ and (b) $3\omega_1 - 2\omega_2$ processes. For details, see the Appendix.

shows possible pathways from the initial Floquet–Liouville state $|aa;00\rangle$ to the final state $|ba;-2,1\rangle$ ($|ba;-3,2\rangle$) by *sequentially* absorption (or emission) of one photon from one of the fields followed by emission (or absorption) of one photon from the other field. The time axis runs vertically upward. For example, the leftmost diagram in Fig. 10(a) indicates, in time order, $|aa;00\rangle \to |ba;-1,0\rangle \to |aa;-1,1\rangle \to |ba;-2,1\rangle$, while the rightmost diagram shows the pathway $|aa;00\rangle \to |ab;0,1\rangle \to |aa;-1,1\rangle \to |ba;-2,1\rangle$. Correction terms beyond the GRWA limit are often much more sophisticated. For example, Figs. 11(a) and 11(b) depict, respectively, all the possible multiphoton pathways (from the initial Floquet–Liouville state $|aa;00\rangle$ to the final state $|ba;-1,0\rangle$) for the third- and fifth-order correction terms of $u_a(\omega_1)$ in Eq. (36) for the simplest one-photon dominant ($\omega=\omega_1$) process. In this case, the third- and fifth-order terms represent higher-order corrections beyond the lowest (first order) GRWA limit. These higher-order terms become significant in strong fields and are responsible for intensity-dependent phenomena. The Feynman diagrams are different for different correction parameters such as u_a, u_a', u_b, and u_b'. But they are related to each other by some symmetry arguments as shown in Eqs. (37)–(39).

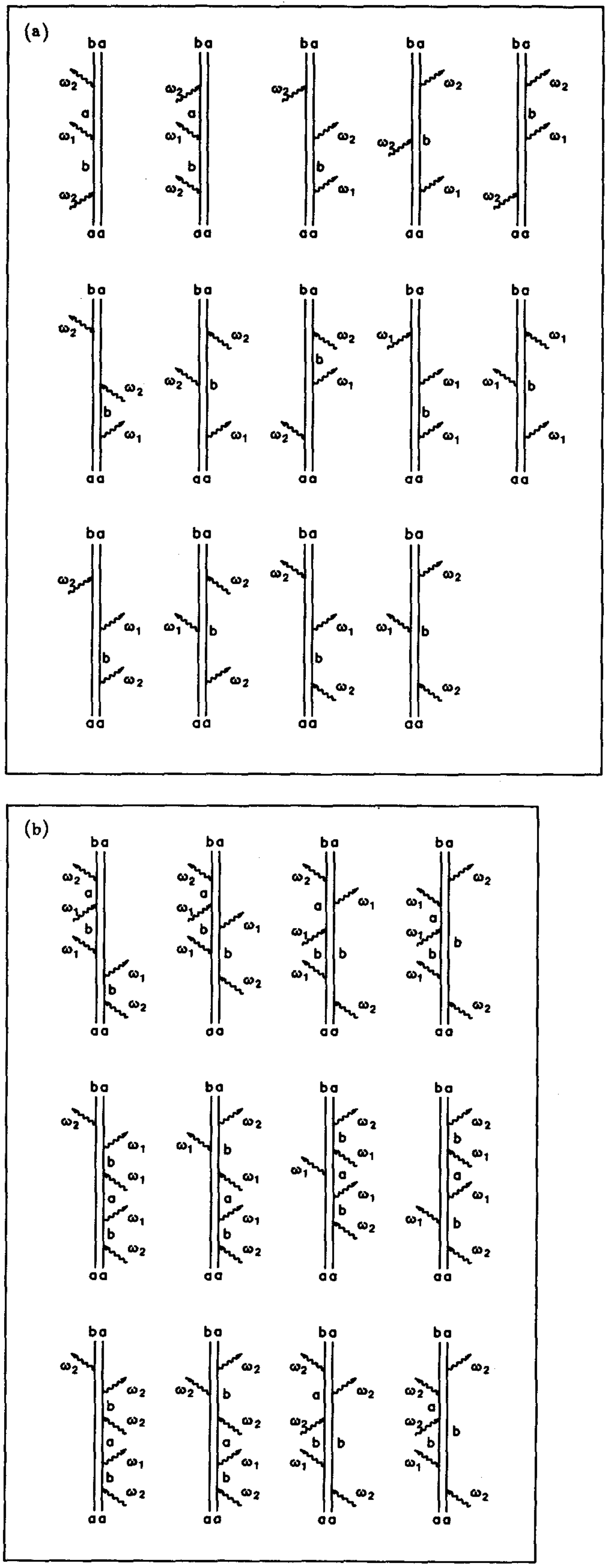

FIG. 11. Feynman diagrams for all the pathways corresponding to (a) the third-order and (b) the fifth-order correction terms in Eq. (36). See the Appendix for details.

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