Models for nonlinear optical spectra of coupled oscillators

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2009

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Nonlinear optical response

The nonlinear response of a sample to a series of laser pulses can be found from response theory. In a sample of randomly oriented molecules, the response functions must be averaged over orientations. In this chapter, we will derive the expression for the response functions in terms of the Green’s functions which describe the time evolution of the sample. Spectra in the NISE approach follow directly from these response functions in the time domain. In the sum over states model, explicit expressions for the response functions in the frequency domain can be obtained.

3.1 Introduction

Optical spectroscopy uses light to study the properties of a sample. In a non-magnetic material, the response follows from the coupling of the electric field $E(t)$ of the light to the polarization $P$ of the material. In typical optical experiments, the photon flux is high enough to make the classical description of light as a field valid. However, typical field strengths are much smaller than the intramolecular forces in the sample. The polarization induced by the radiation can then be expanded in powers of the applied electric field. To first order, $P \propto E$. This is the domain of linear optics, and a linear relationship between field and polarization is used to describe all linear optical experiments.

Continuing the expansion, one obtains higher order contributions [Bloembergen 1965]. The polarization can be written as $P = P^{(1)} + P^{(2)} + P^{(3)} + \ldots$, where $P^{(2)} \propto EE$ and $P^{(3)} \propto EEE$. In a centrosymmetric medium, inversion of the coordinate system shows that the second-order contribution to the polarization vanishes. Consequently, it also vanishes for an isotropic bulk medium composed of randomly
oriented molecules, which are for example found in a liquid or glass. Such samples are centrosymmetric on average. Because there is no contribution from the bulk material, second-order techniques such as sum frequency generation are useful to study interfaces. We will be interested in (on average) isotropic samples, and therefore not consider the second-order polarization.

The lowest order nonlinear techniques that are useful to the study of biomolecules in solution must consequently measure the third-order polarization. These techniques involve the photon echo, pump probe spectroscopy, and two-dimensional spectroscopy. From the expression for the third-order polarization, we see that its components can be measured selectively by controlling three interactions with the electric fields. This can be accomplished by performing an experiment with ultra-short pulses. Each pulse is prepared in such a way that it interacts with the sample at a controlled moment in time, and the polarizations of the pulses perform the selectivity of orientational components. The idea of the selective measurement of the nonlinear polarization is used in 2DIR and 2D visible spectroscopy.

The next sections contain a phenomenological discussion of two-dimensional spectra (Section 3.2), followed by a formal derivation of the nonlinear response functions (Section 3.3). In Section 3.4 we treat the spectra in the sum over states limit. The calculation of spectra in the NISE method is briefly discussed in Section 3.5. Appendix 3A explains the derivation of orientational response coefficients.

### 3.2 Phenomenology

In this section, we introduce the two-dimensional spectrum with the help of two simple examples: the homogeneous two- and three-level systems. The two-level system is the simplest model for an optically accessible electronic transition in a molecule. The two levels are the ground state and the electronic excited state. In its simplest form, the spectroscopy of such a system can be modeled with two parameters: the excited state energy $\epsilon$ (measured from the energy of the ground state, which is taken to be zero) and its homogeneous line width, $\gamma$. The two-level system is a useful model for an electronic transition, where double excitation is forbidden by the Pauli principle. This principle does not apply for vibrations, for which multiple levels are needed. In the description of two-dimensional spectra, however, a three-level model is sufficient. The three-level system is characterized by one extra parameter: the anharmonicity $A$, which is defined as the difference in energy between the doubly excited state and $2\epsilon$. In the systems that we consider we always have $A \ll \epsilon$.

In a pulsed two-dimensional experiment, three pulses are used to excite the sample. The first pulse creates an oscillating dipole, which is left on its own during a time $t_1$. The second pulse hits the system, and leaves it in the ground state or the first excited state. Finally, the third pulse again creates an oscillating dipole. The emitted radiation is collected after a time $t_3$. In this way, the signal $S(t_1, t_2, t_3)$ is measured as a function of the three time variables. The usual way to present the information in the signal follows a double Fourier transformation with respect to $t_1$ and $t_3$. The corresponding frequencies, denoted $\omega_1$ and $\omega_3$, are put on the two axes of a plot, in which the signal is drawn for a fixed value of $t_2$. In a two-level system, only the
Figure 3.1: Cartoon of the two-dimensional spectra of a homogeneous (a) two- and (b) three-level system. Solid lines enclose negative peaks, while positive peaks are drawn with dashed contours.

frequency $\epsilon$ is measured, and the two-dimensional spectrum contains a single peak at $(\omega_1, \omega_3) = (\epsilon, \epsilon)$ (See Figure 3.1 a).

In a three-level system, an additional peak appears due to excited state absorption into the two-quantum state. The first two pulses can bring the system into the first excited state. If the third pulse hits a molecule in this state, three processes will contribute to the nonlinear optical absorption. Because the system is not in the ground state, the transition from the ground state to the first excited state is not possible. This bleaching contribution leads to less absorption. Another process that leads to a negative peak is stimulated emission. Finally, a positive extra absorption process occurs when the third pulse promotes the system from the first to the second excited state.

The two-dimensional spectrum (Figure 3.1 b) shows the frequency of an oscillating dipole in the system after interaction with the first pulse on the horizontal axis, while the vertical axis displays the frequency after interaction with the third pulse. In the bleaching and stimulated emission processes, all interactions couple to transitions between the ground state and the first excited state. These processes will therefore lead to a negative peak on the diagonal of the 2D spectrum, at $\omega_1 = \omega_3 = \epsilon$. In the induced absorption process, the third pulse induces a transition between the first and the second excited state, while the first pulse is still coupled to the ground state - first excited state transition. The induced absorption process will therefore lead to a positive peak at $(\omega_1, \omega_3) = (\epsilon, \epsilon - A)$, a distance $A$ below the bleaching and stimulated emission peak. The induced absorption contribution has the opposite sign of the bleaching and stimulated emission. For harmonic scaling of the transition dipoles, both peaks have the same intensity. Therefore, the two-dimensional spectrum for the ideal harmonic oscillator ($A = 0$) is zero everywhere, as expected.

Interest in two-dimensional spectroscopy does not originate in its ability to dis-
Nonlinear optical response

Figure 3.2: Cartoon of the two-dimensional spectra of (a) three-level systems in an inhomogeneous environment and (b) two coupled three-level systems.

...tistinguish between two- and three-level systems. We therefore very briefly discuss the spectral signatures of interaction with the environment and coupling between oscillators. Interaction with the environment influences the line shape. In particular, an inhomogeneous distribution of oscillator energies will lead to broadening along the diagonal (Figure 3.2 a). The diagonal broadening can easily be understood as a superposition of contributions from individual oscillators, which all lead to a diagonal peak at a slightly different position. In the limit where the width of the inhomogeneous distribution (characterized by a parameter $\sigma$) is much larger than the homogeneous line width $\gamma$, $\sigma$ determines the diagonal width of the peak, while the anti-diagonal width is a measure of $\gamma$.

In a system of coupled modes (Figure 3.2 b), additional peaks appear away from the diagonal. These so-called cross peaks indicate the presence of collective modes which overlap spatially, i.e. which involve the excitation of the same building blocks. The time-dependent interaction between the collective modes, which causes energy flow, can be observed by studying cross peaks for different values of $t_2$. The exact time dependence is a result of the mode coupling as well as the interaction with the environment, and contains detailed information on the dynamics.

3.3 Response functions

The interaction between the sample and the electromagnetic field is given by a matter-light interaction term $H_{ML}$ in the Hamiltonian. In the case of light fields that are weak compared to molecular fields, this interaction term can be treated perturbatively. If the optical transition under study is dipole allowed, and if the coherence size of the excitations that are created in the medium is much smaller than the excitation wavelength, the coupling between medium and light is given by a dipole
term,

\[ H_{\text{ML}}(t) = -\vec{M} \cdot \vec{E}(\vec{r}, t). \]  

(3.1)

The dipole operator is denoted \( \vec{M} \). It can be expanded to first order in terms of the medium coordinates as \( \vec{M} = \sum_n \vec{m}_n (b_n + b_n^\dagger) \), where we assume that no permanent dipoles are present. Care has to be taken in the interpretation of the inner product between the dipole vector and the electric field that appears in Eq. 3.1. The dipole vector is normally given in the coordinate frame of the molecule, while the polarization of the electric field is defined in the lab frame. For a macroscopic sample, the inner product needs to be averaged over all possible orientations of the molecular frame. We will return to this point in Section 3.3.5.

The perturbative expansion of the matter-field interaction is most easily done in the interaction picture with respect to the free evolution of the matter [Mukamel 1995; Boyd 1992]. In the absence of light, the free system dynamics is given by the propagator \( \hat{G} \) as \( \hat{\rho}(t) = \hat{G}(t; t_0)\hat{\rho}(t_0) \). Using the free system propagator, the density matrix in the interaction picture is defined as

\[ \hat{\rho}^I(t) = G^\dagger(t; t_0)\hat{\rho}(t). \]  

(3.2)

Using this definition, the equation of motion becomes (\( \hbar = 1 \))

\[ \frac{d}{dt} \hat{\rho}^I(t) = -i H^\times_{\text{ML}}(t)\hat{\rho}^I(t), \]  

(3.3)

where \( H^\times_{\text{ML}}(t) = G^\dagger(t; t_0)H^\times_{\text{ML}}(t)G(t; t_0) \). The Liouville operator \( H^\times(t) \) is defined as the commutator of the Hamiltonian with whatever follows, \( H^\times(t)A := [H(t), A] \).

The formal solution for the density matrix is then written as a time-ordered exponential,

\[ \hat{\rho}^I(t) = Te^{-i \int_{t_0}^t d\tau H^\times_{\text{ML}}(\tau)} \hat{\rho}^I(t_0), \]  

(3.4)

which can be expanded in the usual way to find the density matrix to any order.

The result for the third-order polarization is

\[ \vec{P}^{(3)}(\vec{r}, t) = \int d\tau_3 d\tau_2 d\tau_1 S^{(3)}(\tau_1, \tau_2, \tau_3)E(\vec{r}, t - \tau_3)E(\vec{r}, t - \tau_3 - \tau_2)E(\vec{r}, t - \tau_3 - \tau_2 - \tau_1), \]  

(3.5)

where the integral is over the interval \((0, \infty)\) for all three time variables. The response function \( S \) is a rank 4 tensor in spatial components, given by

\[ S^{(3)}(\tau_1, \tau_2, \tau_3) = -i^3 \text{tr} \vec{M} G(\tau_3)\vec{M}^\times \vec{M} G(\tau_2)\vec{M}^\times \vec{M} G(\tau_1)\vec{M}^\times \hat{\rho}(t_0), \]  

(3.6)

where \( G(\tau_3), G(\tau_2) \) and \( G(\tau_1) \) are shorthand notation for \( G(t; t - \tau_3), G(t - \tau_3; t - \tau_3 - \tau_2) \) and \( G(t - \tau_3 - \tau_2; t - \tau_3 - \tau_2 - \tau_1) \), respectively. The three propagators de-
Figure 3.3: Pulse parameters in a third-order experiment. The first pulse to hit the sample is pulse one, with wave vector $\vec{k}_1$. After a time delay $t_1$, it is followed by pulse two, which precedes the third pulse by a delay $t_2$. A time interval $t_3$ after the third pulse, the signal is measured.

3.3.1 Short pulses and heterodyne detection

In a pulsed experiment, the sample is irradiated by three ultrashort laser pulses. We label the pulses in such a way that pulse 1 arrives at the sample first, followed by pulses 2 and 3. In most experimental setups, all three pulses originate from the same laser, and optical components are used to control their time delays, denoted $0, t_1$ and $t_1 + t_2$, and wave vectors, which are denoted as $\vec{k}_1, \vec{k}_2$ and $\vec{k}_3$ (See Figure 3.3). Even for very short laser pulses, the bandwidth is much smaller than the central frequency $\omega$. A single pulse centered around time zero is then given by

$$\tilde{E}_i(\vec{r}, t) = \tilde{E}_i(t)e^{i(\vec{k}_i \cdot \vec{r} - \omega t)} + \text{complex conjugate}. \quad (3.7)$$

The separation of the electric field into an envelope $\tilde{E}_i(t)$ and a plane carrier wave is meaningful if the bandwidth of the pulse is small compared to the carrier frequency $\omega$, or in other words, if the pulse is long enough to contain several periods of the carrier wave. The envelope is then a function that varies slowly with time, and it defines the pulse shape. The total electric field that reaches the sample at a time $t$ is the sum of three pulses (the origin of the time axis is chosen at the moment of detection, where $t = 0$),

$$\tilde{E}(\vec{r}, t) = \tilde{E}_1(\vec{r}, t + t_3 + t_2 + t_1) + \tilde{E}_2(\vec{r}, t + t_3 + t_2) + \tilde{E}_3(\vec{r}, t + t_3). \quad (3.8)$$
In writing Eq. 3.8, we assumed that all pulses are in phase. In a typical experimental situation, a single pulse is split into three parts, which are each delayed by a certain time. In an ideal situation, the pulses would therefore be perfectly in phase. However, in practice phase differences occur, and relative phases of the pulses need to be taken into account.

To continue the derivation of the response functions, we assume that the pulses are shorter than the dynamics of the system under study, so that the field envelopes can be approximated by delta functions in time. This appears to make the evaluation of the triple convolution in Eq. 3.5 trivial. However, this is only possible after carefully making the rotating wave approximation [Mukamel 1995; Jonas 2003]. The pulse envelope, which we want to approximate by a delta function, cannot be shorter than the inverse optical frequency. Therefore, before performing the integrations, one makes the approximation that all the fast oscillating terms in Eq. 3.5 are zero. Although care has to be taken [Jonas 2003], this can be rationalized from the fact that such terms tend to average out to zero.

Making the usual rotating wave approximation, we keep only the slowly varying terms in the response, denoted as $S_{\text{rw}}^{(3)}$. After performing the convolution integrals, the third-order polarization becomes

$$
\hat{p}^{(3)}(\vec{r}, t_1, t_2, t_3) = S_{\text{rw}}^{(3)}(t_1, t_2, t_3)(\vec{E}_1 e^{i(\vec{k}_1 \cdot \vec{r} - \omega t)} + \text{c.c.})(\vec{E}_2 e^{i(\vec{k}_2 \cdot \vec{r} - \omega t)} + \text{c.c.})(\vec{E}_3 e^{i(\vec{k}_3 \cdot \vec{r} - \omega t)} + \text{c.c.})
$$

(3.9)

We see that, by using three ultrashort pulses, it is possible to control the three interactions that appear in the formal expression resulting from perturbation theory. In a realistic experiment, achieving a real delta pulse is of course impossible. If the pulse length is important for the description of the experiment, one can find the polarization by explicitly carrying out the convolution with the pulse shape in Eq. 3.5. In the evaluation, care has to be taken when the pulses (partly) overlap in time. In that case, the interaction with the first pulse may happen later than the interaction with the second pulse. An alternative approach that has been used in nonlinear optics to include the effect of finite pulse width is a nonperturbative treatment of the interaction between medium and light [Brüggemann et al. 2007]. The third-order signal is then found by using the phase matching condition, which we will discuss below. In the following, we will use the approximation of delta pulses. This means that we will not be able to describe dynamics that happen faster than the pulse length, and we have to exclude overlapping pulses. In particular, zero waiting time in a calculated 2D spectrum must be interpreted as a waiting time long enough to ensure the correct pulse order, but short compared to the time scale of the system dynamics.

The third-order polarization in Eq. 3.9 can be written as a sum of 8 terms [Mukamel and Abramavicius 2004; Cho 2008],

$$
\hat{p}^{(3)}(\vec{r}, t_1, t_2, t_3) = \sum_{i=1}^{8} \tilde{p}^{(3)}_i(t; t_1, t_2, t_3) e^{\vec{k}_i \cdot \vec{r} - i c_i \omega t},
$$

(3.10)

where $\vec{k}_i = \pm \vec{k}_1 \pm \vec{k}_2 \pm \vec{k}_3$ and $c_i \in \{-3, -1, 1, 3\}$. If the sample is much larger than
the wavelength of the light, as in a bulk sample, the third-order polarization generates a signal in the direction of the wave vectors $\vec{k}_i$ (phase matching) [Mukamel 2000; Cho 2008]. If the three incident pulses fall into the sample from different directions, the terms in the expansion in Eq. 3.10 can therefore be measured separately. This is accomplished by putting a detector in the required phase-matched direction.

The polarization that is induced functions as the source of an electromagnetic field, which is radiated from the sample. The radiated field can be detected directly (homodyne detection) but is more often mixed with a fourth pulse. This technique, called heterodyne detection, is used to increase the weak nonlinear signal. Furthermore, it allows for the measurement of the real and imaginary parts of the response function separately [de Boeij et al. 1995].

The third-order response function $S^{(3)}$ contains nested commutators in Hilbert space. Expanding these commutators gives a total of eight different terms. Each term is multiplied with three electric fields, and each multiplication can be with a positive or a negative frequency. Before making the rotating wave approximation, the third-order polarization can therefore be written as a sum of 64 terms. To keep track of these terms, a diagrammatic technique is introduced.

### 3.3.2 Diagrams

The different terms in the nonlinear response function $S^{(3)}_{\text{rw}}(t_1, t_2, t_3)$ are conveniently expressed in double sided Feynman diagrams. These diagrams follow the evolution of the density matrix in time, which increases from the bottom to the top of the diagram. In a multilevel system, the density matrix is written as an operator in a certain complete basis, which can consist of individual oscillator states (which were labeled with $n$ and $m$ in Chapter 2), eigenstates of the Hamiltonian, or any other convenient set. In this section, we label the one-quantum basis states by $n, m$ and their primed variants, while two-quantum basis states are labeled $w''$ and $w'''$. An interaction with the electric field is drawn as an arrow. Arrows pointing to the right represent interactions with a positive wave vector, while arrows pointing to the left represent interactions with a negative wave vector. It turns out that the only diagrams which survive the rotating wave approximation are those in which an arrow pointing towards the diagram (i.e. a positive wave vector for an interaction at the ket side, or a negative wave vector for an interaction at the bra side) increases the number of excitation quanta, while the number is decreased when interacting with light with a wave vector pointing away from the diagram.

The diagrams relevant for 2D spectra measured in the $\vec{k}_R = \vec{k}_1 + \vec{k}_2 + \vec{k}_3$ and $\vec{k}_{NR} = \vec{k}_1 - \vec{k}_2 + \vec{k}_3$ phase matched directions are shown in Figure 3.4. These two signals are often called rephasing and non-rephasing, respectively. In the rephasing diagrams, the evolution of the phase during the second coherence time $t_3$ is opposite to the evolution during the first coherence time $t_1$. In a static system, all phase differences that have built up between molecules during $t_1$ disappear when $t_3 = t_1$, or, in other words, the system rephases. An actual echo is produced, which is not the case in the non-rephasing signal. There is one additional direction in which signals survive the rotation wave approximation, the $\vec{k}_1 + \vec{k}_2 - \vec{k}_3$ direction. In the diagrams that
3.3: Response functions

Figure 3.4: Feynman diagrams in the rephasing (diagrams (a), (b) and (c)) and non-rephasing (diagrams (d), (e) and (f)) phase matched directions. The indices \( n, m, n', m', n'', m'', m''', \) and \( m'''' \) label elements of the one-quantum basis. Two-quantum basis states are labeled with \( w'' \) and \( w''' \), and 0 denotes the ground state.

Contribute in this direction, the system is in a coherent superposition of the ground state and a two-exciton state during \( t_2 \). We will not consider these diagrams in this thesis (See, for example, the paper by Mukamel et al. [2007] for a proposed application).

3.3.3 Linear absorption

The linear absorption spectrum is given by the imaginary part of the Fourier transform of the linear response function. Only one diagram survives the rotating wave approximation and contributes to the response function. In the Condon approximation, where the transition dipole is time-independent, the spectrum can be written as

\[
S_L(\omega) = \text{Im} i \sum_{nm} \mu_n \mu_m \int_0^\infty dt e^{i\omega t} U_{nm}(t; 0).
\]  

\[ (3.11) \]
The propagator \( U \) for the wave function is the solution of the Schrödinger equation, it is defined in terms of the Liouville propagator as \( U_{nm}(t;0) = G_{n0m0}(t;0) \).

### 3.3.4 Third-order response functions

The rephasing third-order response is the sum of the contributions from three of the diagrams shown in Figure 3.4; a ground state bleach pathway (diagram a), a stimulated emission pathway (diagram b), and an induced absorption pathway (diagram c),

\[
S_R(t_1, t_2, t_3) = (-i)^3 A_{\alpha\beta\gamma\delta} \left( S_{RGB}^{\alpha\beta\gamma\delta}(t_1, t_2, t_3) + S_{RSE}^{\alpha\beta\gamma\delta}(t_1, t_2, t_3) + S_{RIA}^{\alpha\beta\gamma\delta}(t_1, t_2, t_3) \right).
\]

(3.12)

The tensor \( A_{\alpha\beta\gamma\delta} \) contains the orientational components for a given laser polarization; its indices \( \alpha, \beta, \gamma, \) and \( \delta \) are spatial coordinates. The three contributions are given by

\[
S_{RGB}^{\alpha\beta\gamma\delta}(t_1, t_2, t_3) = \mu^\alpha_m \mu^\beta_{m'} \mu^\gamma_{m''} \mu^\delta_{m'''} U_{m'''m'}(t_3) U_{m'm}(t_1),
\]

\[
S_{RSE}^{\alpha\beta\gamma\delta}(t_1, t_2, t_3) = \mu^\alpha_m \mu^\beta_{m'} \mu^\gamma_{m''} \mu^\delta_{m'''} U_{m'''m''}(t_3) G_{m''m'm'}(t_2) U_{m'm}(t_1),
\]

\[
S_{RIA}^{\alpha\beta\gamma\delta}(t_1, t_2, t_3) = -\mu^\alpha_m \mu^\beta_{m'} \mu^\gamma_{m''} \mu^\delta_{m'''} U^{(2)}_{m'''m'}(t_3) U_{m'm}(t_3) G_{m''m'm'}(t_2) U_{m'm}(t_1).
\]

In these expressions, and in the following, we use the Einstein summation convention for all free indices. Similarly, the non-rephasing spectrum is given by

\[
S_{NR}(t_1, t_2, t_3) = (-i)^3 A_{\alpha\beta\gamma\delta} \left( S_{NRGB}^{\alpha\beta\gamma\delta}(t_1, t_2, t_3) + S_{NRSE}^{\alpha\beta\gamma\delta}(t_1, t_2, t_3) + S_{NRIA}^{\alpha\beta\gamma\delta}(t_1, t_2, t_3) \right),
\]

(3.13)

with

\[
S_{NRGB}^{\alpha\beta\gamma\delta}(t_1, t_2, t_3) = \mu^\alpha_m \mu^\beta_{m'} \mu^\gamma_{m''} \mu^\delta_{m'''} U_{m'''m'}(t_3) U_{m'm}(t_1),
\]

\[
S_{NRSE}^{\alpha\beta\gamma\delta}(t_1, t_2, t_3) = \mu^\alpha_m \mu^\beta_{m'} \mu^\gamma_{m''} \mu^\delta_{m'''} U_{m'''m''}(t_3) G_{m''m'm'}(t_2) U_{m'm}(t_1),
\]

\[
S_{NRIA}^{\alpha\beta\gamma\delta}(t_1, t_2, t_3) = -\mu^\alpha_m \mu^\beta_{m'} \mu^\gamma_{m''} \mu^\delta_{m'''} U_{m'''m'}(t_3) G_{m''m'm'}(t_2) U_{m'm}(t_1).
\]

2D spectra in the frequency domain are found by making a Fourier transform with respect to \( t_1 \) and \( t_3 \),

\[
S_R(\omega_1, t_2, \omega_3) = \int_0^\infty dt_1 \int_0^\infty dt_3 e^{-i\omega_1 t_1} e^{i\omega_3 t_3} S_R(t_1, t_2, t_3)
\]

(3.14)

\[
S_{NR}(\omega_1, t_2, \omega_3) = \int_0^\infty dt_1 \int_0^\infty dt_3 e^{i\omega_1 t_1} e^{i\omega_3 t_3} S_{NR}(t_1, t_2, t_3).
\]

(3.15)

Finally, the 2D correlation spectrum is defined to obtain the absorptive part of the response as \(^1 S(\omega_1, t_2, \omega_3) = \text{Im} \left( S_R(\omega_1, t_2, \omega_3) + S_{NR}(\omega_1, t_2, \omega_3) \right) \) [Khalil et al. 2003b].

---

1. In our sign convention, the bleaching and stimulated emission peaks have a negative sign in the
3.4: Spectra in the sum over states limit

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Table 3.1: Orientational coefficients for an isotropic sample. The four columns give the orientational coefficients for four independent combinations of laser polarizations in the laboratory frame. The coefficients are invariant under permutation of the components $x, y, z$, giving 21 nonzero components. All other components are zero.

3.3.5 Polarization dependence

The polarization dependence of the two-dimensional spectrum is contained in the tensor $A$, whose values depend on the choice of the laser pulse polarization. The sensitivity of the spectrum to the combination of pulse polarizations is a useful property: it can be applied to find the angle between oscillator dipoles [Golonzka et al. 2001], and to highlight or suppress spectral features. To derive values for the components of this tensor, we will assume that the sample under study is an isotropic mixture of molecules. The orientational tensor can then be found by averaging the inner product of the four dipoles that appear in the response function with the four electric fields over all orientations of the molecule. The polarizations of the electric fields are given in the fixed lab frame. The projection of a dipole in the molecular frame is given by a rotation, which can be parametrized in terms of three Euler angles. After averaging, one finds the coefficients of $A$ for four independent orientational components (Appendix 3A). These values for $A$ are given in Table 3.1 (see also the paper by Hochstrasser [2001]). Orientational coefficients for other combinations of linear polarized pulses can be found as linear combinations of these coefficients.

3.4 Spectra in the sum over states limit

The sum over states result for the spectra is found by calculating the eigenstates of the Hamiltonian in each realization of the static disorder (See Section 2.3). For eigenstates $|u\rangle$ and $|v\rangle$ in a single realization, the equation of motion (Eq. 2.17) reduces to

$$\dot{q}_{uv}(t) = - (iE_{uv} + \gamma_{uv}) q_{uv}(t),$$  

where $E_{uv} = E_u - E_v$, the difference between two eigenvalues. The fast fluctuations lead to the homogeneous broadening constants $\gamma_{uv}$. The solution for the propagator is then simply $G_{uv,uv'}(t) = \delta_{uu'}\delta_{vv'} \exp \left( - (iE_{uv} + \gamma_{uv}) t \right)$. With knowledge of the propagator, the linear and nonlinear spectra can be calculated.

correlation spectrum.
3.4.1 Linear absorption spectrum

The absorption spectrum, up to a constant defined as the imaginary part of the response function divided by the incident field, is given by

\[
S_L(\omega) \propto -\text{Im}\left\langle \sum_u \frac{\left|\tilde{\mu}_u\right|^2}{\omega - E_u + i\gamma_u}\right\rangle_D = \left\langle \sum_u \frac{\left|\tilde{\mu}_u\right|^2 \gamma_u}{(\omega - E_u)^2 + \gamma_u^2}\right\rangle_D, \tag{3.17}
\]

in units where \(\hbar = 1\). The lineshape is a Lorentzian for each single eigenstate, whose full width at half maximum near a single eigenvalue \(E_u\) is given by \(2\gamma_u = 2\gamma_u^0\). The angular brackets \(\langle \cdots \rangle_D\) denote an average over realizations of the static disorder.

3.4.2 Two-dimensional spectrum

In the sum over states model, the propagator is diagonal, and there is no coherence transfer in the basis of eigenstates during \(t_1\) and \(t_3\). The diagrams contributing to the third-order response functions can then be simplified (in the eigenbasis), as shown in Figure 3.5. As an example, we will calculate the response for the rephasing stimulated emission diagram (Figure 3.5 b). In the time domain, the response function is (summations over one-quantum eigenstates, labeled by \(u\), \(v\) et cetera, are implied)

\[
S_{RSE}(t_1, t_2, t_3) = (-i)^3 A_{\alpha\beta\gamma\delta} \langle \mu^\alpha_u \mu^\beta_v \mu'^\gamma_{u'} \mu'^\delta_{v'} U^\dagger_{u'u}(t_1) G_{v'v'u'u}(t_2) U_{v'v''}(t_3) \rangle_D
\]

\[
= (-i)^3 A_{\alpha\beta\gamma\delta} \langle \mu^\alpha_u \mu^\beta_v \mu'^\gamma_{u'} \mu'^\delta_{v'} e^{i(E_u - \gamma_u) t_1} e^{-i(E_v - \gamma_v) t_3} \rangle_D. \tag{3.18}
\]
The Fourier transforms are evaluated to give

\[ S_{\text{RSE}}(\omega_1, t_2, \omega_3) = iA_{\alpha\beta\gamma\delta} \left( \frac{\mu_{\alpha}^{\alpha} \mu_{\beta}^{\beta} \mu_{\gamma}^{\gamma} \mu_{\delta}^{\delta} G_{\nu'\nu''u'(t_2)}}{(\omega_1 - E_u - i\gamma_u)(\omega_3 - E_{\nu'} + i\gamma_{\nu'})} \right) . \]  

This expression gives the contribution of the stimulated emission process to the rephasing two-dimensional spectrum for a given set of eigenstates. An inhomogeneous distribution of molecules in the sample, which may all have different eigenenergies \( E_u \) and eigenstates, can be handled by averaging the response over this distribution, indicated by \( \langle \cdots \rangle_D \). During the waiting time \( t_2 \), relaxation in the band of one-quantum states can take place. This process is described by the Green’s function \( G(t_2) \). For \( t_2 = 0 \), \( G_{\nu'\nu''u'}(0) = \delta_{\nu'\nu''} \delta_{u'u} \). In the same way, the total rephasing 2D spectrum is found to be

\[ S_R(\omega_1, t_2, \omega_3) = iA_{\alpha\beta\gamma\delta} \left( \frac{\mu_{\alpha}^{\alpha} \mu_{\beta}^{\beta} \mu_{\gamma}^{\gamma} \mu_{\delta}^{\delta} G_{\nu'\nu''u}(t_2)}{(\omega_1 - E_u - i\gamma_u)(\omega_3 - E_{\nu'} + i\gamma_{\nu'})} \right) . \]  

In the second line, summation over the two-exciton states, labeled with \( \nu' \), is implied. The transition dipole matrix element between a one-exciton state \( u \) and a two-exciton state \( \nu \) is given by \( \bar{\mu}_{\nu u} = \langle \nu | \bar{u} | u \rangle \). The non-rephasing diagrams yield

\[ S_{\text{NR}}(\omega_1, t_2, \omega_3) = -iA_{\alpha\beta\gamma\delta} \left( \frac{\mu_{\alpha}^{\alpha} \mu_{\beta}^{\beta} \mu_{\gamma}^{\gamma} \mu_{\delta}^{\delta}}{(\omega_1 - E_u + i\gamma_u)(\omega_3 - E_{\nu'} + i\gamma_{\nu'})} \right) \]

\[ + \left( \frac{\mu_{\alpha}^{\alpha} \mu_{\beta}^{\beta} \mu_{\gamma}^{\gamma} \mu_{\delta}^{\delta} G_{\nu'\nu''u}(t_2)}{(\omega_1 - E_u + i\gamma_u)(\omega_3 - E_{\nu'} + i\gamma_{\nu'})} \right) \]

\[ - \left( \frac{\mu_{\alpha}^{\alpha} \mu_{\beta}^{\beta} \mu_{\gamma}^{\gamma} \mu_{\delta}^{\delta} G_{\nu'\nu''u}(t_2)}{(\omega_1 - E_u + i\gamma_u)(\omega_3 - E_{\nu'} + i\gamma_{\nu'})} \right) . \]

For a single broadening constant (all \( \gamma \) constants equal), the calculation of the spectra can be performed efficiently by collecting the response in frequency bins. The spectrum is then first averaged over disorder, and the homogeneous lineshape is obtained by a convolution with the two-dimensional Lorentzian [Ganin and Tokmakoff 2006].

The two-dimensional Lorentzian line can be visualized by plotting the two-dimensional spectrum of a homogeneous two-level system, shown in Figure 3.6. The real and imaginary parts of both the rephasing and non-rephasing response can be measured separately. The figure demonstrates that a single absorptive line can be obtained by summing the imaginary rephasing and non-rephasing parts into the correlation spectrum [Khalil et al. 2003b]. The same procedure works in a three-level system, as shown in Figure 3.7. However, for multiple coupled oscillators, the can-
Figure 3.6: Two-dimensional spectra of a homogeneous two-level system. Negative contributions are indicated with solid contours, while dashed contours code for positive peaks. Contours are drawn at intervals of $0.1/\gamma^2$ between $-1/\gamma^2$ and $+1/\gamma^2$. The length of the transition dipole is chosen in such a way that $A_{\alpha\beta\gamma\delta} \mu^\alpha \mu^\beta \mu^\gamma \mu^\delta = \frac{1}{2}$.

cancellation of dispersive contributions to the correlation spectrum is not perfect. This is seen explicitly by summing the response functions given in Eqs. 3.20 and 3.21. The dispersive parts of pathways where the system is in a coherent superposition of two different eigenstates during $t_2$ will not vanish.

3.4.3 Inhomogeneous averaging

For a single two-level system in the sum over states limit, the average over the slow dynamics is an single integral which can be performed analytically in the case of a Gaussian frequency distribution. In the time domain, we have (the homogeneous
linewidth is $\gamma$, and $\sigma$ is the standard deviation of the Gaussian distribution)

$$S_R(t_1, 0, t_3) = 2i \langle e^{i\epsilon t_1 - \gamma t_1} e^{-i\epsilon t_3 - \gamma t_3} \rangle_D$$

$$= \frac{2i}{\sigma \sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-\xi^2/2\sigma^2} e^{i\xi(t_1 - t_3)} e^{-\gamma(t_1 + t_3)} d\xi$$

$$= 2i e^{-\sigma^2(t_1 - t_3)^2/2} e^{-\gamma(t_1 + t_3)}.$$  \hfill (3.22)

$$S_{NR}(t_1, 0, t_3) = 2i e^{-\sigma^2(t_1 + t_3)^2/2} e^{-\gamma(t_1 + t_3)}.$$  \hfill (3.23)

Performing the Fourier transformations, the resulting expression for the rephasing 2D spectrum is found in terms of the special function $w(x)$ as

$$S_R(\omega_1, 0, \omega_3) = \sqrt{\frac{2\pi}{\sigma^2}} \frac{i}{2\gamma + i(\omega_1 - \omega_3)} \left( w\left(\frac{\omega_1 + i\gamma}{\sigma \sqrt{2}}\right) + w\left(\frac{\omega_3 + i\gamma}{\sigma \sqrt{2}}\right) \right)$$  \hfill (3.24)

For the non-rephasing spectrum, we find

$$S_{NR}(\omega_1, 0, \omega_3) = \sqrt{\frac{2\pi}{\sigma^2}} \frac{1}{(\omega_1 - \omega_3)} \left( w\left(\frac{\omega_1 + i\gamma}{\sigma \sqrt{2}}\right) - w\left(\frac{\omega_3 + i\gamma}{\sigma \sqrt{2}}\right) \right)$$  \hfill (3.25)

Here, $w(x) = \exp(-x^2)\text{erfc}(-ix)$ is the complex generalization of the complementary error function erfc(x), which is defined as $\text{erfc}(x) = 2/\sqrt{\pi} \int_{-\infty}^{\infty} dy \exp(-y^2)$.

We can use its asymptotic expansion for large $x$, $\text{erfc}(x) \approx \exp(-x^2)/x\sqrt{\pi}$ to find back the spectra in the homogeneous limit ($\sigma \to 0$),

$$S_R(\bar{\omega}, 0, \omega) = \frac{2i}{(\gamma + i\bar{\omega})^2 + \omega^2}$$  \hfill (3.26)

$$S_{NR}(\bar{\omega}, 0, \omega) = \frac{2i}{(\gamma - i\bar{\omega})^2 + \omega^2}.$$  \hfill (3.27)
where $\bar{\omega} = (\omega_1 + \omega_3)/2$ and $\omega = (\omega_1 - \omega_3)/2$.

In larger systems, the average over disorder $\langle \cdots \rangle_D$ can generally not be performed by analytic integration. Instead, we perform Monte Carlo integration by sampling random oscillator energies (and, in some cases, couplings) from a probability distribution. For each set of random values, called realizations, the Hamiltonian is diagonalized to obtain the energies and eigenstates. The complete spectrum is obtained as the average of spectra calculated in each realization.

### 3.5 NISE

The procedure of numerical integration of the Schrödinger equation, described in Section 2.4, can be used to calculate the propagators $U$ and $G$ needed in the expressions for the linear and 2D spectra (Eqs. 3.11 - 3.14). The response functions are found by performing the summations over basis states, which are normally chosen to be the single oscillator states, to obtain the response functions in the time domain. A discrete Fourier transform then produces the spectra in the frequency domain. The dynamics during the waiting time is automatically included, without the need to invoke a perturbative or adiabatic approximation for the interaction with the environment.

In practice, it is not necessary to multiply the actual propagators in each time step in a NISE calculation. To economize on computer time and memory, we rather calculate and store the wave functions using Eq. 2.24.

### Appendix 3A Orientational response coefficients

In this appendix we will calculate the orientational part of the response functions, which fixes the constants $A$ used in the last section. It is necessary to account for the right orientational response, since the experiments that we wish to describe are performed with polarized laser beams. The dipole vectors associated with transitions between different quantum states appear in the response functions in inner products with the incident field (implicit in Eq. 3.5). Would we have a laser pulse polarized precisely perpendicular to some transition dipole vector, then the corresponding transition would not be visible in the spectrum at all, no matter how large the magnitude of the dipole vector may be. In principle, transitions could be excluded from the spectra by choosing the “right” polarization for the incident field. In practice, this will not work because the sample usually consists not of oriented molecules, but rather of a liquid or glass in which the probed molecules have an arbitrary orientation. In the linear absorption spectrum, averaging the response over an isotropic distribution of orientations only leads to a multiplicative factor $1/3$, reflecting the probability that the transition dipole vector is aligned with the electric field of the probe. In the rest of the appendix, we will calculate the orientational contribution to the third-order signal for polarized pulses. We will average over all possible orientations of the molecules in space to obtain the orientational response for a large ensemble of randomly oriented molecules. Molecular rotation during the
The coordinate rotation can be parametrized using three Euler angles. In the zxz-convention, the first rotation is by an angle $\phi$ around the $z$-axis. The second rotation is by an angle $\theta$ around the new $x$-axis. The third rotation is by an angle $\psi$ around the new $z$-axis.

The third-order response functions contain inner products of four transition dipoles with electric fields, of the form

$$\langle (\vec{\mu}_1 \cdot \vec{E}_1)(\vec{\mu}_2 \cdot \vec{E}_2)(\vec{\mu}_3 \cdot \vec{E}_3)(\vec{\mu}_4 \cdot \vec{E}_4) \rangle_O.$$  

(3A.1)

The brackets $\langle \cdot \cdot \cdot \rangle_O$ indicate that, for an isotropic sample, these factors must be averaged over all possible orientations of the sample with respect to the laboratory frame. Labeling coordinates in the frame of a molecule with $\alpha, \beta, \gamma, \delta$ and coordinates in the lab frame with $\alpha', \beta', \gamma', \delta'$, the orientational factors can be rewritten as $\mu_1^\alpha \mu_2^\beta \mu_3^\gamma \mu_4^\delta E_1^\alpha' E_2^\beta' E_3^\gamma' E_4^\delta' \langle R^{\alpha\alpha'} R^{\beta\beta'} R^{\gamma\gamma'} R^{\delta\delta'} \rangle_O$. The matrices $R$ are transformations between the two coordinate frames. For a specified combination of laser polarizations, the orientational coefficients can be defined as $A_{\alpha\beta\gamma\delta} = \langle R^{\alpha\alpha'} R^{\beta\beta'} R^{\gamma\gamma'} R^{\delta\delta'} \rangle_O \hat{E}_1^\alpha' \hat{E}_2^\beta' \hat{E}_3^\gamma' \hat{E}_4^\delta'$, where $\hat{E}_1^\alpha'$ is the $\alpha'$ component of a unit vector in the direction of $\vec{E}_1$.

The rotation matrix $R$ can be parametrized in terms of three angles. Here, we use the Euler angles $\phi, \theta$ and $\psi$ in the zxz-convention (Figure 3A.1). The coordinate system is rotated over an angle $0 \leq \phi \leq 2\pi$ around the $z$-axis, followed by a rotation over an angle $0 \leq \theta \leq \pi$ around the new $x$-axis, and a final rotation around the new $z$-axis over an angle $0 \leq \psi \leq 2\pi$. In this convention, the rotation matrix is

$$R(\phi, \theta, \psi) = \begin{pmatrix} \cos \psi \cos \phi - \cos \theta \sin \phi \sin \psi & \cos \psi \sin \phi + \cos \theta \cos \phi \sin \psi & \sin \psi \sin \theta \\ - \sin \psi \cos \phi - \cos \theta \sin \phi \cos \psi & \cos \theta \cos \phi \cos \psi - \sin \psi \sin \phi & \cos \psi \sin \theta \\ \sin \theta \sin \phi & \cos \theta \sin \phi & \cos \theta \end{pmatrix}.$$  

(3A.2)

Averaging over all possible rotations means we have to integrate with respect to a measure defined on the group SO(3), which is represented by $R$. There is a unique rotationally invariant measure on this group the Haar measure with total mass 1.
More precisely, this means that if \( g, h \in SO(3) \) and \( f : SO(3) \rightarrow \mathbb{R} \) is a function on the group, there is a unique measure \( dg \) such that

\[
(f)_O = \int dg f(gh) = \int dg f(g)
\]  
(3A.3)

and

\[
\int dg = 1.
\]  
(3A.4)

Averaging over all rotations means integrating with respect to this measure. To find the rotationally invariant measure in terms of the Euler angles, we parametrize a group element \( g \) with angles \( \phi_g, \theta_g \) and \( \psi_g \) [Gel’fand et al. 1963; Naimark 1964]. The function \( f \) can then be expressed in these angles, \( f(g) = f(\phi_g, \theta_g, \psi_g) \). The integration of \( f \) with respect to \( dg \) can be expressed as

\[
\int dg f(\phi_g, \theta_g, \psi_g) = \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} \omega(\phi_g, \theta_g, \psi_g) d\phi_g d\theta_g d\psi_g f(\phi_g, \theta_g, \psi_g),
\]  
(3A.5)

where we wrote \( dg = \omega(\phi_g, \theta_g, \psi_g) d\phi_g d\theta_g d\psi_g \). The rotationally invariant measure \( \omega(\phi_g, \theta_g, \psi_g) d\phi_g d\theta_g d\psi_g \) is uniquely given by

\[
\omega(\phi, \theta, \psi) = \frac{1}{8\pi^2} \sin \theta.
\]  
(3A.6)

The orientational coefficients are found by calculating triple integrals of products of four rotation matrices. As an example, we will calculate the coefficients in the ZZYY-polarization. The first and second pulses are polarized along the \( z \)-axis of the lab frame, while the polarization of the second pulse and of the signal are along the lab’s \( y \)-axis. The orientational coefficients for this polarization condition are given by

\[
A_{\alpha\beta\gamma\delta} \mu_1^\alpha \mu_2^\beta \mu_3^\gamma \mu_4^\delta = \frac{1}{8\pi^2} \int_{\psi=0}^{2\pi} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \sin \theta d\theta d\phi d\psi \\
\hat{z}(\mu_{1x} \sin \psi \sin \theta + \mu_{1y} \cos \psi \sin \theta + \mu_{1z} \cos \theta) \\
\times \hat{z}(\mu_{2x} \sin \psi \sin \theta + \mu_{2y} \cos \psi \sin \theta + \mu_{2z} \cos \theta) \\
\times \hat{y}(\mu_{3x} (\cos \psi \sin \phi + \cos \theta \cos \phi \sin \psi) + \mu_{3y} (-\sin \psi \sin \phi + \cos \theta \cos \phi \cos \psi) - \mu_{3z} \sin \theta \cos \phi) \\
\times \hat{y}(\mu_{4x} (\cos \psi \sin \phi + \cos \theta \cos \phi \sin \psi) + \mu_{4y} (-\sin \psi \sin \phi + \cos \theta \cos \phi \cos \psi) - \mu_{4z} \sin \theta \cos \phi).
\]  
(3A.7)
Performing the triple integration, one finds

\[ A_{\alpha\beta\gamma\delta}^{\alpha_{1}\beta_{2}\gamma_{3}\delta_{4}} = \frac{1}{30} \left\{ 4(\vec{\mu}_{1} \cdot \vec{\mu}_{2})(\vec{\mu}_{3} \cdot \vec{\mu}_{4}) - (\vec{\mu}_{1} \cdot \vec{\mu}_{3})(\vec{\mu}_{2} \cdot \vec{\mu}_{4}) - (\vec{\mu}_{1} \cdot \vec{\mu}_{4})(\vec{\mu}_{2} \cdot \vec{\mu}_{3}) \right\} , \]  

(3A.8)

from which the coefficients given in the first column of Table 3.1 can be read off. The coefficients for other laser polarizations are found from a similar calculation.