

Chapter 2

Nonlinear Optical Signals

In this chapter we introduce the background necessary to discuss nonlinear optical signals in a diagrammatic, fully quantum mechanical framework. Before providing a rigorous derivation of the nonlinear signals and their perturbative calculation, we first motivate our approach intuitively and discuss why it is best suited for the problem at hand. Afterwards, we define the basic interaction Hamiltonian and the Liouville space notation we adopt in this dissertation. Then we derive general expressions for arbitrary field observables, and an effective Hamiltonian for the creation and annihilation of local phonons in an ion trap. These results will be accompanied by an introduction into the diagrammatic theory of nonlinear optical signals, and a generalization of the relation between transition amplitudes and susceptibilities for the quantum domain. We will see that it is then no longer possible to define susceptibilities without the specification of the initial quantum state of the field, since the quantum treatment of the field takes the back-action of the matter system onto the field into account. Hence, each interaction depends on all other interactions preceding it. Instead, they can be reformulated as quantum field operators. Finally, we briefly review the perturbative approach in a short synopsis.

2.1 Motivation and Overview

Since this chapter presents the rather abstract formalism, we will first take one step back, and briefly point out the different steps in our derivation. We also refer to the sections, in which the underlying rigorous derivations can be found.

Light-matter interaction: In this dissertation, we consider an interaction Hamiltonian in the dipole approximation, which is well justified in the optical regime. We are mostly interested in the interaction with complex quantum systems such as photosynthetic aggregates. The optically active components are easily photodamaged under strong illumination [Kok56], such that spectroscopy of such systems needs to be carried out with the smallest intensity possible to minimize the photodamage. In this regime, it is sufficient to only consider processes in the interaction Hamiltonian, in which an excitation of the sample (denoted by the operator $V^\dagger$) is accompanied by the destruction of a photon from the light field (denoted E), or, vice versa, a matter de-excitation V and a photon creation $E^\dagger$. This Hamiltonian will be introduced in detail in Sect. 2.2.

The signal: Having introduced the interaction Hamiltonian, our first task is to figure out how the electromagnetic field is influenced by this Hamiltonian. In a first naive approach, we could assume, for instance, - as in our previous discussion of the Hamiltonian - that the field creating the signal has to be connected to the de-excitation of the sample system,

$$E_{\text{signal}}^\dagger \sim V. \quad (2.1)$$

Measuring the intensity of this field is then given by

$$\langle E_{\text{signal}}^\dagger E_{\text{signal}} \rangle \sim \langle V V^\dagger \rangle. \quad (2.2)$$

As we will see, this reasoning is essentially correct when the fluorescence from the sample is collected. In case the electric field is initially populated and in the case of more involved measurement setups, a more abstract approach is called for, and it is presented in Sect. 2.3.

The system evolution: Having derived the observables pertaining to a given experimental setup, the final step in our theory consists in the evaluation of the expectation value in Eq.(2.2). A direct approach might consist of the evaluation of expectation values of a (closed) set of operators using the Heisenberg–Langevin formalism [Gardiner85]. This would also allow for the description of saturation effects under strong driving conditions [Lehmberg70, Shatokhin05]. However, we will mostly focus on signals induced by short light pulses, in which the finite bandwidth of the pulses will be important, and where interactions alternate with periods of field-free evolution periods. Taking further into account that we focus on very weak fields with only few photons, a perturbative approach suggests itself for the present study. It will be elaborated in Sect. 2.5, where we also introduce the diagrammatic representation of the perturbative expansions, which may provide intuition for the construction of measurement protocols.

2.2 Light-Matter Hamiltonian and Liouville Space Notation

2.2.1 Light-Matter Interaction

We consider a system described by the total Hamiltonian

$$H_{\text{tot}} = H_{\text{matter}} + H_{\text{field}} + H_{\text{int}}, \quad (2.3)$$

which decomposes into components describing the matter, the electromagnetic field, and the interaction between them. Depending on the sample to be probed, the matter Hamiltonians may exhibit variable structures, so they will be specified later in this dissertation. Most examples however feature a band structure as depicted in Fig. 2.1; an initial ground state g with well-separated excited state manifolds e and f .¹ Neighboring manifolds are coupled by the interaction with the light field.

The starting point of our calculations is the light-matter interaction Hamiltonian in the dipole approximation [Loudon00]. Since this dissertation deals with the interaction of light with sample systems which are typically much smaller than the wavelength of the light beams, we neglect the spatial dependence of both matter and field to write the interaction Hamiltonian as

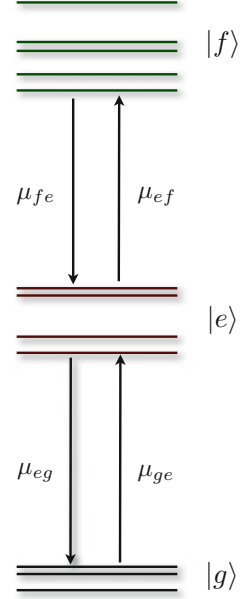
$$H_{\text{int}} = \vec{\epsilon} \vec{\mathcal{V}}, \quad (2.4)$$

where $\vec{\mathcal{V}} = (\vec{V} + \vec{V}^\dagger)$ denotes the dipole operator of the sample. Its two components $\vec{V}$ and $\vec{V}^\dagger$ denote the de-excitation (excitation) part of the dipole operator, respectively. In Fig. 2.1, $\vec{V}$ determines the transitions $f \rightarrow e \rightarrow g$, and $\vec{V}^\dagger$ the inverse direction $g \rightarrow e \rightarrow f$.

Similarly, $\vec{\epsilon} = (\vec{E} + \vec{E}^\dagger)$ denotes the electromagnetic field operator, and $\vec{E}$ and $\vec{E}^\dagger$ the positive-(negative-)frequency component of the field, respectively. The action of $\vec{E}$ destroys a photon in the quantum state, and $\vec{E}^\dagger$ creates one. Depending on the setup under consideration, we may distinguish different fields by their propagation direction or polarization, such that the total electromagnetic field will be given by the sum $\vec{E} = \vec{E}_1 + \vec{E}_2 + \dots$. We adopt the field quantization as presented in Ref. [Blow90] where light propagation along well-defined spatial directions is considered. In this situation, the modes are characterized by the quantization area A_0 perpendicular to the propagation direction, and continuous frequency distributions due to an effectively infinite mode extension along the propagation direction. The positive-frequency component of the field reads in the interaction picture with respect to H_{field} [Loudon00]

¹We only consider signals with up to four interactions with the system. In this regime, it is sufficient to only consider these two manifolds since higher-excited states can only be accessed with higher-order signals, as we will see.

Fig. 2.1 The level scheme in most scenarios considered in the course of this dissertation: three bands of well-separated level manifolds, g , e , and f are connected by the coupling to the electromagnetic field, described by the dipole moments μ_{ij} . The states may be electronic or vibrational levels



$$\vec{E}(t) = i\hat{e}\sqrt{\frac{\pi\hbar\omega}{\epsilon_0 c A_0}} \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} a(\omega') e^{-i\omega' t}, \quad (2.5)$$

where ϵ_0 denotes the dielectric constant, c the vacuum speed of light, and $\hat{e}$ is the polarization unit vector. The photon annihilation operator $a(\omega)$ obeys the usual bosonic commutation relation, $[a(\omega), a^\dagger(\omega')] = \delta(\omega - \omega')$. In writing Eq. (2.5), we have adopted the *slowly-varying envelope approximation*. It assumes that the central frequency ω of the electric field is much larger than the spectral width of the fields, which is usually fulfilled in the optical regime. This has two consequences: First, it allows us to evaluate the mode normalization $\sqrt{\hbar\omega'/4\pi\epsilon_0 c A_0}$ at ω , and take it out of the frequency integral. Hence, by employing this approximation, the field normalization turns into a constant number, which can be neglected in the overwhelming part of this dissertation. Since we only compare perturbative signals with identical numbers of interactions, each signal carries identical field normalization constants, and we will therefore refrain from explicitly mentioning them in the following calculations, since all our signals will be shown normalized. Second, the same reasoning that lead to the constant field normalization in Eq. (2.5) allows to extend the frequency integration over the entire real axis [remember, Eq. (2.5) represents only the positive-frequency component of the electric field]. This approximation yields great practical simplifications in later calculations, since integrations over the entire frequency axis often turn into simple Fourier integrals, which may be evaluated analytically (see, e.g., Appendix A).

Changing to the interaction picture with respect to the matter and the field Hamiltonian, we may employ the rotating wave approximation (RWA) [Loudon00]: The photon annihilation operator $\vec{E}(t)$ oscillates as $e^{-i\omega't}$ [see Eq. (2.5)], and similarly the excitation operator $\vec{V}^\dagger(t)$ oscillates as $e^{i\omega_{ca}t}$, where $\omega_{ca} > 0$ denotes the energy difference between the final state c and the initial state a . Hence, the product $\vec{E}(t)\vec{V}^\dagger(t)$ oscillates only very slowly near the resonance $\omega' = \omega_{ca}$. In contrast, the terms $\vec{E}^\dagger(t)\vec{V}^\dagger(t)$ and $\vec{E}(t)\vec{V}(t)$ always oscillate very rapidly, and their contribution to final signals may therefore be neglected near resonance. Physically, this means we neglect non-energy-conserving terms, where a photon is created (destroyed) and the sample excited (de-excited) at the same time. Within this approximation, we write the scalar version of the interaction Hamiltonian as

$$H_{\text{int}} = E(t)V^\dagger(t) + E^\dagger(t)V(t), \quad (2.6)$$

where $V = \hat{e} \cdot \vec{V}$ and $V^\dagger = \hat{e} \cdot \vec{V}^\dagger$ denote the excitation annihilation and creation operators, respectively.

As mentioned above, in the course of this dissertation, we typically consider level schemes as depicted in Fig. 2.1: three well-separated electronic manifolds denoted g , e and f , which are dipole-coupled to neighboring manifolds. We may then write the exciton annihilation operator (in the Schrödinger picture) as

$$V = \sum_{g,e} \mu_{eg} |g\rangle\langle e| + \sum_{e,f} \mu_{fe} |e\rangle\langle f|, \quad (2.7)$$

and, of course, $V^\dagger$ is given by the Hermitian conjugate of V .

2.2.2 Liouville Space Notation

Consider the space of linear operators $\mathcal{L}$ acting on the matter-field Hilbert space $\mathcal{H}_{\text{tot}}$. By virtue of the Hilbert–Schmidt product, which for two operators A and B is given by [Reed81]

$$\langle\langle A|B \rangle\rangle \equiv \text{tr} \{A^\dagger B\}, \quad (2.8)$$

$\mathcal{L}$ inherits the Hilbert space structure from the original Hilbert space, and operators A acting on $\mathcal{H}_{\text{tot}}$, are vectors $|A\rangle\rangle$ in $\mathcal{L}$. This space is often called the *Liouville space* [Fano64], and operators acting on it are termed *superoperators*.

The density matrix ϱ of the combined matter-field system is an element in $\mathcal{L}$. In the interaction picture with respect to $H_{\text{matter}} + H_{\text{field}}$, its time evolution is given by the von-Neumann equation

$$\frac{d}{dt} \varrho(t) = -\frac{i}{\hbar} [H_{\text{int}}(t), \varrho(t)]. \quad (2.9)$$

Defining the superoperator $H_{\text{int},-}$ by its action on arbitrary operators $X \in \mathcal{L}$,

$$H_{\text{int},-}X \equiv H_{\text{int}}X - XH_{\text{int}}, \quad (2.10)$$

we write the formal solution of Eq. (2.9) as a Dyson series in Liouville space. Hence, we obtain the density matrix

$$\varrho(t) = \mathcal{G}(t, t_0)\varrho(t_0), \quad (2.11)$$

with the Liouville space Green's function

$$\mathcal{G}(t, t_0) = \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int},-} \right], \quad (2.12)$$

and $\mathcal{T}$ the time-ordering operator defined by

$$\mathcal{T}A(t_1)B(t_2) \equiv \Theta(t_1 - t_2)A(t_1)B(t_2) + \Theta(t_2 - t_1)B(t_2)A(t_1), \quad (2.13)$$

where

$$\Theta(t) = \begin{cases} 1 & t \geq 0 \\ 0 & t < 0 \end{cases} \quad (2.14)$$

is the Heaviside function. To contrast the Liouville space Green's function (2.12) from its Hilbert space counterpart, we will denote the latter one by

$$G(t, t_0) = \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int}}(\tau) \right]. \quad (2.15)$$

As initial conditions in (2.9), we always assume factorizing initial conditions, i.e.

$$\varrho(t_0) = \varrho_{\text{matter}}(t_0) \otimes \varrho_{\text{field}}(t_0), \quad (2.16)$$

in the course of this dissertation. While this factorization is not necessary for the validity of our considerations, it greatly simplifies the analysis of optical signals, since nonlinear signals will always factorize into individual field- and matter-correlation functions which may be treated separately. Furthermore, our main interest lies in the interaction of matter with *pulsed light*. Hence, we can safely assume that there is a time t_0 prior to the pulse passage through the sample where fields and matter have not yet interacted. Unless specified differently, we further assume the matter part of the system to be (prepared) in its ground state,

$$\varrho_{\text{matter}}(t_0) = |g\rangle\langle g|, \quad (2.17)$$

which is an excellent approximation for the thermal state of the electronic degrees of freedom in a molecular aggregate.² In case we deal with a manifold of ground states as depicted in Fig. 2.1, however, the initial state may be a thermal mixture of this ground manifold. This case is not considered in the present dissertation.

Similar to our definition of $H_{\text{int},-}$, we may of course associate with each Hilbert space operator A a Liouville space operator by defining its action on elements of $\mathcal{L}$. Specifically, we will also need the anti-commutator superoperator A_+ , which we define by

$$A_+X \equiv \frac{1}{2} (AX + XA), \quad (2.18)$$

and the left-/right-superoperators via

$$A_L \equiv 2A_+ + A_-, \quad (2.19)$$

$$A_R \equiv 2A_+ - A_-. \quad (2.20)$$

2.3 Quantum Optical Field Measurements

This section develops general superoperator expressions for optical signals based on a fully quantum treatment of the fields. We distinguish between two cases: We refer to field measurements whenever the detected field is initially populated (i.e. not in the vacuum), and fluorescence detection otherwise. In both experimental scenarios, our goal consists in the calculation of a time-dependent observable $A(t)$ acting only on the field Hilbert space. Our focus in this section is to determine, how the observable is influenced by the interaction of the detected field(s) with the sample system prior to their detection.

We denote the expectation value with respect to the density matrix at time t , Eq. (2.11), by

$$\langle A(t) \rangle_{\text{final}} \equiv \text{tr}\{A(t)\varrho(t)\}, \quad (2.21)$$

where, we employ this nomenclature to clarify that the field measurement takes place *after* the fields have interacted with the sample system, and the expectation value with respect to the initial state by

$$\langle A(t) \rangle \equiv \text{tr}\{A(t)\varrho(t_0)\}. \quad (2.22)$$

²In photosynthetic complexes, the excited state manifold can only be excited optically, i.e. in a temperature regime similar to the surface of the sun.

Using Eq. (2.11), we can relate the two as

$$\langle A(t) \rangle_{\text{final}} = \left\langle \mathcal{T} A(t) \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int},-} \right] \right\rangle. \quad (2.23)$$

Here, we have exchanged the position of the time-ordering operator $\mathcal{T}$ and the measured quantity $A(t)$, which does not affect the outcome, since - by virtue of definition (2.13) - all the interactions in the exponential are placed to the right of the measured quantity. By expanding the exponential in Eq. (2.23), we will later in Sect. 2.5 obtain perturbative signals in the number of light-matter interactions, which are then evaluated with respect to the *initial* state of the matter-light system. For the sake of simplicity of our notation, we will not distinguish between expectation values of the matter, the field, or the combined system. Due to our choice of factorizing initial conditions (2.16), correlation functions with respect to the initial state factorize into separate field and matter correlation functions. If only operators in one of the two spaces are contained in the correlation function, the trace with respect to the other Hilbert space only yields a factor of one.

For the derivation of the signals, we will work with the interaction Hamiltonian (2.4), and invoke the RWA only at the end of the calculation. We extensively use the following identity, which holds for commuting operators ϵ and $\mathcal{V}$ [Harbola08]

$$H_{\text{int},-}(t) = \epsilon_+(t)\mathcal{V}_-(t) + \epsilon_-(t)\mathcal{V}_+(t), \quad (2.24)$$

where $\epsilon_{\pm}$ and $\mathcal{V}_{\pm}$ are defined by Eqs. (2.10) and (2.18), respectively.³ This identity will be regularly employed in the subsequent derivations.

2.3.1 Field Measurements

Consider an arbitrary time-dependent operator $A(t)$ acting only on the field Hilbert space. In Liouville space notation, its expectation value S is given by

$$S = \langle A_+(t) \rangle_{\text{final}} = \left\langle \mathcal{T} A_+(t) \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int},-}(\tau) \right] \right\rangle \quad (2.25)$$

$$= S_0 - \frac{i}{\hbar} \int_{t_0}^t d\tau \left\langle \mathcal{T} A_+(t) H_{\text{int},-}(\tau) \exp \left[-\frac{i}{\hbar} \int_{t_0}^{\tau} d\tau' H_{\text{int},-}(\tau') \right] \right\rangle, \quad (2.26)$$

where in the second line, we simply wrote out explicitly the final time integration of the Dyson series. S_0 represents the observable's value without any interaction with the matter, and without loss of generality we may set it to zero. Since the observable

³This identity can be verified by straightforward calculation.

A acts only on the field, the only contribution from $H_{\text{int},-}$ is $\epsilon_- \mathcal{V}_+$ (the expectation value of $\mathcal{V}_-$, i.e. of a commutator, vanishes, $\langle \mathcal{V}_- \rangle = \text{tr}\{\mathcal{V}_- \rho\} - \text{tr}\{\rho \mathcal{V}_-\} = 0$). Thus, we obtain

$$S = -\frac{i}{\hbar} \int_{t_0}^t d\tau \left\langle \mathcal{T} A_+(t) \epsilon_-(\tau) \mathcal{V}_+(\tau) \exp \left[-\frac{i}{\hbar} \int_{t_0}^{\tau} d\tau' H_{\text{int},-}(\tau') \right] \right\rangle. \quad (2.27)$$

Furthermore, using the cyclicity of the trace, we can write for any density matrix

$$\text{tr}\{A_+ \epsilon_- \rho\} = \frac{1}{2} \text{tr}\{A \epsilon \rho + \epsilon \rho A - A \rho \epsilon - \rho \epsilon A\} \quad (2.28)$$

$$= \text{tr}\{(A\epsilon - \epsilon A) \rho\} \quad (2.29)$$

$$= \text{tr}\{[A, \epsilon]_+ \rho\} = \text{tr}\{[A, \epsilon]_+ \rho\}. \quad (2.30)$$

Note that $[A, \epsilon]_+$ denotes the “+” superoperator of the operator $[A, \epsilon]$ as defined in Eq. (2.18). Therefore, we obtain the leading-order interaction-induced contribution in the number of matter-field interactions to the observable’s expectation value,

$$S = -\frac{i}{\hbar} \int_{t_0}^t d\tau \langle [A(t), \epsilon(\tau)]_+ \mathcal{V}_+(\tau) \rangle_{\text{final}}. \quad (2.31)$$

Hence, to assess the impact of the interaction with the matter system onto *any* field observable $A(t)$, we only need to evaluate the commutator with the field operator ϵ . In the following, we will carry out this calculation for several prominent examples of $A(t)$, as sketched in Fig. 2.2. First, we discuss transmission measurements, where

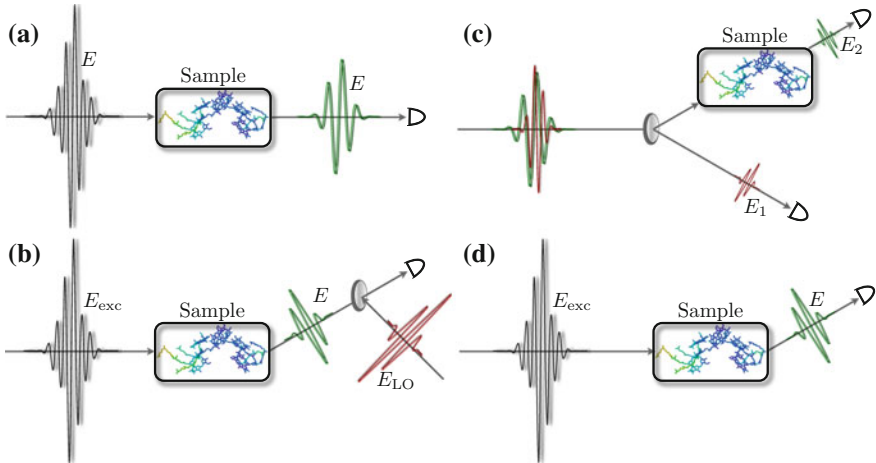


Fig. 2.2 Different measurement setups discussed in this section: **a** Intensity measurement in transmission. **b** Heterodyne detection of the signal field. **c** Two-photon coincidence counting. **d** Fluorescence measurement

the field is either detected directly [panel (a)] or superposed with a local oscillator field before detection. These two signals constitute standard signals in the semiclassical calculation of the nonlinear signals, and we rederive them using our quantum-mechanical approach. Having thus verified the validity of our formalism, we then discuss observables that escape a semiclassical treatment: two-photon counting and fluorescence signals.

Intensity Measurement in Transmission

We first consider the measurement setup depicted in Fig. 2.2a: An optical pulse is transmitted through a sample, and its intensity after the interaction is recorded. The change in intensity is often termed transient absorption, or self-heterodyned detection [Mukamel00]. The intensity at time t is described by the observable $A(t) = a^\dagger(t)a(t)$, where the photon annihilation operator is defined by⁴

$$a(t) = \int \frac{d\omega}{\sqrt{2\pi}} a(\omega) e^{-i\omega t}, \quad (2.32)$$

and we recall the commutation relation $[a(\omega), a^\dagger(\omega')] = \delta(\omega - \omega')$. Thus, we obtain for an explicit evaluation of the commutator in Eq. (2.31) [recall the definition of ϵ through E and $E^\dagger$ on p. 37]

$$\begin{aligned} [A(t), \epsilon(\tau)] &= \sqrt{\frac{\pi \hbar \omega}{\epsilon_0 c A_0}} \int \frac{d\omega}{\sqrt{2\pi}} \int \frac{d\omega'}{\sqrt{2\pi}} \int \frac{d\omega''}{2\pi} e^{i(\omega - \omega')t} \left[a^\dagger(\omega) a(\omega'), ia(\omega'') e^{-i\omega''\tau} + (-i)a^\dagger(\omega'') e^{i\omega''\tau} \right] \\ & \quad (2.33) \end{aligned}$$

$$= \frac{1}{(2\pi)^2} \sqrt{\frac{\pi \hbar \omega}{\epsilon_0 c A_0}} \int d\omega \int d\omega' e^{i(\omega - \omega')t} \left(-ia(\omega') e^{-i\omega'\tau} + (-i)a^\dagger(\omega) e^{-i\omega'\tau} \right) \quad (2.34)$$

Using the decomposition of unity, $\int d\omega \exp[i\omega(t - \tau)] = 2\pi\delta(t - \tau)$, we can write

$$[A(t), \epsilon(\tau)] = (-E(t) + E^\dagger(t)) \delta(t - \tau). \quad (2.35)$$

This yields, in Eq. (2.31),

$$S = -\frac{i}{\hbar} \left\langle \left(-E_+(t) + E_+^\dagger(t) \right) \mathcal{V}_+(t) \right\rangle_{\text{final}}, \quad (2.36)$$

and, neglecting non-RWA terms EV and $E^\dagger V^\dagger$, where a photon is emitted and the sample excited simultaneously (or, vice versa, a photon is absorbed and the sample de-excited), we recover the known result [Rahav10]

⁴Our choice of normalization with $1/\sqrt{2\pi}$ - as well as $1/(2\pi)$ in Eq. (2.5) - may seem unnecessarily complicated. As we will see, it is chosen such that the final expressions of signals do not contain those factors any more.

$$\begin{aligned}
S &= -\frac{i}{\hbar} \left(\langle -E_+(t) V_+^\dagger(t) \rangle_{\text{final}} + \langle E_+^\dagger(t) V_+(t) \rangle_{\text{final}} \right) \\
&= \frac{2}{\hbar} \Im \langle E_+^\dagger(t) V_+(t) \rangle_{\text{final}}.
\end{aligned} \tag{2.37}$$

In many realistic cases, the time resolution of the photodetectors (≥ 100 fs [Gan13]) is much weaker than the time scales of typically employed ultrashort pulses (few fs). The detector then effectively measures the time-integrated signal

$$S' = \frac{2}{\hbar} \int_{-\infty}^{\infty} dt \Im \langle E_+^\dagger(t) V_+(t) \rangle_{\text{final}}, \tag{2.38}$$

as we will employ at the beginning of Chap. 4.

Note that we encounter an apparent ambiguity in the derivation of Eq. (2.37): We could have also picked the signal

$$S' = -\frac{2}{\hbar} \Im \langle E_+(t) V_+^\dagger(t) \rangle_{\text{final}}. \tag{2.39}$$

Both definitions are mathematically equivalent, since $\Im \langle E V^\dagger \rangle = -\Im \langle E^\dagger V \rangle$. However, their physical interpretation in terms of the underlying process in the sample differs: In Eq. (2.37), the last interaction corresponds to a de-excitation, and the creation of a photon which yields the signal, whereas in Eq. (2.39) the final interaction is an absorption of a photon from the detected pulse. So even though it is irrelevant in terms of the simulation of optical signals (one may choose either convention), it is still worthwhile to understand what the underlying physical process really is. The resolution to this apparent contradiction is given in Ref. [Mukamel10b] for classical light fields, and will be presented in Sect. 2.6 for quantum light.

Frequency-Dispersed Intensity Measurement

We still discuss the setup depicted in Fig. 2.2a, but now assume that the field is spectrally dispersed, and then detected. In this case, the observable is given by $A(\omega) = a^\dagger(\omega)a(\omega)$, and the signal, in analogy to Eq. (2.25), by

$$S = \left\langle \mathcal{T} \left(a^\dagger(\omega) a(\omega) \right)_+ \exp \left[-\frac{i}{\hbar} \int_{t_0}^{\infty} d\tau H_{\text{int},-}(\tau) \right] \right\rangle, \tag{2.40}$$

where the unitary evolution is carried out to $t = \infty$, since the detected signal shows no time resolution, and photons emitted at any instant in time may contribute to it. The change of the frequency-dispersed intensity induced by the interaction with the matter is again given by Eq. (2.31). The commutator is calculated just like in our previous calculation, Eq. (2.34), and we obtain

$$[A(\omega), \epsilon(\tau)] = -E(\omega) e^{-i\omega\tau} + E^\dagger(\omega) e^{i\omega\tau}, \tag{2.41}$$

and Eq. (2.31) then reads

$$S = -\frac{i}{\hbar} \int_{t_0}^{\infty} d\tau \langle (-E(\omega)e^{-i\omega\tau} + E^\dagger(\omega)e^{i\omega\tau})_+ \mathcal{V}_+(\tau) \rangle. \quad (2.42)$$

Neglecting non-RWA terms, and sending $t_0 \rightarrow -\infty$, which is justified as long as t_0 clearly precedes the transmitted pulse(s), we arrive at

$$S = \frac{2}{\hbar} \Im \langle E^\dagger(\omega) V(\omega) \rangle_{\text{final}}. \quad (2.43)$$

Here, we have of course the same ambiguity as in the time-resolved signal above. Note also that Eq. (2.43) is not simply the Fourier transform of Eq. (2.37): In the time domain, Eq. (2.43) must be written as

$$S = \frac{2}{\hbar} \Im \int dt_1 \int dt_2 e^{i\omega(t_1-t_2)} \langle E^\dagger(t_1) V(t_2) \rangle_{\text{final}}. \quad (2.44)$$

It contains contributions from two different times t_1 and t_2 , and may therefore not be obtained from Eq. (2.37) which contains only one time. This is one manifestation of the simple fact that time-resolved and frequency-resolved signals do not contain the same information, in general. We will encounter frequency-resolved signals later in Sect. 3.6, as well as in Chaps. 4 and 5.

Heterodyne Detection

In this detection scheme, the signal is created by the interaction with one or several excitation pulses E_{exc} which are not detected (see also the discussion in Sect. 1.2. The signal is superimposed with a local oscillator field, and then detected [see Fig. 2.2b]. If the phase of the local oscillator can be controlled, the state of the signal field may be reconstructed [Lvovsky09]. The precise technique underlying the reconstruction shall not be our concern here, such that we take the observable in this case to be the positive-frequency component of the electric field itself, $A(t) = a(t)$. The evaluation of the commutator in Eq. (2.31) yields

$$[a(t), \epsilon(\tau)] = \sqrt{\frac{\hbar\omega}{2\epsilon_0 c A_0}} \delta(t - \tau). \quad (2.45)$$

The result (2.31) then takes the form

$$S = \frac{2}{\hbar} \sqrt{\frac{\hbar\omega}{2\epsilon_0 c A_0}} \Im \langle V_+(t) \rangle_{\text{final}}. \quad (2.46)$$

Apart from the field normalization, Eq. (2.46) coincides with the semiclassical expression [Mukamel99], where the matter dipole operator is the source of the non-linear polarization, as does the intensity signal we have derived above. We will not discuss heterodyne-detected signals in this dissertation.

Two-Photon Counting

Consider two (possibly correlated) fields E_1 and E_2 . They may be populated by entangled photons created in collinear parametric downconversion, and separated with a beam splitter, as sketched in Fig. 2.2c. We assume that only field E_2 interacts with the matter system [and thus enters solely in the field $\epsilon_{\pm}(t)$ in Eq. (2.6)], and E_1 is detected to exploit its quantum correlations with E_2 . The two-photon counting signal is given by the operator $A(t, t') = a_1^\dagger(t')a_2^\dagger(t)a_2(t)a_1(t')$, and hence, using Eq. (2.35)

$$[A(t, t'), \epsilon_2(\tau)] = a_1^\dagger(t') \left(-E_2(t) + E_2^\dagger(t) \right) a_1(t') \delta(t - \tau). \quad (2.47)$$

Therefore, the signal reads

$$S = \frac{2}{\hbar} \Im \left(\left(a_1^\dagger(t')a_1(t')E_2^\dagger(t) \right)_+ V_+(t) \right)_{\text{final}}. \quad (2.48)$$

Similarly, when the two fields are spectrally dispersed, and then detected, we measure the quantity $A(\omega, \omega') = a_1^\dagger(\omega')a_2^\dagger(\omega)a_2(\omega)a_1(\omega')$, in which case an identical calculation as the one leading to Eq. (2.43) yields

$$S = \frac{2}{\hbar} \Im \left(\left(a_1^\dagger(\omega')a_1(\omega')E^\dagger(\omega) \right)_+ V_+(\omega) \right)_{\text{final}}. \quad (2.49)$$

This signal will be discussed in Chap. 5.

2.3.2 Fluorescence Signals

Fluorescence signals correspond to measuring the intensity of the spontaneously emitted light field, i.e. of the observable $A(t) = a^\dagger(t)a(t)$, just like in transmission measurements, Eq. (2.37). However, the sample is excited by interaction pulses E_{exc} which are not detected, and the signal is created by the spontaneous decay of the molecular excitation into the vacuum [see Fig. 2.2d]. To derive the signal, we do not take the excitation pulses into account, since they are not detected and merely create the molecular excitations. So whereas in Eq. (2.37) we calculated the change in intensity of an initially populated field, our goal is now to calculate the intensity $a^\dagger(t)a(t)$, when the field is initially in the vacuum state $|0\rangle$. The lowest-order, non-vanishing correlation function of the vacuum electric field is given by the anti-normally ordered correlation function $\langle 0|EE^\dagger|0\rangle$, which is created by two interactions with the matter system. So even though Eq. (2.37) is still formally correct, it is misleading, since the linear term vanishes. We need to expand Eq. (2.25) to second order in the interaction Hamiltonian with the vacuum field,

$$S = \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \langle A_+(t) H_{\text{int},-}(\tau_2) H_{\text{int},-}(\tau_1) \rangle_{\text{final}} \quad (2.50)$$

$$= \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \langle [A(t), \epsilon(\tau_2)]_+ \mathcal{V}_+(\tau_2) H_{\text{int},-}(\tau_1) \rangle_{\text{final}} \quad (2.51)$$

$$= \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \langle [A(t), \epsilon(\tau_2)]_+ \mathcal{V}_+(\tau_2) (\epsilon_-(\tau_1) \mathcal{V}_+(\tau_1) + \epsilon_+(\tau_1) \mathcal{V}_-(\tau_1)) \rangle_{\text{final}}. \quad (2.52)$$

To obtain Eq. (2.52), we have used our previous result, Eq. (2.31) in the second line. Here, in contrast to the derivation of Eq. (2.37), both terms $\sim \epsilon_- \mathcal{V}_+$ and $\sim \epsilon_+ \mathcal{V}_-$ in Eq. (2.52) need to be taken into account. However, it turns out that the field correlation function $\langle [A(t), \epsilon(\tau_2)]_+ \epsilon_+(\tau_1) \rangle$ vanishes for the vacuum state: Using the definitions (2.10) and (2.18) as well as the result (2.41), the superoperator expression reads

$$\begin{aligned} & \langle [A(t), \epsilon(\tau_2)]_+ \epsilon_+(\tau_1) \rangle \\ &= \delta(t - \tau_2) \langle 0 | (-E(t) + E^\dagger(t)) (E(\tau_1) + E^\dagger(\tau_1)) \\ &+ (E(\tau_1) + E^\dagger(\tau_1)) (-E(t) + E^\dagger(t)) | 0 \rangle \end{aligned} \quad (2.53)$$

$$= \delta(t - \tau_2) \langle 0 | -E(t)E^\dagger(\tau_1) + E(\tau_1)E^\dagger(t) | 0 \rangle \quad (2.54)$$

Within the slowly-varying envelope approximation [see Eq. (2.5)] employed in this dissertation, the two terms yield identical results,

$$\langle 0 | E(t)E^\dagger(\tau_1) | 0 \rangle = \langle 0 | E(\tau_1)E^\dagger(t) | 0 \rangle = \frac{\hbar\omega}{2\epsilon_0 c A_0} \delta(t - \tau_1), \quad (2.55)$$

such that their difference vanishes. It is important to keep in mind that the simplification between Eqs. (2.53) and (2.54) rests on the fact that the field is in the vacuum state, and normally-ordered correlation functions vanish. In transmission measurements (2.37), additional terms need to be taken into account.

The second field correlation function in Eq. (2.52) evaluates to

$$\begin{aligned} & \langle [A(t), \epsilon(\tau_2)]_+ \epsilon_-(\tau_1) \rangle \\ &= \delta(t - \tau_2) \langle 0 | -E(t)E^\dagger(\tau_1) - E(\tau_1)E^\dagger(t) | 0 \rangle, \end{aligned} \quad (2.56)$$

where the two terms now add up constructively. Hence, the resulting signal reads

$$S = -\left(-\frac{i}{\hbar}\right)^2 \frac{\hbar\omega}{2\epsilon_0 c A_0} \langle \mathcal{V}_+(t) \mathcal{V}_+(t) \rangle_{\text{final}}. \quad (2.57)$$

As discussed following Eq. (2.37), since the photodetectors collecting the fluorescence often possess insufficient time resolution to obtain time-resolved signals, it may be more appropriate to integrate Eq. (2.57) over time,

$$S' = \frac{\omega}{2\hbar\epsilon_0 c A_0} \int dt \langle \mathcal{V}_+(t) \mathcal{V}_+(t) \rangle_{\text{final}}. \quad (2.58)$$

Employing the interaction Hamiltonian (2.6) in the RWA again, we note that the nonvanishing contributions to the field correlation function (2.56) are given by, each, one de-excitation and one excitation operator with the field excitation operator being the rightmost operator, such that the matter de-excitation operator V needs to be the rightmost operator as well (i.e. the corresponding matter operators are given by $V^\dagger(t)V(\tau_1)$ in the first term, and $V^\dagger(\tau_1)V(t)$ in the second term). This reasoning means, we may write the signal as

$$S = \frac{\omega}{2\hbar\epsilon_0 c A_0} \langle V_L(t) V_R^\dagger(t) \rangle_{\text{final}}. \quad (2.59)$$

This result also justifies one further simplification which we will use in Chaps. 3 and 7: Consider the expression for the excitation annihilation operator (2.7), which is valid for the level schemes considered in this dissertation. It is straightforward to verify that in this case, the product $V_L(t) V_R^\dagger(t)$ is given by the sum over projections on the excited state populations at time t , and weighted by the dipole moments of the transitions the excitation may decay with. This approximation will be employed in Sect. 3.6.

2.3.3 Classical Versus Quantum Response Functions

In the preceding section, we have derived optical signals in a fully quantum-mechanical treatment. This approach always involves a contribution of a ϵ_- operator. The physical intuition is clear: In order to create a signal, the sample system first has to emit a photon, and this photon has to be reabsorbed at the detector. In the semiclassical treatment we sketched in Sect. 1.2, the signals are derived by solving Maxwell's equations, in which the matter correlation functions enter as source terms for the polarization $\sim \langle \mathcal{V} \rangle$. This means, the field operators in Eq. (2.6) are replaced by c-numbers, for which commutator terms vanish. In our formalism this amounts to setting $\epsilon_- = 0$. But there are further important effects which are not captured by the semiclassical approach: Neglecting the ϵ_- term in Eq. (2.24), the semiclassical interaction Hamiltonian is simply given by

$$H_{\text{semiclassical}}(t) = \epsilon_+(t) \mathcal{V}_-(t), \quad (2.60)$$

and the matter correlation functions therefore read [Mukamel11]

$$R^{(n)}(t, \dots, \tau_1) \propto \langle \mathcal{V}_+(t) \mathcal{V}_-(\tau_n) \dots \mathcal{V}_-(\tau_1) \rangle, \quad (2.61)$$

which were called *classical response functions* in the above reference.⁵ These functions are however incapable of describing photon-mediated interactions between otherwise noninteracting constituents - say, molecules, of the sample, where one molecule emits a photon, which is then reabsorbed by another molecule. Such processes lead to noticeable effects in the ensemble signal, such as cascading and local field corrections [Bennett14], where two (or, in principle, more) products of lower-order susceptibilities appear like one higher-order susceptibility, satisfying the same phase-matching conditions, but not containing the same information content, as well as dipole forces [Buhmann07] such as Förster resonant energy transfer [Förster48]. Typically, these effects are added phenomenologically, either as additional source terms in the Maxwell equations in the former case, or as effective master equations in the system dynamics in the latter case. The fully quantum mechanical treatment presented here is able to capture all of these effects in one consistent approach.

Except for Chap. 4, Eq. (4.18), however, we will be concerned with signals associated with classical response functions in the remainder of this dissertation, and nonclassicality will enter through the initial quantum state of the light field.

2.4 Effective Interactions in Ion Chains

In the previous section, we have established a framework to describe the impact of the interaction with a material system for general field observables - using only the dipole Hamiltonian (2.4), and properties of the Liouville space superoperators. In principle, these ingredients are sufficient to derive formally correct expressions for arbitrary nonlinear optical signals. However, the description on the basis of the dipole Hamiltonian is often unnecessarily complicated, and - even worse - may cloud the essential physics in the relevant degrees of freedom. Hence, we devote this section to a simplification, which we will use extensively in Chap. 7: the development of effective interactions in ion chains, which will greatly simplify the development of nonlinear signals in these well-controlled systems. The basic idea follows in spirit the development of the theory of quantum computation and simulation with trapped ions: Instead of explicitly treating the full Hamiltonian of an ion chain, which comprises the motional and electronic degrees of freedom as well as their laser-induced coupling, such that even for few ions the Hamiltonian has an enormous dimension, we derive a set of effective interaction operators that suffice to calculate nonlinear signals with manageable overhead.⁶

⁵The left-most operator $\mathcal{V}_+$ stems from the signal, and the other operators $\mathcal{V}_-$ from the expansion of the Dyson series (2.12) with the semiclassical Hamiltonian (2.60).

⁶A notable example of such effective interactions from the literature includes the Mølmer-Sørensen Hamiltonian, which will be discussed in Chap. 7 (see Eq. (7.8)). It describes an interaction that can drive pairs of qubits into entangled states. Even though the interaction is facilitated via laser coupling of the spin states to the motional degrees of freedom, the explicit treatment of the latter is subsumed into the effective Hamiltonian, thus greatly reducing the dimensionality of the problem.

To derive the effective interactions, we consider a single trapped ion. We take into account three electronic states: two long-lived states, which we denote by $|\downarrow\rangle$ and $|\uparrow\rangle$, respectively, as well as a short-lived state $|\chi\rangle$. In the case of $^{40}\text{Ca}^+$, for instance, we identify $|\downarrow\rangle$ with the ground state $S_{1/2}$, and $|\uparrow\rangle$ with the state $D_{3/2}$ or $D_{5/2}$. The decay of both excited states to the ground state is dipole-forbidden by selection rules, such that they show extremely long lifetimes of ~ 1.2 s. The short-lived state $|\chi\rangle$ in this case is provided by $P_{1/2}$, with a lifetime of only 7 ns [Ramm13].

As we will show in the following derivation, due to the short lifetime of $|\chi\rangle$, population in $|\chi\rangle$ can be neglected, and the state can therefore be eliminated from the theoretical description. It will be used implicitly in our theory, for instance in the measurement of the spin population, but will never be treated explicitly. Furthermore, when the ions are cooled close to their motional ground state, the confinement in the trap potential may be approximated by a harmonic potential [Leibfried03]. The frequency ν_x of the ion chain's center-of-mass vibrations is directly controlled by the strength of this external potential.

2.4.1 Phonon Excitation by Stimulated Raman Scattering

We now present two derivations for the effective phonon (de-)excitation operator - one following standard approaches in the trapped ion community, which we call the “quantum-optical derivation”, and one following a standard approach in nonlinear spectroscopy, the “spectroscopic derivation”. Finally, we compare differences and similarities between the two approaches.

Quantum-Optical Derivation

Our first goal consists in the effective description of the controlled creation or annihilation of vibrations in the trap potential. To this end, we imagine a setup as described in Fig. 2.3a. Two laser fields E_1 and E_2 with central frequencies ω_1 and ω_2 couple the vibrational states via an off-resonant Raman transition, which is why we choose $\omega_2 = \omega_1 - \nu_x$ (where ν_x is the trap potential frequency, and hence, the vibrational transition's energy). We neglect the finite bandwidth of the excitation pulses, and instead treat the two fields as plane waves,

$$E_i(t) = E_i e^{i(\vec{k}\vec{x} - i\omega_i t)} + c.c. \quad (2.62)$$

We further introduce the Pauli operators $\sigma_+ = |\chi\rangle\langle\downarrow|$ and $\sigma_- = |\downarrow\rangle\langle\chi|$ to describe the electronic transitions, as well as the phonon creation (annihilation) operators $a^\dagger(a)$. This allows us to write the Hamiltonian (in the interaction picture with respect to the electromagnetic field Hamiltonian) as

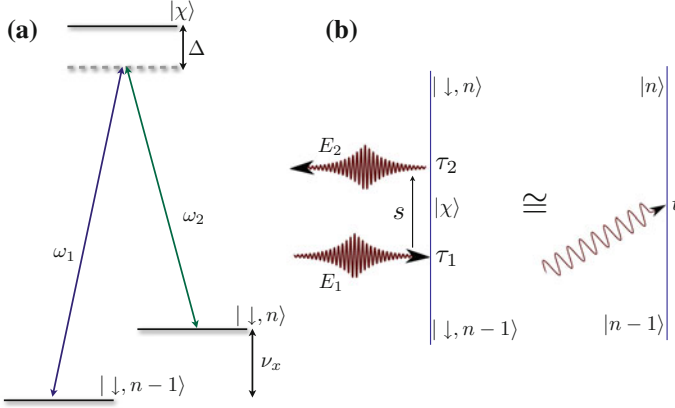


Fig. 2.3 **a** Level scheme for the creation of local phonons via stimulated Raman scattering. **b** Diagrammatic representation of the Raman scattering process. The two-photon process may be described by the effective interaction, Eq. (2.101), which will be described by a *single wavy line*

$$\begin{aligned}
 H_{\text{int}}(t) = & \hbar\omega_e\sigma_+\sigma_- + \hbar\nu_x a^\dagger a \\
 & + \sigma_+ \left(\hbar\Omega_1 e^{i(\vec{k}_1\vec{r}-\omega_1 t+\phi_1)} + \hbar\Omega_2 e^{i(\vec{k}_2\vec{r}-\omega_2 t+\phi_2)} \right) \\
 & + \sigma_- \left(\hbar\Omega_1 e^{-i(\vec{k}_1\vec{r}-\omega_1 t+\phi_1)} + \hbar\Omega_2 e^{-i(\vec{k}_2\vec{r}-\omega_2 t+\phi_2)} \right), \quad (2.63)
 \end{aligned}$$

where ω_e denotes the transition frequency between $|\chi\rangle$ and $|\downarrow\rangle$. In the spirit of the conventional (nonperturbative) formalism, we further introduced the Rabi frequencies $\Omega_j \equiv \mu E_j / \hbar$ pertaining to the coupling between the field j and the electronic transition. In contrast to our “spectroscopic” derivation, which we will present later, the transition dipole μ is not dressed with the vibrational eigenstates. Instead, the spatial dependence of the interaction Hamiltonian - and hence, its coupling to the motional degrees of freedom - is accounted for by the exponential $\exp(i\vec{k}_j\vec{r})$, where $\vec{r}$ denotes the position of the ion. Assuming that the light fields are polarized such that they only couple to the axial vibration we wish to excite, we may write the exponential as [Leibfried03]

$$e^{i\vec{k}_j\vec{r}} = e^{i\eta_j(a+a^\dagger)}, \quad (2.64)$$

where $\eta_j = k\sqrt{\hbar/2m\nu_x}$ is the Lamb–Dicke parameter [Dicke53], and m the mass of the ion [Leibfried03]. In the present case, we only consider the Lamb–Dicke limit $\eta_j(2\langle a^\dagger a \rangle + 1) \ll 1$ of low phonon numbers and weak recoil from the interaction with the laser fields, in which case we may approximate the exponential (2.64) by its linear contribution

$$e^{i\eta_j(a+a^\dagger)} \approx 1 + i\eta_j(a + a^\dagger), \quad (2.65)$$

i.e., one can restrict the theoretical treatment to the excitation or annihilation of individual phonons.

The Hamiltonian (2.63) describes the dipole interaction between the ion and the two laser fields, which are both detuned by $\Delta = \omega_e - \omega_1$ from the electronic transition ω_e , and we further restrict our attention to the strongly detuned case where $\Delta \gg \nu_x$. To obtain an effective Hamiltonian for the excitation and destruction of phonons, we proceed in two steps: First, we transform into a rotating frame in order to identify rapidly oscillating terms. Second, we employ the Magnus expansion to obtain multiphoton processes, which do not oscillate as rapidly, and therefore yield the dominant contribution to the full evolution

$$U_{\text{field}}(t) = \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_0^t d\tau H_{\text{int}}(\tau) \right]. \quad (2.66)$$

A similar derivation can be found in Ref. [Roos08]. Our goal in this derivation is to replace the time-ordered integrations in Eq. (2.66) by an effective interaction,

$$U_{\text{field}}(t) \simeq \exp \left[-\frac{i}{\hbar} V_{\text{phonon}} t \right]. \quad (2.67)$$

Step 1: We change to the interaction picture with respect to the ion Hamiltonian described by the transformation

$$U_0(t) = e^{-i(\omega_e \sigma_+ \sigma_- + \nu_x a^\dagger a)t}, \quad (2.68)$$

such that we obtain

$$H'(t) = U_0^\dagger(t) H_{\text{int}}(t) U_0(t) - \hbar \omega_e \sigma_+ \sigma_- - \hbar \nu_x a^\dagger a \quad (2.69)$$

$$= \sigma_+ \left(\frac{\hbar \Omega_1}{2} e^{-i\Delta t} e^{i(\eta_1(ae^{-i\nu_x t} + a^\dagger e^{i\nu_x t}) + \phi_1)} + \frac{\hbar \Omega_2}{2} e^{-i(\Delta - \nu_x)t} e^{i(\eta_2(ae^{-i\nu_x t} + a^\dagger e^{i\nu_x t}) + \phi_2)} \right) + H.c. \quad (2.70)$$

Here, we have used the fact that $\omega_2 = \omega_1 - \nu_x$, which is why the second term oscillates with the frequency $\Delta - \nu_x$ (compared to the frequency Δ in the first term).

Step 2: As mentioned before, we assume that the two laser fields are far detuned from the electronic transition, i.e. $\Delta \gg \nu_x$. Hence, clearly all the terms in Eq. (2.70) oscillate very rapidly, and only products of two interactions can contribute significantly to Eq. (2.66). This hand-waving argument is made precise by the *Magnus* series [Magnus54], which replaces the time-ordered exponential in Eq. (2.66) by the exponential of a series expansion,

$$\mathcal{T} \exp \left[-\frac{i}{\hbar} \int_0^t d\tau H'(\tau) \right] = \exp \left[\sum_{n=1}^{\infty} F_n(t) \right], \quad (2.71)$$

which may be terminated after some finite N in most practical applications. The first two terms are given by [Mukamel99]

$$F_1(t) = -\frac{i}{\hbar} \int_0^t d\tau_1 H'(\tau_1), \quad (2.72)$$

and

$$F_2(t) = \frac{1}{2} \left(-\frac{i}{\hbar} \right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 [H'(\tau_2), H'(\tau_1)]. \quad (2.73)$$

The integrand of Eq. (2.72) oscillates rapidly between the initial time 0 and the final time t . As we will see, Eq. (2.73) on the other hand contains terms, which only oscillate rapidly between the first and the second interaction [see also Fig. 2.3b], thus yielding the dominant contribution to the Magnus series. The evaluation of Eq. (2.73) will result in the effective interaction operator we wish to obtain. Before evaluating the commutator, we carry out the time integrals first. Inserting Eq. (2.70) in Eq. (2.73), we note that it is sufficient to evaluate integrals of the form

$$h_{k,l}(t) = \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 e^{-i\Delta(\tau_2-\tau_1)} e^{ik\nu_x\tau_2} e^{-il\nu_x\tau_1}, \quad (2.74)$$

where the terms $\exp(ik\nu_x\tau_2)$ and $\exp(-il\nu_x\tau_1)$, $k, l = \pm 1$, stem from the expansion of the exponentials $\exp(i\eta(ae^{-i\nu_x\tau} + a^\dagger e^{i\nu_x\tau}))$ in Eq. (2.70), and $\exp(-i\Delta(\tau_2 - \tau_1))$ from the two involved electronic transitions. To disentangle the two time integrations, we change to the variable $s = \tau_2 - \tau_1$, and obtain

$$h_{k,l}(t) = \int_0^t d\tau_2 e^{-i(\Delta-l\nu_x)s} \int_0^t ds e^{i(k-l)\nu_x\tau_2}. \quad (2.75)$$

The τ_2 -integration yields

$$\int_0^t d\tau_2 e^{-i(\Delta-l\nu_x)s} = \frac{e^{-i(\Delta-l\nu_x)t} - 1}{-i(\Delta-l\nu_x)} \approx \frac{-i}{\Delta}, \quad (2.76)$$

where we assumed again that the laser fields are far off-resonant, hence $\Delta \gg |l\nu_x|$. Furthermore, we neglected the rapidly oscillating term $\exp(-i\Delta t)$. The same reasoning applies to the s -integration, which creates a rapidly oscillating signal $\sim \exp(i(k-l)\nu_x t)$ - unless $k = l$, in which case the result simply reads $\int_0^t d\tau_2 = t$. We only retain this dominant contribution, and therefore arrive at approximate time dependence

$$h_{k,l}(t) \approx \frac{1}{\Delta} [-i\delta_{k,l}t + \mathcal{O}(1/\nu_x)]. \quad (2.77)$$

This linear time dependence of $F_2(t)$ shows that the resulting operator may be interpreted as the action of an effective Hamiltonian, i.e.

$$F_2(t) \approx -iV_{\text{eff}}t/\hbar, \quad (2.78)$$

as discussed in Eq. (2.67).

The evaluation of the commutator terms in Eq. (2.73) is now straightforward: Inserting the Hamiltonian (2.70) in Eq. (2.73), we obtain four different terms,

$$F_2(t) = F_2^{(1,1)}(t) + F_2^{(2,2)}(t) + F_2^{(1,2)}(t) + F_2^{(2,1)}(t) \quad (2.79)$$

Here, the brackets indicate the light fields involved, i.e. $F^{(2,2)}$ corresponds to two interaction with field E_2 etc. Two of these correspond to two interactions of the ion with either of the light fields 1 and 2, $F_2^{(1,1)}(t) + F_2^{(2,2)}(t)$, and are independent of the laser phases ϕ_1 and ϕ_2 , and - as we shall see - are responsible for elastic light scattering, thereby only creating an additional phase shift in the ion. The remaining two terms $F_2^{(1,2)}(t) + F_2^{(2,1)}(t)$ depend on the phase difference $\pm(\phi_1 - \phi_2)$, and create or destroy phonons in the system. The first phase-independent term in the Lamb–Dicke limit (2.65) is given by

$$F_2^{(1,1)}(t) = \frac{1}{2} \left(-\frac{i}{\hbar} \right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 e^{-i\Delta(\tau_2 - \tau_1)} \\ \times \left[\sigma_+ \left(1 + i\eta_1 (ae^{-i\nu_x\tau_2} + a^\dagger e^{i\nu_x\tau_2}) \right), \sigma_- \left(1 - i\eta_1 (ae^{-i\nu_x\tau_1} + a^\dagger e^{i\nu_x\tau_1}) \right) \right] + H.c., \quad (2.80)$$

which yields in total eighteen different terms. According to Eq. (2.77), only those terms dominate in the final propagator, in which the frequency in the left argument of the commutator (2.67), $k\nu_x$, and in the right argument, $-l\nu_x$, cancel one another. Hence, we obtain

$$F_2^{(1,1)}(t) = \frac{1}{2} \left(-\frac{i}{\hbar} \frac{\hbar\Omega_1}{2} \right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 e^{-i\Delta(\tau_2 - \tau_1)} \\ \times \left([\sigma_+, \sigma_-] + \eta_1^2 [\sigma_+ a, \sigma_- a^\dagger] e^{-i\nu_x(\tau_2 - \tau_1)} + \eta_1^2 [\sigma_+ a^\dagger, \sigma_- a] e^{i\nu_x(\tau_2 - \tau_1)} \right) + H.c. \quad (2.81)$$

$$= \left(-\frac{i\Omega_1}{2} \right)^2 \frac{-it}{\Delta} 2\sigma_z \left(1 + \eta_1^2 (2a^\dagger a + 1) \right) - H.c. \quad (2.82)$$

$$= i \frac{\Omega_1^2 t}{2\Delta} \sigma_z \left(1 + \eta_1^2 (2a^\dagger a + 1) \right) \simeq i \frac{\Omega_1^2 t}{2\Delta} \sigma_z, \quad (2.83)$$

where we neglected corrections to the Lamb–Dicke limit (2.65) in the final step. The factor Ω_1^2/Δ describes the effective two-photon coupling strength of the ion to the laser field. It only couples via σ_z to the ion, thus causing the optical Stark effect

[Cohen-Tannoudji92]. Apparently, Eq. (2.83) does not change the phononic (nor the electronic) population, but merely adds a population-dependent phase. Similarly, we obtain for the interaction with field 2,

$$F_2^{(2,2)}(t) = i \frac{\Omega_2^2 t}{2\Delta} \sigma_z (1 + \eta_1^2 (2a^\dagger a + 1)) \simeq i \frac{\Omega_2^2 t}{2\Delta} \sigma_z. \quad (2.84)$$

While these contributions may be used to, e.g., induce electronic dephasing artificially [Gessner14b], they are not of interest for our present purpose. Instead, we are mostly interested in the phase-dependent terms, such as

$$\begin{aligned} F_2^{(1,2)}(t) = & \frac{1}{2} \left(-\frac{i}{\hbar} \right)^2 \frac{\hbar\Omega_1}{2} \frac{\hbar\Omega_2}{2} \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 e^{-i\Delta(\tau_2-\tau_1)} e^{i(\phi_1-\phi_2)} \\ & \times e^{-i\nu_x\tau_1} \left[\sigma_+ \left(1 + i\eta_1 (ae^{-i\nu_x\tau_2} + a^\dagger e^{i\nu_x\tau_2}) \right), \sigma_- \left(1 - i\eta_2 (ae^{-i\nu_x\tau_1} + a^\dagger e^{i\nu_x\tau_1}) \right) \right] \\ & + H.c. \end{aligned} \quad (2.85)$$

The only relevant difference (apart from the different Lamb–Dicke parameter η_2 and Rabi frequency Ω_2) with respect to Eq. (2.80) consists in the additional factor $\exp(-i\nu_x\tau_1)$ in the second line of Eq. (2.85), which stems from the frequency difference between the two laser fields E_1 and E_2 [see Eq. (2.70)]. This factor changes the dominant contributions to $F^{1,2}(t)$. Using Eq. (2.77), we again only retain those commutator terms satisfying $k = l$,

$$\begin{aligned} F_2^{(1,2)}(t) = & -\frac{\Omega_1\Omega_2}{8} \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 e^{-i\Delta(\tau_2-\tau_1)} e^{i(\phi_1-\phi_2)} \\ & \times ([\sigma_+, -i\eta_2\sigma_-a^\dagger] + [i\eta_1\sigma_+a^\dagger, \sigma_-] e^{i\nu_x(\tau_2-\tau_1)}) + H.c. \end{aligned} \quad (2.86)$$

$$= \frac{\Omega_1\Omega_2(\eta_1 - \eta_2)t}{4\Delta} \sigma_z (ae^{-i(\phi_1-\phi_2)} - a^\dagger e^{i(\phi_1-\phi_2)}). \quad (2.87)$$

We obtain the same result for $F_2^{(2,1)}(t)$, such that the full effective phononic interaction reads

$$F_2^{(1,2)}(t) + F_2^{(2,1)}(t) = -\frac{i}{\hbar} \left(i \frac{\hbar\Omega_1\Omega_2(\eta_1 - \eta_2)t}{2\Delta} \sigma_z (ae^{-i\phi} - a^\dagger e^{i\phi}) \right) t, \quad (2.88)$$

where

$$\phi = \phi_1 - \phi_2. \quad (2.89)$$

Since we never populate the upper state $|\chi\rangle$, we can eliminate this state from the explicit treatment, and remove the electronic operator σ_z from the result. With regard to our initial goal (2.67), we arrive at

$$V_{\text{phonon}} = i \frac{\hbar \Omega_1 \Omega_2 (\eta_1 - \eta_2)}{2\Delta} (a e^{-i\phi} - a^\dagger e^{i\phi}). \quad (2.90)$$

Our present approach yields the maximal effective interaction when $\eta_1 = -\eta_2$, i.e. when the two fields are counter-propagating. This is in agreement with similar calculations for the excitation of electronic states in trapped ions using Raman coupling [Wineland98]. Note that due to the imaginary factor i in Eq. (2.90), the phonon annihilation operator enters with opposite sign (remember, the phonon annihilation is the Hermitian conjugated process of the phonon creation). This relative sign is a direct consequence of the two-photon nature of the phonon excitation/annihilation process. As we will describe in greater detail in Chap. 7, this structure will determine the relative signs of different Feynman diagrams in nonlinear measurement protocols.

“Spectroscopic” Derivation

In our second derivation, we provide an alternative path to obtain (2.67), which follows similar calculations in chemical physics [Mukamel09]. We take the finite bandwidth of the two laser fields into account, which creates an explicit time dependence of the effective interaction, as we will discuss in the following. The light-ion interaction Hamiltonians then read in the interaction picture with respect to the free evolution of matter and field,

$$H_{\text{int},i}(t) = E_i(t) \sum_n \mu_n |\chi\rangle \langle \downarrow, n | e^{i\omega_{\chi n} t} + h.c. \quad i \in 1, 2, \quad (2.91)$$

where μ_n denotes the dipole matrix element coupling the n -th vibrational state with the short-lived state $|\chi\rangle$, and $\omega_{\chi n}$ the energy difference between the states $|\chi\rangle$ and $|\downarrow, n\rangle$. We reiterate that here, in contrast to Eq. (2.62), the fields $E_i(t)$ are *not* plane waves, but finite-bandwidth pulses. The Raman transition amplitude may be obtained by a perturbative expansion in the interaction Hamiltonian to second order, where the wavefunction first interacts with E_1 , and then with E_2 ,

$$\begin{aligned} |\psi_{\text{final}}(t)\rangle &= \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 H_{\text{int},2}(\tau_2) H_{\text{int},1}(\tau_1) |\downarrow, n-1\rangle + \dots \\ &= \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 E_2^*(\tau_2) E_1(\tau_1) \mu_{n-1} \mu_n e^{-i\omega_{\chi n} \tau_2} e^{i\omega_{\chi n-1} \tau_1} |\downarrow, n\rangle + \dots \end{aligned} \quad (2.92)$$

Here, the dots represent other second-order processes such as elastic scattering, which we describe by two interactions with the same field, i.e. $\sim \mu_n^2 E_i^*(\tau_2) E_i(\tau_1)$, which were treated in our previous derivation in Eqs. (2.83) and (2.84), and whose derivation we will not repeat. The other relevant term is the phonon annihilation, which is simply the inverse process of Eq. (2.92), in which the system ends in the state $|\downarrow, n-2\rangle$. Our process of interest is represented diagrammatically in Fig. 2.3b: In this representation, the evolution of the wavefunction is represented by the vertical line, where time runs from bottom to top, and excitations (de-excitations) are depicted by arrows pointing towards (away from) the solid line, respectively. To evaluate the

nested time integrations in the above expression, we first write the fields in their frequency decomposition,

$$E_i(t) = \int \frac{d\omega}{2\pi} A_i(\omega) e^{-i\omega(t-t_i^{(0)})-i\phi_i}, \quad (2.93)$$

where we introduce the central time of the pulse $t_i^{(0)}$, and an additional phase ϕ_i . We further introduced the pulse amplitude $A_1(\omega)$. Furthermore, we will denote the pulse's center frequency ω_i . Both control parameters will be used in Chap. 7 to design measurement protocols.

To simplify Eq. (2.92), we may extend the integration over the interaction time $\tau_2 \rightarrow \infty$, since the next interactions will be well separated from the interaction with these two fields [Mukamel09]. The field envelope will drop to zero after the fields have interacted with the system, such that the integration to ∞ yields the same result. Furthermore, sending the initial time $t_0 \rightarrow -\infty$ using the same argument, together with the substitution to the integration variable $s = \tau_2 - \tau_1$, we obtain

$$\begin{aligned} |\psi_{\text{final}}\rangle &= \left(-\frac{i}{\hbar}\right)^2 \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} \mu_{n-1} \mu_n A_1(\omega) A_2^*(\omega') e^{i(\phi_2 - \phi_1)} \\ &\quad \times 2\pi \delta(\omega - \omega' - \nu_x) \frac{ie^{i(\omega - \omega')t_1^{(0)}}}{\omega - \omega_{\chi_{n-1}} + i\eta} |\downarrow, n\rangle + \dots \end{aligned} \quad (2.94)$$

$$\begin{aligned} &= \left(-\frac{i}{\hbar}\right)^2 \int \frac{d\omega}{2\pi} \mu_{n-1} \mu_n A_1(\omega) A_2^*(\omega - \nu_x) e^{i(\phi_2 - \phi_1)} \\ &\quad \times \frac{ie^{i\nu_x t_1^{(0)}}}{\omega - \omega_{\chi_{n-1}} + i\eta} |\downarrow, n\rangle + \dots \end{aligned} \quad (2.95)$$

where we introduced the infinitesimal imaginary factor $i\eta$. Since we sent the final time $t \rightarrow \infty$, the final state no longer explicitly depends on time. Without this approximation, the second time integration may not be carried out explicitly, and the “exact” time dependence is contained in this τ_2 -integration. To maximize the Raman amplitude, we choose the central time of the two pulses to coincide, i.e. $t_2^{(0)} = t_1^{(0)}$. We further used that $\omega_{\chi, n} = \omega_{\chi, n-1} - \nu_x$ (see Fig. 2.3) to combine the exponentials $\exp(-i\omega_{\chi_n}\tau_2)$ and $\exp(i\omega_{\chi_{n-1}}\tau_1)$ in Eq. (2.92).

To further simplify Eq. (2.95), we note that the detuning $\Delta = |\omega_1 - \omega_{\chi_{n-1}}|$ is much larger than the bandwidth of both E_1 and E_2 . Hence, the integrand in Eq. (2.95) is non-zero only on the tails of the Lorentzian $1/(\omega - \omega_{\chi_{n-1}} + i\eta)$. This allows us to replace it by the detuning Δ , and take it out of the integration,

$$|\psi_{\text{final}}\rangle = -i \frac{\mu_n \mu_{n-1}}{\hbar^2 \Delta} e^{i(\phi_2 - \phi_1) + i\nu_x t_1^{(0)}} \delta(t - t_1^{(0)}) \int \frac{d\omega}{2\pi} A_1(\omega) A_2^*(\omega - \nu_x) |\downarrow, n\rangle + \dots \quad (2.96)$$

Hence, we have derived the transition amplitude, which connects the initial state $|\downarrow, n-1\rangle$ with the state $|\downarrow, n\rangle$ due to the interaction with the two pulse amplitudes

A_1 and A_2 . In contrast to our previous derivation, the two fields are accounted for via their spectral overlap, $\int d\omega A_1(\omega)A_2^*(\omega - \nu_x)$, which clearly has maximal strength when the central frequencies of the two fields satisfy $\omega_1 = \omega_2 + \nu_x$. Furthermore, the transition amplitude carries the phase $\phi \equiv \phi_2 - \phi_1$, which may be controlled experimentally, and which we will use in Chap. 7 for pathway selection in nonlinear measurements. Since we are only interested in the phononic dynamics, we now combine the quantities referring to the electronic degrees of freedom in a prefactor $\tilde{\kappa}$, which only depends very weakly on the vibrational state of the system. This allows us to write the transition amplitude in Eq. (2.96) (which, in molecular spectroscopy would be called a *polarizability* [Mukamel09]) as

$$\alpha_{n,n-1}(t) = i\tilde{\kappa}e^{i\phi}\delta(t - t_1^{(0)})|\downarrow, n\rangle\langle\downarrow, n-1| \quad (2.97)$$

We can now write $|\downarrow, n\rangle\langle\downarrow, n-1| = a^\dagger|\downarrow, n-1\rangle\langle\downarrow, n-1|/\sqrt{n}$, and obtain

$$\alpha_{n,n-1}(t) = i\frac{\tilde{\kappa}}{\sqrt{n}}e^{i\phi}\delta(t - t_1^{(0)})a^\dagger|\downarrow, n-1\rangle\langle\downarrow, n-1| \quad (2.98)$$

Combining this quantity for all vibrational states n , we notice that in the presented limit (off-resonant single-photon transitions, fast pulses compared to the vibrational dynamics), the combination of the two fields effectively creates the operator $\sim \sum_n \kappa_n a^\dagger|\downarrow, n-1\rangle\langle\downarrow, n-1|$, where κ_n depends only weakly on the phonon number n , i.e. $\kappa_n \approx \kappa$: The only n -dependent terms are - apart from the factor $1/\sqrt{n}$ - the dipole moments μ_n and μ_{n-1} . These were defined without reference to the vibrational state to which they couple, which is clearly a weakness of the present derivation. We can however estimate their dependence on n by invoking the Franck-Condon factor [May04]. It relates transition dipole moments between electronic states with different phononic quantum number to the spatial overlap to the overlap of the two involved vibrational states - which are both determined by the same external trap potential in the present case. It is easy to see that the maximal contribution to Eq. (2.98) stems from the coupling to excited states with either n or $n-1$ phonons, which implies that $\mu_n\mu_{n-1} \sim \sqrt{n}$: Since, for instance, the transition $|\downarrow, n-1\rangle \rightarrow |\chi, n-1\rangle$, which is quantified by the dipole moment

$$\mu_{n-1} \propto \langle\downarrow, n-1|\sigma_+|\chi, n-1\rangle = \mu \propto \langle\downarrow|\sigma_+|\chi\rangle\langle n-1|n-1\rangle, \quad (2.99)$$

is independent of n , the subsequent de-excitation process $|\chi, n\rangle \rightarrow |\downarrow, n\rangle$ is described by

$$\mu_n \propto \langle\chi, n-1|\sigma^-a|\downarrow, n\rangle = \langle\chi|\sigma^-|\downarrow\rangle\langle n-1|a|n\rangle \sim \sqrt{n}, \quad (2.100)$$

which is thus proportional to $\sqrt{n}$. Taken together, this factor cancels the contribution from the factor $1/\sqrt{n}$ in Eq. (2.98), and $\tilde{\kappa}$ is indeed independent of n .

Since we assumed the two pulses to interact with the sample simultaneously, we also need to consider the inverse process, where a phonon is destroyed. It is given by the Hermitian conjugate process of Eq. (2.97), such that we obtain the effective interaction operator

$$\tilde{V}_{\text{Phonon}}(t) = \kappa (a^\dagger e^{i\phi} - a e^{-i\phi}) \delta(t - t_1^{(0)}), \quad (2.101)$$

where $\kappa = i\tilde{\kappa}/\sqrt{n}$, a denotes the phonon annihilation operator, and we recall the phase ϕ is defined in Eq. (2.89).

Our above derivation of the excitation of phonons was carried out for an individual trapped ion. As we will see in Chap. 7, when several ions are trapped in a linear chain, their individual vibrational modes are coupled [see, e.g., Eq. (7.1)], i.e. local vibrations are not eigenstates of the chain's Hamiltonian. In order to nevertheless excite localized wavepackets, and monitor their spreading over the chain, it is necessary to excite faster than the excitation spreads over the chain. Spectrally, this implies that the laser fields need to have sufficient bandwidth to access all delocalized vibrational eigenstates of the entire chain, whose superposition creates a localized wavepacket.

Note that there exist other methods to excite phonons in ion chains. They include strong resonant pulses [Harlander11, Brown11, Haze12, Toyoda13], or trains of pulses [Mizrahi13], which directly excite vibrations in the ion chain due to the momentum transfer during the light scattering. Again, if the pulse durations are short compared to the tunnel rates between the ions, these methods may induce the same instantaneous excitation or destruction of phonons as the Raman process described here.

Comparison

We have presented two possible derivations of the effective interaction operator for the creation or destruction of phonons: One derivation closely followed similar approaches in the trapped ion community, and by neglecting the pulse bandwidths resulted in Eq. (2.90). The other derivation explicitly takes the finite bandwidths into account, and by following similar derivations in chemical physics [Mukamel09], we obtained Eq. (2.101). Both approaches yielded the same functional dependence on the phonon operators.

The first derivation offers some clear advantages: By explicit evaluation of the propagator (2.66), we obtain the effective Hamiltonian (2.90), whose validity is only limited by the Lamb–Dicke limit (2.65). This allows, for instance, for the definition of a displacement operator, in case one is interested in the study of macroscopic superposition states [Monroe96]. By taking additional orders on the expansion of the exponential in Eq. (2.65) into account, it is, in principle, possible to obtain results beyond the Lamb–Dicke limit. Furthermore, the explicit treatment of the spatial dependence of the light-ion interaction enabled us to obtain the explicit dependence of the Raman process on the beam geometry: The factor $\eta_1 - \eta_2$ in Eq. (2.90) clarifies that it is most efficient to excite vibrations in a non-collinear geometry (when the recoil of the first interaction can be counteracted by the interaction with the other beam), which maximizes the difference between the two factors. This cannot be seen

from the “spectroscopic derivation”, where the information is hidden in the dipole moments, which would have to be obtained separately.

On the other hand, in our use of the effective interaction in Chap. 7, we investigate the creation of local phonons in an ion chain. Due to the Coulomb interaction between the ions, local phonons are not eigenstates of the full system. Hence, a finite bandwidth is essential to excite them, and in this sense the “spectroscopic derivation” can be employed to calculate the influence of a given pulse bandwidth on the phonon excitation, by virtue of the spectral overlap in Eq. (2.96), and an evaluation of the Franck–Condon factor in Eqs. (2.99) and (2.100) could be employed to obtain the precise coupling constants. This demonstrates that - in situations, where the finite bandwidth is relevant (as will be the case in most of this dissertation) - a perturbative approach comprises the only viable option.

2.4.2 Electronic Transitions

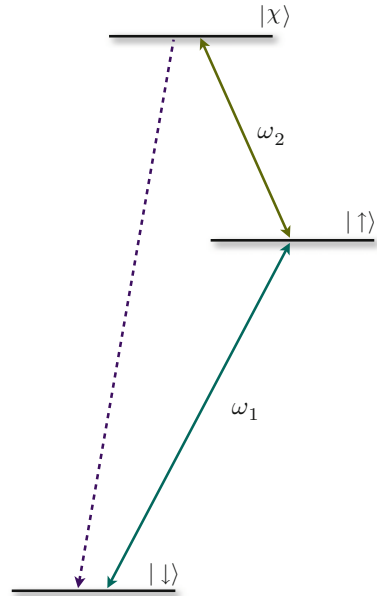
Apart from the vibrations, we will also consider nonlinear spectroscopy of the electronic degrees of freedom of the trapped ions. Using narrowband laser pulses, it is possible to selectively couple only two or three electronic states. In this situation, it is possible to restrict the necessary theoretical treatment to these two or three states. The resulting level scheme we will consider is depicted in Fig. 2.4. The long-lived electronic states $|\uparrow\rangle$ and $|\downarrow\rangle$ may be directly coupled using narrow-band lasers [Leibfried03], where, as before, the laser phase may be controlled to extract signals. By coupling $|\uparrow\rangle$ to a short-lived state $|\chi\rangle$, and collecting fluorescence from the $|\chi\rangle \rightarrow |\downarrow\rangle$ transition, the electronic populations may be assessed: As described at the end of Sect. 2.3.2 in the derivation of fluorescence signals, this measurement is proportional to the population in the upper state, such that the populations in both states may be identified with close to unit efficiency [Leibfried03] (i.e. ion bright $\rightarrow |\uparrow\rangle$, ion dark $\rightarrow |\downarrow\rangle$). This measurement is then described by the observable σ_z .⁷ By driving the electronic transition between $|\downarrow\rangle$ and $|\uparrow\rangle$ for the time $t^* = \pi/2\Omega$, where Ω denotes the Rabi frequency of the process, we can generate the effective interaction

$$V_{\text{el}} = \frac{1}{\sqrt{2}} (\sigma^+ e^{i\phi} - \sigma^- e^{-i\phi}), \quad (2.102)$$

where $\sigma_- = |\downarrow\rangle\langle\uparrow|$ and $\sigma_+ = |\uparrow\rangle\langle\downarrow|$ denote the transition operators between the two states. We assume that the Rabi frequency is much faster than the induced dynamics, such that we may again - just like in our derivation of the phononic interaction (2.90) - take the excitation (2.102) to be instantaneous, i.e. that the excitation

⁷Note that more elaborate measurement schemes allow for the measurement of electronic coherence as well, see e.g. [Häffner08].

Fig. 2.4 Level scheme of the relevant electronic states: The two long-lived states $|\downarrow\rangle$ and $|\uparrow\rangle$ are coupled by a narrow-band laser with frequency ω_1 . To measure the electronic state populations, population in $|\uparrow\rangle$ is pumped to the short-lived state $|\chi\rangle$, and fluorescence from $|\chi\rangle$ to $|\downarrow\rangle$ is collected



takes place at a well-defined moment during the system's evolution. In contrast to Eq. (2.90), however, the present interaction need not be weak.

2.5 Diagram Construction

We now turn to the final step of our approach sketched in Sect. 2.1: the evaluation of optical signals. We give a concise introduction to the diagrammatic representation of nonlinear signals, and also touch upon the interpretation of individual diagrams. To facilitate an intuitive understanding, all the diagrams are derived exemplarily at hand of the absorption detection, Eq. (2.37), or of fluorescence signals, Eq. (2.57). As we shall see, depending on whether we expand wavefunctions or density matrices, we naturally obtain different types of diagrams, which, of course, can be transformed into one another.

2.5.1 Loop Diagrams

Loop diagrams are the natural description of nonlinear optical signals based on the propagation of a combined matter-field wavefunction,⁸

⁸For a concise introduction via the Schwinger loop, see, e.g., Ref. [Hansen12].

$$|\psi(t)\rangle = \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int}}(\tau) \right] |\psi(t_0)\rangle. \quad (2.103)$$

Note that in contrast to the superoperator Dyson series, Eq. (2.12), here we deal with the Dyson series (2.15) of the Hamiltonian operator in the lower-dimensional Hilbert space. As we have seen before, the absorption signal is given by Eq. (2.37), where we recall that the expectation value is taken with respect to the final density matrix $\varrho(t)$. In the present case, we have $\varrho(t) = |\psi(t)\rangle\langle\psi(t)|$, such that the signal reads

$$S(t, \Gamma) = \frac{2}{\hbar} \Im \langle \psi(t) | E^\dagger(t) V(t) | \psi(t) \rangle, \quad (2.104)$$

where Γ summarizes the set of external control parameters. Expansion of the exponential in Eq. (2.103) to the desired order in H_{int} generates approximate expressions for the signal S . Hence, the n -th order signal reads

$$S^{(n)}(\Gamma) = \frac{2}{\hbar} \Im \sum_{k+l=n} \langle \psi^{(k)}(t) | E^\dagger(t) V(t) | \psi^{(l)}(t) \rangle, \quad (2.105)$$

where the k -th order wavefunction in the interaction picture is given by

$$|\psi^{(k)}(t)\rangle = \left(-\frac{i}{\hbar} \right)^k \int_{t_0}^t d\tau_k \int_{t_0}^{\tau_k} d\tau_{k-1} \dots \int_{t_0}^{\tau_2} d\tau_1 H_{\text{int}}(\tau_k) \dots H_{\text{int}}(\tau_1) |\psi(t_0)\rangle. \quad (2.106)$$

Using the definition of the interaction Hamiltonian in the rotating wave approximation (2.6), and the initial condition (2.16), the terms in the n -th order signal may be written as convolutions of $n+1$ -point matter, and $n+1$ -point field correlation functions [where the “+1” is due to the interaction creating the signal in Eq. (2.104)],

$$\begin{aligned} S^{(k,l)}(\Gamma) &= \langle \psi^{(k)}(t) | E^\dagger(t) V(t) | \psi^{(l)}(t) \rangle \\ &= (-1)^k \left(-\frac{i}{\hbar} \right)^n \int_{t_0}^t d\tau'_k \dots \int_{t_0}^{\tau'_2} d\tau'_1 \int_{t_0}^t d\tau_l \dots \int_{t_0}^{\tau_l} d\tau_1 \\ &\quad \times \langle \mathcal{V}(\tau'_1) \dots \mathcal{V}(\tau'_k) V(t) \mathcal{V}(\tau_l) \dots \mathcal{V}(\tau_1) \rangle \\ &\quad \times \langle \epsilon(\tau'_1) \dots \epsilon(\tau'_k) E^\dagger(t) \epsilon(\tau_l) \dots \epsilon(\tau_1) \rangle. \end{aligned} \quad (2.107)$$

Note that, for simplicity of notation, we have not yet employed the rotating wave approximation in Eq. (2.107), such that we work with the quantities $\epsilon = E + E^\dagger$ and $\mathcal{V} = V + V^\dagger$ [recall Eq. (2.24)]. The signal contribution (2.107) is written as a time-ordered sequence of integrations over the so-called *interaction times*. It is possible to decouple the integrations by changing to the *loop times*, which are defined by the time delays between consecutive interactions, $s_j = \tau_{j+1} - \tau_j$, and sending the initial time $t_0 \rightarrow -\infty$, which is justified as long as t_0 clearly predates the interaction with

the first pulse [see also our discussion of the Raman polarizability in the preceding section leading to Eq. (2.95)]. Rewriting the signal in the Schrödinger picture with respect to the matter Hamiltonian,

$$\mathcal{V}_{\text{interaction}}(t) = G^\dagger(t) \mathcal{V}_{\text{Schrödinger}} G(t), \quad (2.108)$$

and using the properties of the time propagator $G^\dagger(t) = G(-t)$ as well as $G(t_1)G(t_2) = G(t_1 + t_2)$, we may rewrite the signal in terms of the propagators $G(\tau_{j+1} - \tau_j)$,

$$\begin{aligned} S^{(k,l)}(\Gamma) &= (-1)^k \left(-\frac{i}{\hbar}\right)^n \int_0^\infty ds_n \dots \int_0^\infty ds_1 \\ &\times \langle \mathcal{V} G^\dagger(s_n) \mathcal{V} \dots G^\dagger(s_{l+1}) V G(s_l) \mathcal{V} \dots G(s_1) \mathcal{V} \rangle \\ &\times \langle \epsilon(t - s_{l+1} \dots - s_n) \epsilon(t - \dots s_{n-1}) \dots E^\dagger(t) \epsilon(t - s_l) \dots \epsilon(t - \dots - s_1) \rangle. \end{aligned} \quad (2.109)$$

The time integrations along the *ket* have been transformed into the loop variables $s_1, \dots, s_l$, and the integrations along the *bra* into $s_{l+1}, \dots, s_n$. This way, the time arguments of the field correlations functions have become more involved. For instance, τ_1 has turned into $t - s_l - \dots - s_1$, and τ'_1 into $t - s_{l+1} - \dots - s_n$. In the course of this dissertation, we will nonetheless see that this representation in terms of loop times is beneficial in the evaluation of optical signals: Matter correlation functions are typically more expensive to evaluate, and it is therefore helpful to choose a basis in which they are particularly simple.

Note that to obtain the semiclassical expression for nonlinear signals, which we briefly sketched in Sect. 1.2 we simply need to replace the field correlation function in Eq. (2.109) by classical field amplitudes $\mathcal{A} = A + A^*$,

$$\begin{aligned} &\langle \epsilon(t - s_{l+1} \dots - s_n) \epsilon(t - \dots s_{n-1}) \dots E^\dagger(t) \epsilon(t - s_l) \dots \epsilon(t - \dots - s_1) \rangle_{\text{semiclassical}} \\ &= \mathcal{A}(t - s_{l+1} \dots - s_n) \mathcal{A}(t - \dots s_{n-1}) \dots A^*(t) \mathcal{A}(t - s_l) \dots \mathcal{A}(t - \dots - s_1). \end{aligned} \quad (2.110)$$

Therefore, the current approach naturally encompasses this semiclassical theory, and we will employ classical field amplitudes on several occasions in the course of this dissertation, for comparison to signals induced by quantum light.

Diagrammatic representation So far, we simply applied standard perturbation theory to the signal in Eq. (2.104). However, a straightforward evaluation of Eq. (2.109) quickly runs into problems, since - by definition $\mathcal{V} = V + V^\dagger$ - we have 2^n possible terms [even using the RWA (2.6)], which may contribute to Eq. (2.109). To circumvent this problem, it is simpler to represent the different terms (pathways) by diagrams which immediately tell the experienced reader, which pathways contribute - and what the underlying physical processes are (for problems regarding the interpretation, see Sect. 2.6).

Specifically, we now discuss in detail the case where $n = 3$ pulses are injected, since this includes classical four-wave mixing signals [Boyd03] such as the photon echo [Brixner04, Ginsberg09], which are of special importance in nonlinear spectroscopy. For this case, we have to consider four possible terms in Eq. (2.105), $S^{(3,0)}$, $S^{(2,1)}$, $S^{(1,2)}$, and $S^{(0,3)}$, which read, for instance,

$$S^{(3,0)} = (-1)^3 \left(-\frac{i}{\hbar}\right)^3 \int_0^\infty ds_3 \int_0^\infty ds_2 \int_0^\infty ds_1 \langle \mathcal{V} G^\dagger(s_3) \mathcal{V} G^\dagger(s_2) \mathcal{V} G^\dagger(s_1) V \rangle \\ \times \langle \epsilon(t - s_1 - s_2 - s_3) \epsilon(t - s_1 - s_2) \epsilon(t - s_1) E^\dagger(t) \rangle, \quad (2.111)$$

$$S^{(1,2)} = (-1)^1 \left(-\frac{i}{\hbar}\right)^3 \int_0^\infty ds_3 \int_0^\infty ds_2 \int_0^\infty ds_1 \langle \mathcal{V} G^\dagger(s_3) \mathcal{V} G(s_2) V G(s_1) \mathcal{V} \rangle \\ \times \langle \epsilon(t - s_3) E^\dagger(t) \epsilon(t - s_2) \epsilon(t - s_2 - s_1) \rangle, \quad (2.112)$$

and the other two cases may be obtained similarly.

To reduce the number of terms that need to be taken into account, we can now apply the rotating wave approximation, meaning that each matter excitation is accompanied by a field de-excitation and vice versa. But still, since we have $\mathcal{V} = V + V^\dagger$, each matter correlation function above contains $2^3 = 8$ different contributions, yielding a total of $3 \times 8 = 24$ possible excitation pathways. However, in many situations this number may be reduced substantially by employing, e.g. phase matching or selection rules: In this dissertation, we will typically deal with electronic transitions between neighboring manifolds, such that, e.g., direct transitions between the g - and f -manifold (recall the level scheme of Fig. 2.1) may be neglected, which is a good approximation, since such transitions are dipole-forbidden. Furthermore, the system is initially in the electronic ground state, such that the first excitation has to be an excitation of the system. As we will show now in detail, these restrictions together with the fact that the excitation pathway along the loop has to end up in the initial state again (since otherwise the matter correlation function would vanish) allow us to describe optical signals with at most four diagrams in this dissertation.

To construct the diagrammatic representation of such expressions, we restrict our discussion to one specific quantum pathway (i.e. one specific sequence of excitations and de-excitations in the matter correlation function) contributing to the $S^{(1,2)}$ signal (2.112),

$$S_{\text{example}} = \langle \psi^{(1)}(t) | E^\dagger(t) V(t) | \psi^{(2)}(t) \rangle, \quad (2.113)$$

which we derive in the Schrödinger representation. We start with the propagation of the wavefunction along the *ket*, taking us from the initial state $|\psi(t_0)\rangle$ to $|\psi^{(2)}(t)\rangle$, according to Eq. (2.106). We recall that ψ lives in the combined field-matter Hilbert space, such that - using the factorizing initial conditions (2.16) in the wavefunction description $|\psi(t_0)\rangle = |\psi_{\text{matter}}(t_0)\rangle \otimes |\psi_{\text{field}}(t_0)\rangle$ - the final state is given by

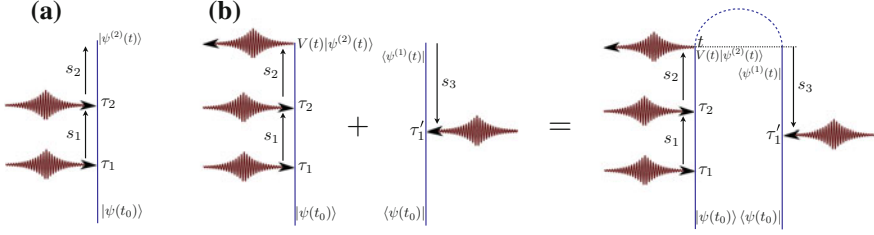


Fig. 2.5 Construction of the third-order loop diagram pertaining to Eq. (2.116): **a** The evolution of the wavefunction according to Eq. (2.103) is represented by a vertical line, where time is running from bottom to top. Interactions between matter and field are indicated by arrows pointing to - or away from - the wavefunction. **b** The loop diagram representing the amplitude (2.113) is obtained from the evolution of two wavefunctions $|\psi^{(2)}\rangle$ and $\langle\psi^{(1)}|$, see Eqs. (2.114) and (2.115), as well as the final interaction $E^\dagger V$ (only V is made explicit in the diagram) at time t . The loop times s_j (i.e. time delays between successive interactions) and the interaction times τ_j are indicated

$$|\psi^{(2)}(t)\rangle = \left(-\frac{i}{\hbar}\right)^2 \int_0^\infty ds_2 \int_0^\infty ds_1 G(s_2) V^\dagger G(s_1) V^\dagger |\psi_{\text{matter}}(t_0)\rangle \\ \times E(t - s_2) E(t - s_2 - s_1) |\psi_{\text{field}}(t_0)\rangle. \quad (2.114)$$

It is easy to realize that the only contribution to $|\psi^{(2)}(t)\rangle$ consists of the two excitations in Eq. (2.114): We start in the electronic ground state, so the first interaction has to be an excitation. If the second interaction de-excites the sample again, the final interaction $V(t)$, that creates the signal, acts on the ground state, and destroys the signal. Hence, the only remaining contribution to $|\psi^{(2)}(t)\rangle$ consists of two excitations.⁹ This process is depicted by the Feynman diagram in Fig. 2.5a, where time is running from bottom to top. Each excitation of the matter (and simultaneous de-excitation of the field) is represented by an arrow pointing towards the *ket*. Note that this representation originates in the semiclassical picture, where only the evolution of the matter system has to be treated quantum mechanically, and therefore the de-excitation of the field is not explicitly accounted for. But of course, the field correlation function may be obtained just as straightforwardly from this representation, by keeping in mind that each excitation of the matter system is accompanied by a de-excitation of the field, and vice versa.

Similarly, the evolution of the *bra*-side is given by

$$\langle\psi^{(1)}(t)| = -\left(-\frac{i}{\hbar}\right) \int_0^\infty ds_3 \langle\psi_{\text{matter}}(t_0)| V G^\dagger(s_3) \\ \times \langle\psi_{\text{field}}(t_0)| E^\dagger(t - s_3), \quad (2.115)$$

and represented by the right transition amplitude in Fig. 2.5b. The minus-sign in Eq. (2.115) stems from taking the Hermitian conjugate of $|\psi^{(1)}\rangle$.

⁹We did not specify $|\psi_{\text{field}}\rangle$, which could further restrict the number of relevant pathways.

The final signal $E^\dagger V$ (which is time-independent in the Schrödinger picture), see Eq. (2.113), is sandwiched between these two expressions to yield

$$S_{\text{example}} = - \left(-\frac{i}{\hbar} \right)^3 \int_0^\infty ds_3 \int_0^\infty ds_2 \int_0^\infty ds_1 \langle V G^\dagger(s_3) V G(s_2) V^\dagger G(s_1) V^\dagger \rangle \\ \times \langle E^\dagger(t - s_3) E^\dagger(t) E(t - s_2) E(t - s_2 - s_1) \rangle. \quad (2.116)$$

By convention,¹⁰ this final interaction is added to the *ket*-side of the diagram, and the two evolutions are connected by a dotted half-circle, indicating that their combination creates the contribution to the absorption signal (2.113).

Note that interactions are ordered *along the loop*: If we follow the evolution clockwise along the loop, i.e. following the evolution of the *ket* from t_0 to t , and then the evolution of the *bra* back from t to t_0 . Mathematically, this forward and backward time integration may be described by a closed contour integration - a so-called *Schwinger-loop* (or Schwinger-Keldysh loop) [Schwinger61, Keldysh65] - in the complex plane (where the physical time is the real axis), which lends the diagram its name. There is no time ordering between interactions on the *bra* and the *ket* side.

2.5.2 Unrestricted Loop Diagrams

One is not always interested solely in the evaluation of specific nonlinear signals, i.e. of specific observables. For instance, in Chap. 3, we mostly simulate excited state population distributions, without reference to a specific measurement setup. Furthermore, as discussed at hand of Eq. (2.37) on p. 45, optical signals may be ambiguous, and accordingly, so is their diagrammatic representation. To understand what is *really* going on in the matter system, we need to compare these optical signals to transition amplitudes between states in the matter system. Their calculation naturally leads us to different expressions, which are termed *unrestricted loop diagrams* in [Mukamel10b], which we will discuss in the following.

Suppose we want to calculate a molecular transition from an initial molecular state i to a final molecular state f , perturbatively in the matter-field interaction. After evaluating the matrix elements with respect to the matter degree of freedom, one is left with transition operators acting on the field space,

$$T_{fi}(t) = \langle f(t) | \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int}}(\tau) \right] | i(t_0) \rangle \\ = T_{fi}^{(1)}(t) + T_{fi}^{(2)}(t) + T_{fi}^{(3)}(t) \dots \quad (2.117)$$

¹⁰We could have also added the final interaction to the propagation of the *bra*, and depicted it by an excitation of the bra at time t . This ambiguity in the description of nonlinear signals will be elaborated further in Sect. 2.6.

where we obtain, for instance,¹¹ the first-order transition amplitude [Cohen-Tannoudji92]

$$T_{fi}^{(1)}(t) = -\frac{i}{\hbar} \int_{t_0}^t d\tau \langle f(t) | \mathcal{V}(\tau) | i(t_0) \rangle \epsilon(\tau). \quad (2.118)$$

The probability for the transition between the state $|i\rangle$ and $|f\rangle$ will be the modulus square of Eq. (2.117), when averaged with respect to the initial state of the electromagnetic fields,

$$p_{fi}(t) = \langle T_{fi}^\dagger(t) T_{fi}(t) \rangle \equiv \text{tr} \left\{ T_{fi}^\dagger(t) T_{fi}(t) \varrho_{\text{field}}(t_0) \right\}, \quad (2.119)$$

where ϱ_{field} denotes the initial state of the electromagnetic field. Expansion of Eq. (2.119) in the form of Eq. (2.117), and evaluation thereof will lead to expressions of the form

$$\begin{aligned} p_{fi,\text{example}}(t) &= \langle T_{fi}^{\dagger(1)}(t) T_{fi}^{(3)}(t) \rangle \\ &= \left(-\frac{i}{\hbar} \right)^3 \left(\frac{i}{\hbar} \right) \int_{t_0}^t d\tau_3 \int_{t_0}^{\tau_3} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^{\tau_1} d\tau'_1 \\ &\quad \times \langle i(t_0) | V(\tau'_1) P_f(t) V(\tau_3) V^\dagger(\tau_2) V^\dagger(\tau_1) | i(t_0) \rangle \\ &\quad \times \langle E^\dagger(\tau'_1) E^\dagger(\tau_3) E(\tau_2) E(\tau_1) \rangle, \end{aligned} \quad (2.120)$$

where we introduce the projector onto the final state $P_f(t) = |f(t)\rangle \langle f(t)|$. In loop times, Eq. (2.120) reads

$$\begin{aligned} p_{fi,\text{example}}(t) &= -\left(-\frac{i}{\hbar} \right)^4 \int_0^\infty ds_4 \int_0^\infty ds_3 \int_0^\infty ds_2 \int_0^\infty ds_1 \\ &\quad \times \langle V G^\dagger(s_4) P_f G(s_3) V G(s_2) V^\dagger G(s_1) V^\dagger \rangle \\ &\quad \times \langle E^\dagger(t-s_4) E^\dagger(t-s_3) E(t-s_3-s_2) E(t-s_3-s_2-s_1) \rangle, \end{aligned} \quad (2.121)$$

which looks indeed very similar to the integral expressions of our previous example of a loop diagram, Eq. (2.116), except that the two transition amplitudes are no longer connected by a final matter-field interaction creating the signal. The diagrammatic representation in Fig. 2.6 of the above expression is straightforward, using our derivation of the loop diagram (2.112): Each (k -th order) transition amplitude $T_{fi}^{(k)}$ is represented by a vertical blue line, in analogy to Fig. 2.5a, in which each of the k interactions is represented by an arrow. The two transition amplitudes are finally

¹¹ Note that the states carry explicit time dependence since the transition amplitudes are formulated in the interaction picture with respect to the free Hamiltonians of matter and field.

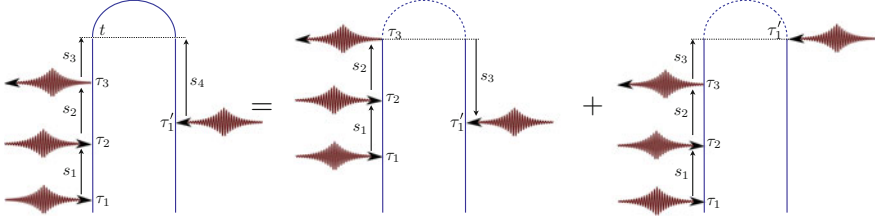


Fig. 2.6 Splitting of an unrestricted loop diagram, i.e. of a process that does not end with a measurement, pertaining to Eq. (2.120) as the sum of two loop diagrams, according to Eq. (2.123). The loop times s_j and the interaction times τ_j are indicated

connected by a solid semicircle to signify the projector $p_f(t)$. Therefore, its diagrammatic representation does not feature a final interaction at time t , and to distinguish this process from the loop diagram before, it is usually termed an unrestricted loop diagram [Mukamel10b].

As noted above, the final interaction creating the signal is the only difference between the loop diagrams discussed in the previous section and the present unrestricted loops. Hence, it is quite intuitive that we can relate any unrestricted diagram to regular loop diagrams by introducing time-ordering between the final interactions on both sides of the density matrix, as we will show in the following. Let us start again with Eq. (2.120), where the final interactions at times τ'_1 and τ_3 are not time-ordered, since they are both integrated between the initial time t_0 and the final time t . We now introduce the time-ordering artificially, by writing

$$\int_{t_0}^t d\tau_3 \int_{t_0}^t d\tau'_1 = \int_{t_0}^t d\tau_3 \int_{t_0}^{\tau_3} d\tau'_1 + \int_{t_0}^t d\tau'_1 \int_{t_0}^{\tau'_1} d\tau_3. \quad (2.122)$$

This procedure splits Eq. (2.120) in two terms

$$p_{fi, \text{example}}(t) = \left(-\frac{i}{\hbar}\right) \int_{t_0}^t d\tau_3 \tilde{p}_{(a)}(\tau_3) + \left(\frac{i}{\hbar}\right) \int_{t_0}^t d\tau'_1 \tilde{p}_{(b)}(\tau'_1), \quad (2.123)$$

where each of the two terms is given by a “regular” loop diagram,

$$\begin{aligned} \tilde{p}_{(a)}(\tau_3) &= -\left(-\frac{i}{\hbar}\right)^3 \int_{t_0}^{\tau_3} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^{\tau_3} d\tau'_1 \\ &\quad \times \langle i(t_0) | V(\tau'_1) P_f(t) V(\tau_3) V^\dagger(\tau_2) V^\dagger(\tau_1) | i(t_0) \rangle \\ &\quad \times \langle E^\dagger(\tau'_1) E^\dagger(\tau_3) E(\tau_2) E(\tau_1) \rangle, \end{aligned} \quad (2.124)$$

and

$$\begin{aligned}
\tilde{p}_{(b)}(\tau'_1) &= \left(-\frac{i}{\hbar}\right)^3 \int_{t_0}^{\tau'_1} d\tau_3 \int_{t_0}^{\tau_3} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \\
&\times \langle i(t_0) | V(\tau'_1) P_f(t) V(\tau_3) V^\dagger(\tau_2) V^\dagger(\tau_1) | i(t_0) \rangle \\
&\times \langle E^\dagger(\tau'_1) E^\dagger(\tau_3) E(\tau_2) E(\tau_1) \rangle,
\end{aligned} \tag{2.125}$$

We have thus expressed the transition probability between state $|i\rangle$ and state $|f\rangle$ in terms of loop diagrams, which may be evaluated using the rules of the previous Sect. 2.5.1. One small difference between the two still remains: Since we only considered a single final state f , the resulting loops (2.124) and (2.125) still contain the projector onto this state. In an optical measurement, of course, all possible final states contribute to the signal. This amounts to a summation over all final states $\sum_f P_f(t)$ in Eqs. (2.124) and (2.125), which yields the identity. Hence, in this rather abstract calculation, we showed how to relate loop diagrams (from optical measurements) with unrestricted loop diagrams (from transition amplitudes). In Sect. 2.6, we will follow the derivation in the opposite direction to express optical signals in terms of transition amplitudes.

2.5.3 Ladder Diagrams

So far, we have been concerned with the development of nonlinear signals based on the propagation of wavefunctions, and did not take advantage of the Liouville space notation introduced in Sect. 2.2. When we expand the entire density matrix (2.12), we obtain fully time-ordered expressions [Mukamel08]. This is necessary, for instance, when the system is coupled to a dissipative environment, and the time evolution is described by an effective quantum master equation [Breuer02]. Typically, this environmental noise drives the system into a thermal equilibrium state, thereby decreasing the purity of the initial state. On a formal level, it implies that backwards time propagation along the loop is no longer possible ($\mathcal{G}^\dagger$ as defined in Eq. (2.12) is, in an open system, no longer a trace-reserving, completely positive map [Breuer02]).

It is possible to obtain fully time-ordered expressions from loop diagrams in two steps: First, one has to rewrite Hilbert space expressions such as Eq. (2.116) as time-ordered Liouville space expressions,

$$\begin{aligned}
S_{\text{example}} &= (-1) \left(-\frac{i}{\hbar}\right)^3 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^{\tau_1} d\tau'_1 \langle V_R(\tau'_1) V_L(t) V_L^\dagger(\tau_2) V_L^\dagger(\tau_1) \rangle \\
&\times \langle E_R^\dagger(\tau'_1) E_L^\dagger(t) E_L(\tau_2) E_L(\tau_1) \rangle,
\end{aligned} \tag{2.126}$$

where we have adopted the “left” and “right” Liouville superoperators, Eqs. (2.19) and (2.20), which simply tell us whether the interaction takes place on the *ket* or on the *bra* side of the density matrix. Note that the original Hilbert space expression (2.116) may be obtained again from Eq. (2.126) by employing the definition of the

left- and right-superoperators: We assume that our initial density matrix is given by the pure state $\varrho(t_0) = |\psi(t_0)\rangle\langle\psi(t_0)|$ (as was used in the derivation of the loop diagrams), and write

$$\langle V_R(\tau'_1) V_L(t) V_L^\dagger(\tau_2) V_L^\dagger(\tau_1) \rangle = \text{tr} \left\{ V(t) V^\dagger(\tau_2) V^\dagger(\tau_1) \varrho(t_0) V(\tau'_1) \right\} \quad (2.127)$$

$$= \text{tr} \left\{ V(\tau'_1) V(t) V^\dagger(\tau_2) V^\dagger(\tau_1) \varrho(t_0) \right\}, \quad (2.128)$$

which coincides with the matter correlation function in Eq. (2.116), when changing to loop time variables s_j (Of course, the same calculation may be carried out with the field correlation function). Since “left” and “right” superoperators commute, $[V_L, V_R^\dagger] = 0$, which may be verified by straightforward calculation, we may change the position of the right-operator $V_R(\tau'_1)$ in the matter correlation function to obtain the different possible full time-orderings, without altering the correlation function itself. This allows us in the final step to break up the time integrations into all fully time-ordered combinations,

$$\begin{aligned} S_{\text{example}} &= (-1) \left(-\frac{i}{\hbar} \right)^3 \\ &\times \left(\int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^{\tau_1} d\tau'_1 + \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau'_1 \int_{t_0}^{\tau_1} d\tau_1 + \int_{t_0}^t d\tau'_1 \int_{t_0}^{\tau'_1} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \right) \\ &\times \langle V_R(\tau'_1) V_L(t) V_L^\dagger(\tau_2) V_L^\dagger(\tau_1) \rangle \langle E_R^\dagger(\tau'_1) E_L^\dagger(t) E_L(\tau_2) E_L(\tau_1) \rangle. \end{aligned} \quad (2.129)$$

One usually relabels the time integrations to $\tau_1, \dots, \tau_3$ in ascending chronological order as depicted in Fig. 2.7,

$$\begin{aligned} S_{\text{example}} &= (-1) \left(-\frac{i}{\hbar} \right)^3 \int_{t_0}^t d\tau_3 \int_{t_0}^{\tau_3} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \\ &\times \left(\langle V_L(t) V_L^\dagger(\tau_3) V_L^\dagger(\tau_2) V_R(\tau_1) \rangle \langle E_L^\dagger(t) E_L(\tau_3) E_L(\tau_2) E_R^\dagger(\tau_1) \rangle \right) \end{aligned} \quad (2.130)$$

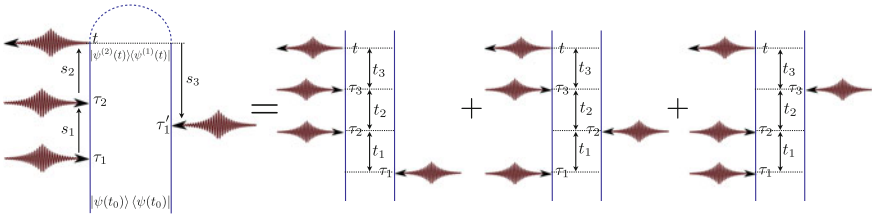


Fig. 2.7 The loop diagram, Eq. (2.116), may be written as the sum (2.129) of three fully time-ordered ladder diagrams. Instead of time-ordering along the loop, ladder diagrams describe fully time-ordered expressions, which can describe dissipative dynamics. The loop times s_j , the interaction times τ_j , and the ladder times t_j are indicated

$$+ \langle V_L(t) V_L^\dagger(\tau_3) V_R(\tau_2) V_L^\dagger(\tau_1) \rangle \langle E_L^\dagger(t) E_L(\tau_3) E_R^\dagger(\tau_2) E_L(\tau_1) \rangle \quad (2.131)$$

$$+ \langle V_L(t) V_R(\tau_3) V_L^\dagger(\tau_2) V_L^\dagger(\tau_1) \rangle \langle E_L^\dagger(t) E_R^\dagger(\tau_3) E_L(\tau_2) E_L(\tau_1) \rangle \Big). \quad (2.132)$$

In analogy to the loop times [see their introduction following Eq. (2.107)], we may also simplify the evaluation of these nested integrals by changing to the time delays between interactions (now in physical time),

$$t_j \equiv \tau_{j+1} - \tau_j, \quad (2.133)$$

and sending $t_0 \rightarrow -\infty$. The resulting expression in the Schrödinger picture with respect to the matter Hamiltonian reads

$$\begin{aligned} S_{\text{example}} = & (-1) \left(-\frac{i}{\hbar} \right)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \times \\ & \left(\langle V_L \mathcal{G}(t_3) V_L^\dagger \mathcal{G}(t) V_L^\dagger \mathcal{G}(t_1) V_R \rangle \langle E^\dagger(t - t_3 - t_2 - t_1) E^\dagger(t) E(t - t_4) E(t - t_3 - t_2) \rangle + \right. \\ & \langle V_L \mathcal{G}(t_3) V_L^\dagger \mathcal{G}(t_2) V_R \mathcal{G}(t_1) V_L^\dagger \rangle \langle E^\dagger(t - t_3 - t_2) E^\dagger(t) E(t - t_3) E(t - t_3 - t_2 - t_1) \rangle + \\ & \left. \langle V_L \mathcal{G}(t_3) V_R \mathcal{G}(t_2) V_L^\dagger \mathcal{G}(t_1) V_L^\dagger \rangle \langle E^\dagger(t - t_3) E^\dagger(t) E(t - t_3 - t_2) E(t - t_3 - t_2 - t_1) \rangle \right). \end{aligned} \quad (2.134)$$

Even though the expressions in Eq. (2.134) look rather deterrently, they may be easily visualized by their Feynman diagrams. To that end, let us discuss the second line of Eq. (2.134) in more detail, which is represented by the left-most ladder diagram in Fig. 2.7. Its matter correlation function $\langle V_L \mathcal{G}(t_3) V_L^\dagger \mathcal{G}(t_2) V_L^\dagger \mathcal{G}(t_1) V_R \rangle$ is to be read from right to left: First, the *bra* side of the density matrix is excited by V_R , represented by the arrow pointing from the right towards the density matrix in the diagrammatic representation. After the first free evolution period t_1 with the Liouville space propagator $\mathcal{G}(t_1)$, the interaction $V_L^\dagger$ creates an excitation on the *ket*-side, represented by the arrow pointing towards the density matrix from the left. The next free evolution t_2 is followed by the third interaction $V_L^\dagger$, and - after the final free evolution t_3 - the last interaction V_L creates the signal.

In the course of this dissertation, we do not take dissipative effects on the propagating light fields into account. In actual experimental setups, fluctuations in the laser systems, the optical instruments, or the like will most certainly affect the quantum state of the light to some extent. Here, we present proof-of-principle demonstrations of the effects of quantum correlations of the light onto optical signals, which are not degraded by fluctuations. Hence, the field correlation functions in Eq. (2.134) may still be evaluated in Hilbert space, yielding the same correlation functions as in Eq. (2.116), albeit written in the ladder diagram variables $t_1, \dots, t_4$. Hence, the field operator $E_R^\dagger$ associated with the matter interaction V_R may be pulled over to the right in each of the terms in Eq. (2.132)

$$\begin{aligned} & \text{tr} \left\{ E_L^\dagger(t) E_L(t - t_3) E_L(t - t_3 - t_2) E_R^\dagger(t - t_3 - t_2 - t_1) \varrho_{\text{field}} \right\} \\ &= \text{tr} \left\{ E^\dagger(t - t_3 - t_2 - t_1) E^\dagger(t) E(t - t_4) E(t - t_3 - t_2) \varrho_{\text{field}} \right\}. \end{aligned} \quad (2.135)$$

This is the reason all the field correlation functions in Eq. (2.134) may be written in normally ordered form.

Despite their apparent greater complexity, ladder diagrams of the type (2.134), depicted in Fig. 2.7, offer several major advantages compared to loop diagrams: First and foremost, they allow for the treatment of open quantum systems since the Liouville space propagator $\mathcal{G}(t)$ in Eq. (2.12) may also describe dissipative dynamics. Second, the propagation happens in real time such that we know the quantum state of the combined matter field system at any instant in time. This is not the case for loops, where we do not know at which point in time interactions on the *bra* side occur with respect to those on the *ket* side.

2.5.4 Time Versus Frequency Domain Expressions

It is of course possible to express the nested time integrals in terms of multiple frequency integrals. In the course of this dissertation, we will use both cases depending on the specific problem.

Let us consider Eq. (2.116) as a concrete example. To obtain the frequency domain expression, we decompose the field correlation into its Fourier components

$$\begin{aligned} & \langle E^\dagger(t - s_3) E^\dagger(t) E(t - s_2) E(t - s_2 - s_1) \rangle \\ &= \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} e^{i(\omega'_a + \omega'_b - \omega_a - \omega_b)t} e^{i\omega_a s_1} e^{i(\omega_a + \omega_b) s_2} e^{-i\omega'_a s_3} \\ & \times \langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle, \end{aligned} \quad (2.136)$$

which allows us to carry out the time integrations in Eq. (2.116), and replace the time-dependent propagators $G(s_1)$, $G(s_2)$, and $G^\dagger(s_3)$ by the frequency domain Green's functions

$$G(\omega) \equiv \int_0^\infty ds e^{i\omega s} G(s) \quad (2.137)$$

$$= \frac{i}{\omega - H_{\text{matter}}/\hbar + i\eta}. \quad (2.138)$$

Equation (2.116) then takes the form

$$\begin{aligned}
S_{\text{example}} = & \left(-\frac{i}{\hbar}\right)^3 \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} e^{i(\omega'_a + \omega'_b - \omega_a - \omega_b)t} \\
& \times \langle V G^\dagger(\omega'_a) V G(\omega_a + \omega_b) V^\dagger G(\omega_a) V^\dagger \rangle \\
& \times \langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle.
\end{aligned} \tag{2.139}$$

As one can see from Eq. (2.139), the frequency domain representation may be beneficial in the case of time-integrated signals such as Eq. (2.38): Integrating over t in Eq. (2.139) directly yields a delta-function $2\pi\delta(\omega'_a + \omega'_b - \omega_a - \omega_b)$. As a rule of thumb, it is typically more convenient to evaluate signals in the time domain when the matter correlation function is more complicated than the field correlation function, and in the frequency domain otherwise.

2.5.5 Impulsive Limit

In many standard nonlinear optical signals, the pulse durations of the excitation pulses are very short compared to the relevant dynamics in the matter system. The impulsive limit then often yields an excellent approximation to simulate the signal, and greatly simplifies its numerical evaluation: One assumes that the pulses are given by delta pulses,

$$E_i(t) \simeq \delta(t - (t_i^{(0)} - t_{i-1}^{(0)})). \tag{2.140}$$

We may then carry out the time integrations in any perturbative signal. For instance, we obtain for Eq. (2.134)

$$\begin{aligned}
S_{\text{example}} = & (-1) \left(-\frac{i}{\hbar}\right)^3 \left(\langle V_L \mathcal{G}(t_3^{(0)}) V_L^\dagger \mathcal{G}(t_2^{(0)}) V_L^\dagger \mathcal{G}(t_1^{(0)}) V_R \rangle \right. \\
& \left. + \langle V_L \mathcal{G}(t_3^{(0)}) V_L^\dagger \mathcal{G}(t_2^{(0)}) V_R \mathcal{G}(t_1^{(0)}) V_L^\dagger \rangle + \langle V_L \mathcal{G}(t_3^{(0)}) V_R \mathcal{G}(t_2^{(0)}) V_L^\dagger \mathcal{G}(t_1^{(0)}) V_L^\dagger \rangle \right)
\end{aligned} \tag{2.141}$$

where the times $t_1^{(0)}, t_2^{(0)}, t_3^{(0)}$ denote the time delays between the laser pulses, and not integration variables. Hence, in this limit we obtain direct access to the matter response function, and Fourier transform of the time delays reveals the true line broadening of resonances, and is not perturbed by finite pulse bandwidths. Of course, it also represents a great technical simplification since the previous multiple time integrations are no longer necessary.

2.6 Susceptibilities Versus Transition Amplitudes in the Quantum Domain

Nonlinear (quantum) optics is mainly concerned with the evolution of the electromagnetic fields, and matter systems typically enter the description in terms of *susceptibilities* [Boyd03]. As mentioned in the derivation of Eq. (2.37), this approach suffers from important drawbacks since the interpretation of the underlying, physical processes in the matter system seems ambiguous. This ambiguity may be resolved by calculating *transition amplitudes* between energy levels of the sample system, where the final state is clearly unambiguous. However, it is not at all obvious how to relate these transition amplitudes to optical signals since those also contain parametric processes where system and light do not exchange energy, but rather contribute to dispersion of light inside the sample medium.

In the diagrammatic representation of optical signals, the connection between these two approaches becomes evident: One has to relate the loop diagrams describing optical signals with the unrestricted loop diagrams describing products of transition amplitudes. This will be elaborated in the following for the first- and third-order contribution of intensity measurements, Eq. (2.37). We again consider a three-level system consisting of a ground state manifold g , a single-exciton manifold e , and the two-exciton manifold f (see Fig. 2.1). We first discuss the first-order contribution, which serves as a showcase example to illustrate the perturbative construction of optical signals, and will therefore be discussed in quite some detail.

As pointed out in Ref. [Mukamel10b], the transition amplitudes are connected to the energy exchanged between field and matter system. To measure the total transferred energy, we integrate Eq. (2.37) over time. We further aim to address the described ambiguity in the representation of optical signals, which we had noted in Sect. 2.3. To this end, we symmetrize the signal with respect to the two possible representations, Eqs. (2.37) and (2.39), of the final interaction,

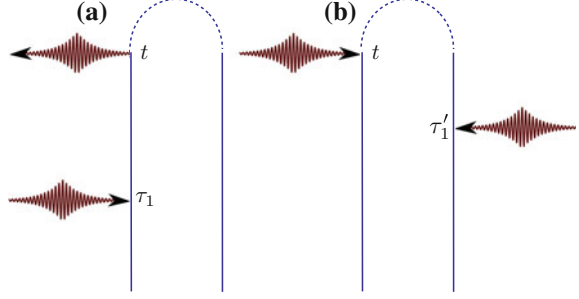
$$S(\Gamma) = \frac{1}{2} \int_{-\infty}^{\infty} dt \left(\frac{2}{\hbar} \Im \langle E_+^\dagger(t) V_+(t) \rangle_{\text{final}} - \frac{2}{\hbar} \Im \langle E_+(t) V_+^\dagger(t) \rangle_{\text{final}} \right). \quad (2.142)$$

We only consider unitary evolution, such that we can use a Hilbert space description, replace the Liouville space expectation value above by a Hilbert space expectation value (i.e. we simply replace $E_+ \rightarrow E$ etc.), and obtain the result in terms of loop diagrams.

2.6.1 Linear Absorption

We first analyze the first term in Eq. (2.142), $\langle E^\dagger(t) V(t) \rangle$. The linear absorption signal is obtained by expanding the exponential (2.15) to first order, which leaves us with two possible contributions,

Fig. 2.8 The loop diagrams comprising the symmetrized linear absorption signal (2.142). Diagram **a** is obtained from the expansion (2.145) of $\langle E^\dagger V \rangle$, and diagram **b** from the expansion of $\langle EV^\dagger \rangle$



$$S^{(1,0)}(\Gamma) = \frac{1}{\hbar} \int_{-\infty}^{\infty} dt \Im \langle \psi^{(1)}(t) | E^\dagger(t) V(t) | \psi^{(0)}(t) \rangle, \quad (2.143)$$

$$S^{(0,1)}(\Gamma) = \frac{1}{\hbar} \int_{-\infty}^{\infty} dt \Im \langle \psi^{(0)}(t) | E^\dagger(t) V(t) | \psi^{(1)}(t) \rangle, \quad (2.144)$$

where we recall our definition (2.106) of the k -th wavefunction. In Eq. (2.143), the de-excitation operator $V(t)$ acts on the ground state, and this contribution therefore vanishes.¹² To avoid this situation in Eq. (2.144), the one interaction with the field has to create an excitation in the sample. Hence, the linear signal is given by $S^{(0,1)}$, and we can write

$$S^{(0,1)}(\Gamma) = \frac{1}{\hbar} \int_{-\infty}^{\infty} dt \int_{t_0}^t d\tau_1 \Im \left(-\frac{i}{\hbar} \right) \langle \psi^{(0)}(t_0) | E^\dagger(t) V(t) E(\tau_1) V^\dagger(\tau_1) | \psi^{(0)}(t_0) \rangle. \quad (2.145)$$

This expression may be represented by diagram (a) in Fig. 2.8. Using the initial factorizing condition $|\psi^{(0)}(t_0)\rangle = |g\rangle \otimes |\psi_{\text{field}}\rangle$, and changing to the Schrödinger picture of the sample system, we obtain

$$S^{(0,1)}(\Gamma) = \frac{1}{\hbar} \int_{-\infty}^{\infty} dt \int_{t_0}^t d\tau_1 \Im \left(-\frac{i}{\hbar} \right) \langle g | V G(t - \tau_1) V^\dagger | g \rangle \langle E^\dagger(t) E(\tau_1) \rangle, \quad (2.146)$$

where we abbreviate $\langle E^\dagger(t) E(\tau_1) \rangle = \langle \psi_{\text{field}} | E^\dagger(t) E(\tau_1) | \psi_{\text{field}} \rangle$. Using the definition of V as in Fig. 2.1, Eq. (2.7), the matter correlation function is given by the sum-over-states expression

$$\langle g | V G(t - \tau_1) V^\dagger | g \rangle = \sum_e |\mu_{ge}|^2 e^{-i\omega_e(t-\tau_1)}, \quad (2.147)$$

¹²Note, however, that if we discussed a situation in which the system is *not* prepared in the ground state, this contribution would have to be taken into account as well.

where the sum e runs over all the single exciton states in the associated manifold in Fig. 2.1.¹³ To evaluate the signal, we now change to the loop time $s = t - \tau_1$, and decompose the field correlation function as

$$\langle E^\dagger(t)E(t-s) \rangle = \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} e^{i\omega t - i\omega'(t-s)} \langle E^\dagger(\omega)E(\omega') \rangle, \quad (2.148)$$

and, after inserting Eqs. (2.147) and (2.148) in (2.146), we can carry out the time integrations, and obtain

$$S^{(0,1)}(\Gamma) = \frac{1}{\hbar^2} \Im \int \frac{d\omega}{2\pi} \frac{|\mu_{ge}|^2}{\omega - \omega_e + i\eta} \langle E^\dagger(\omega)E(\omega) \rangle. \quad (2.149)$$

Here, we have added the infinitesimal complex factor $i\eta$ to evaluate the s -integration in Eq. (2.146), after the substitution $s = t - \tau_1$. The t -integration yielded a delta function $2\pi\delta(\omega - \omega')$.

To rewrite Eq. (2.149) as the modulus square of a transition amplitude, we now define the first-order transition amplitude operator acting on the field Hilbert space,

$$T_{eg}^{(1)}(\omega) = \sum_e \frac{\mu_{eg}}{\hbar} E(\omega). \quad (2.150)$$

This allows us to write the signal as

$$S^{(0,1)}(\Gamma) = \sum_e \Im \int \frac{d\omega}{2\pi} \frac{1}{\omega - \omega_e + i\eta} \langle T_{eg}^{(1)\dagger}(\omega) T_{eg}^{(1)}(\omega) \rangle. \quad (2.151)$$

Finally, we employ the identity (also known as the *Sokhotski-Plemelj theorem*) [Weinberg95, Cohen-Tannoudji92]

$$\frac{1}{\omega + i\eta} = \text{PP} \frac{1}{\omega} - i\pi\delta(\omega), \quad (2.152)$$

where PP denotes the principal value, and $\delta(\omega)$ the delta distribution. The field correlation function is a real number $\langle T^\dagger T \rangle$, since it is simply the norm of the vector $T^{(1)}(\omega)|\psi_{\text{field}}\rangle$, so we arrive at

$$S^{(0,1)}(\Gamma) = -\frac{1}{2} \sum_e \langle |T_{eg}^{(1)}(\omega_e)|^2 \rangle, \quad (2.153)$$

where we used the short-hand notation $|T|^2 \equiv T^\dagger T$.

¹³ Similarly, we will denote summations over the other state manifolds in Fig. 2.1 by summation indices g, f , etc. in the following.

In an identical derivation, we can express the second term in Eq. (2.142) by the single Feynman diagram (b) in Fig. 2.8. In contrast to Eqs. (2.143) and (2.144), only the first-order function $\langle \psi^{(1)} | EV^\dagger | \psi^{(0)} \rangle$ yields a signal, such that the diagram features its single excitation of the right (*bra*) side. A very similar calculation as before yields the same result as for $S^{(0,1)}$, Eq. (2.153). Hence, the full linear absorption signal is given by

$$S^{(1)}(\Gamma) = - \sum_e \langle |T_{eg}^{(1)}(\omega_e)|^2 \rangle. \quad (2.154)$$

We have thus related the linear susceptibility responsible for the linear absorption with the modulus square of the transition operator acting on the field Hilbert space, which simultaneously promotes the matter system from the ground state g to the excited state e . This result should not come as a surprise, but - apart from being a clean example, in which we could derive the diagrammatic representation of the signal in detail - we can already draw some useful conclusions from Eq. (2.154): The sign of the linear absorption is negative due to our definition (2.31) of the signal. The linear absorption always reduces the number of photons in the field (keeping in mind that we assumed the matter system to be initialized in its ground state). Therefore, the change of photon number (2.37) is negative. We have also seen that, in fact, both terms in Eq. (2.142) yield the same transition amplitude $\langle |T_{eg}^{(1)}(\omega_e)|^2 \rangle$, even though their diagrammatic representation in Fig. 2.8 could give the false impression that they corresponded to different processes, for instance, diagram (a) to a scattering process, while diagram (b) indeed described an absorption event.

2.6.2 Third-Order Absorption

We now turn to the next order in the number of matter-field interactions. This will be especially relevant for the rest of the dissertation, since it features four-point field correlation functions. It is those correlation functions that are responsible for the entangled photon effects described in Sect. 1.3, and therefore this is the lowest order where we can expect to see entanglement effects in optical signals. Expanding the time evolution operator (2.15) to third order, we obtain the loop diagrams depicted in Fig. 2.9. Diagrams (Ia)–(IVa) are obtained by expanding the first term in Eq. (2.142), and the convention that the final interaction happens on the *ket*-side. Similarly, the second line, diagrams (Ib)–(IVb), stem from the expansion of the second term in Eq. (2.142). Diagrams (I) and (II) will be termed *two-photon absorption (TPA)* pathways since the system evolves through a doubly excited state at some fraction of the time evolution. They feature matter correlation functions of the form $\langle VVV^\dagger V^\dagger \rangle$, i.e. (reading from right to left) two excitations (or photon absorptions, represented by arrows pointing towards the density matrix) followed by two de-excitations (arrows pointing away from it) when following the propagation around the loop. Similarly, diagrams (III) and (IV) will be called *Raman* pathways, since they show a succession

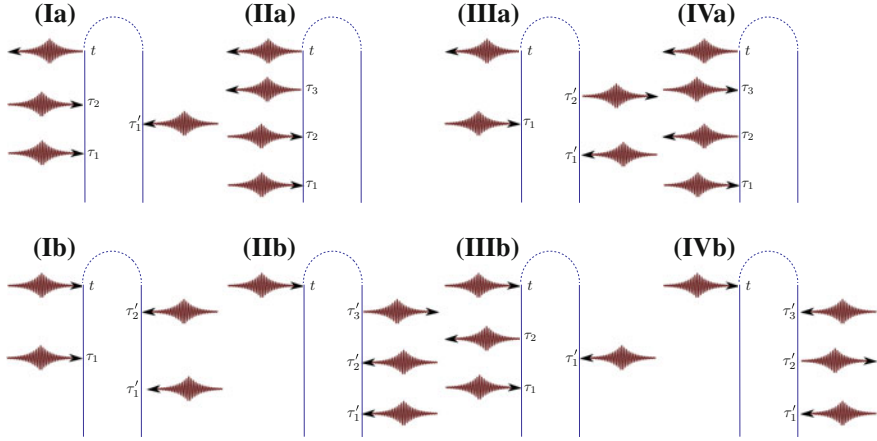


Fig. 2.9 The loop diagrams comprising the symmetrized third-order absorption signal contributing to Eq. (2.142). Diagrams (I) and (II) represent two-photon absorption (TPA) pathways, where the system evolves through a double excited state, and diagrams (III) and (IV) are Raman contributions, where the system can reveal vibrational resonances

of excitations and de-excitations, $\langle V V^\dagger V V^\dagger \rangle$. When the ground state of the system contains a ladder of vibrational states, these may be accessed in these transition pathways via a two-photon process. For instance, in our derivation of the effective phonon interaction in ion traps, Eq. (2.90), the polarizability consisted of a succession of electronic excitation and de-excitation, i.e. $V V^\dagger$, and we will later encounter this quantity in Chap. 6. It is in this spirit that the four-point correlation functions $\langle V V^\dagger V V^\dagger \rangle$ in diagrams (III) and (IV) are called Raman pathways.

We reiterate (see our previous discussion of the linear absorption signal) that each line of diagrams in Fig. 2.9 separately allows the calculation of the third-order signal $S^{(3)}(\Gamma)$. But we will now show how their combination allows us to express the signal in terms of transition amplitudes.

Two-Photon Absorption Pathways

We start with the calculation of diagram (Ia),

$$S_{(Ia)}^{(3)} = -\frac{1}{\hbar} \Im \left[\left(-\frac{i}{\hbar} \right)^3 \int_{-\infty}^{\infty} dt \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^{\tau_1} d\tau'_1 \langle V(\tau'_1) V(t) V^\dagger(\tau_2) V^\dagger(\tau_1) \rangle \right. \\ \left. \times \langle E^\dagger(\tau'_1) E^\dagger(t) E(\tau_2) E(\tau_1) \rangle \right] \quad (2.155)$$

(Note that the factor -1 stems from the single interaction acting on the *bra*). To proceed, we decompose the field correlation function into frequency components,

$$\begin{aligned} \langle E^\dagger(\tau'_1)E^\dagger(t)E(\tau_2)E(\tau_1) \rangle &= \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} e^{i\omega'_a\tau'_1 + i\omega'_b t - i\omega_b\tau_2 - i\omega_a\tau_1} \\ &\times \langle E^\dagger(\omega'_a)E^\dagger(\omega'_b)E(\omega_b)E(\omega_a) \rangle. \end{aligned} \quad (2.156)$$

By changing to the loop times defined in Sect. 2.5, and evaluating the matter correlation function in a sum-over-states expression, using Eq. (2.7),

$$\langle V G^\dagger(s_3) V G(s_2) V^\dagger G(s_1) V^\dagger \rangle = \sum_{g,e,f,e'} \mu_{ge} e^{-i\omega_e s_1} \mu_{ef} e^{-i\omega_f s_2} \mu_{fe'} e^{i\omega_{e'} s_3} \mu_{e'g}, \quad (2.157)$$

we may carry out the time integrations,

$$\begin{aligned} S_{(\text{la})}^{(3)} &= -\frac{1}{\hbar} \Im \left[\left(-\frac{i}{\hbar} \right)^3 \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} 2\pi \delta(\omega_a + \omega_b - \omega'_a - \omega'_b) \right. \\ &\times \langle E^\dagger(\omega'_a)E^\dagger(\omega'_b)E(\omega_b)E(\omega_a) \rangle \frac{i\mu_{ge}}{\omega_a - \omega_e + i\eta} \frac{i\mu_{ef}}{\omega_a + \omega_b - \omega_f + i\eta} \\ &\times \left. \frac{-i\mu_{fe'}}{\omega'_a - \omega_{e'} - i\eta} \mu_{e'g} \right], \end{aligned} \quad (2.158)$$

where we again introduced the usual infinitesimal factor η to write the matter propagators in frequency domain [see Eq. (2.138)]. Changing to the integration variable $\omega_{\text{sum}} = \omega_a + \omega_b$, and defining the second-order transition operator acting on the field space as

$$T_{fg}^{(2)}(\omega_{\text{sum}}) = \frac{1}{\hbar^2} \sum_e \int \frac{d\omega_a}{2\pi} \frac{\mu_{ge}\mu_{ef}}{\omega_a - \omega_e + i\eta} E(\omega_{\text{sum}} - \omega_a) E(\omega_a), \quad (2.159)$$

we may rewrite the signal as

$$S_{(\text{la})}^{(3)}(\Gamma) = \Im \left[\sum_f \int \frac{d\omega_{\text{sum}}}{2\pi} \langle T_{fg}^{(2)\dagger}(\omega_{\text{sum}}) T_{fg}^{(2)}(\omega_{\text{sum}}) \rangle \frac{1}{\omega_{\text{sum}} - \omega_f + i\eta} \right]. \quad (2.160)$$

Finally, as in our derivation of Eq. (2.154), we use the identity (2.152) to express Eq. (2.160) as the modulus square of transition amplitude operators acting on the initial quantum state of the light,

$$S_{(\text{la})}^{(3)}(\Gamma) = -\frac{1}{2} \sum_f \langle |T_{fg}^{(2)}(\omega_f)|^2 \rangle. \quad (2.161)$$

In an identical calculation, we obtain

$$S_{(\text{Ib})}^{(3)} = -\frac{1}{2} \sum_f \langle |T_{fg}^{(2)}(\omega_f)|^2 \rangle. \quad (2.162)$$

Hence, the final third-order contribution to the signal (2.142), which contains their sum, yields exactly the contribution of the absorption of two photon pairs, which promote the system from the ground state manifold g to the two-exciton manifold f , and calculating either of the two possibilities contains the full information content on this particular excitation pathway. Just like the linear absorption signal, this contribution is always negative, since two photons need to be absorbed to promote the system into the f -manifold, thereby reducing the number of photons in the light field.

For diagrams (IIa) and (IIb), we obtain similarly

$$S_{(\text{IIa})}^{(3)}(\Gamma) = \Im \left[\sum_{e'} \int \frac{d\omega}{2\pi} \langle T_{e'g}^{(1)\dagger}(\omega) T_{e'g}^{(3)}(\omega) \rangle \frac{1}{\omega - \omega_{e'} + i\eta} \right], \quad (2.163)$$

and

$$S_{(\text{IIb})}^{(3)}(\Gamma) = -\Im \left[\sum_{e'} \int \frac{d\omega}{2\pi} \langle T_{e'g}^{(3)\dagger}(\omega) T_{e'g}^{(1)}(\omega) \rangle \frac{1}{\omega - \omega_{e'} - i\eta} \right], \quad (2.164)$$

with the first- and third-order transition amplitude operators

$$T_{e'g}^{(1)}(\omega) = \frac{\mu_{e'g}}{\hbar} E(\omega), \quad (2.165)$$

$$T_{e'g}^{(3)}(\omega) = \frac{1}{\hbar^3} \sum_{ef} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_x}{2\pi} \frac{\mu_{ge}}{\omega_a - \omega_e + i\eta} \frac{\mu_{ef} \mu_{fe'}}{\omega_x - \omega_f + i\eta} \\ \times E^\dagger(\omega_x - \omega) E(\omega_x - \omega_a) E(\omega_a). \quad (2.166)$$

Thus, employing Eq. (2.152), the sum of the these two diagrams may be written as,

$$S_{(\text{IIa})}^{(3)}(\Gamma) + S_{(\text{IIb})}^{(3)}(\Gamma) \\ = \Im \sum_{e'} \int \frac{d\omega}{2\pi} \left[-i\pi \delta(\omega - \omega_{e'}) \langle T_{e'g}^{(1)\dagger}(\omega) T_{e'g}^{(3)}(\omega) + T_{e'g}^{(3)\dagger}(\omega) T_{e'g}^{(1)}(\omega) \rangle \right. \\ \left. \text{PP} \frac{1}{\omega - \omega_{e'}} \langle T_{e'g}^{(1)\dagger}(\omega) T_{e'g}^{(3)}(\omega) - T_{e'g}^{(3)\dagger}(\omega) T_{e'g}^{(1)}(\omega) \rangle \right] \quad (2.167)$$

The second line vanishes, since the principal value returns a real number. Hence, we finally arrive at

$$S_{(\text{IIa})}^{(3)}(\Gamma) + S_{(\text{IIb})}^{(3)}(\Gamma) = -2\Re \sum_{e'} \langle T_{e'g}^{(1)\dagger}(\omega_{e'}) T_{e'g}^{(3)}(\omega_{e'}) \rangle, \quad (2.168)$$

and the sum of the TPA pathways yields

$$S_{\text{TPA}}^{(3)}(\Gamma) = - \sum_f \langle |T_{fg}^{(2)}(\omega_f)|^2 \rangle - 2\Re \sum_{e'} \langle T_{e'g}^{(1)\dagger}(\omega_{e'}) T_{e'g}^{(3)}(\omega_{e'}) \rangle. \quad (2.169)$$

The second term also enters with a negative sign. However, since it is the real part of the product of two different operators, it may become positive, as we will see in Chap. 4.

Raman Pathways

In addition to our previous definitions, we introduce the transition amplitude operators

$$T_{g'g}^{(2)}(\omega) = \frac{1}{\hbar^2} \sum_e \int \frac{d\omega_a}{2\pi} \frac{\mu_{ge}\mu_{eg'}}{\omega_a - \omega_e + i\eta} E^\dagger(\omega_a - \omega) E(\omega_a), \quad (2.170)$$

$$T_{e'g}^{\prime(3)}(\omega) = \frac{1}{\hbar^3} \sum_{e,g'} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_-}{2\pi} \frac{\mu_{ge}}{\omega_a - \omega_e + i\eta} \frac{\mu_{eg'}\mu_{g'e'}}{\omega_- - \omega_{g'} + i\eta} \\ \times E(\omega - \omega_-) E^\dagger(\omega_a - \omega_-) E(\omega_a). \quad (2.171)$$

$T_{g'g}^{(2)}$ describes a generalization of the Raman process we described in the derivation of the effective interaction operators earlier in Sect. 2.4. In the case of an off-resonant excited state, we may take the denominator $\omega_a - \omega_e + i\eta$ out of the integration, and obtain a quantized version of Eq. (2.97). $T^{\prime(3)}$ corresponds to a Raman process where the system evolves in the ground state after the first two interactions, whereas $T^{(3)}$ defined in Eq. (2.166) describes the two-photon absorption (TPA) process. After similar calculations as before, we obtain the final result

$$S_{\text{Raman}}^{(3)}(\Gamma) = \sum_{g'} \langle |T_{g'g}^{(2)}(\omega_{g'})|^2 \rangle - 2\Re \sum_{e'} \langle T_{e'g}^{(1)\dagger}(\omega_{e'}) T_{e'g}^{\prime(3)}(\omega_{e'}) \rangle. \quad (2.172)$$

Here, the first term enters with a positive sign. It creates a positive contribution to the third-order signal, since the second photon in the Raman process $g \rightarrow g'$ is emitted, and thereby increases the number of photons in the detected field. The $T^{(1)\dagger}T^{\prime(3)}$ -contribution has the same sign as its TPA analog in Eq. (2.168). However, note that the $T^{(3)}$ amplitude (2.166) has a photon creation operator as leftmost operator. Hence, it finishes with a photon emission. The $T^{\prime(3)}$ -pathway in the Raman signals finishes with a photon annihilation. As we will show in Chap. 4, this difference causes the two contributions to have opposite signs after all.

In conclusion, Eqs. (2.169) and (2.172) express the time-integrated third-order response in terms of transition amplitudes of the matter system, evaluated for a given initial quantum state of light, which enters via the expectation value $\langle \dots \rangle$. It is not straightforward to connect the diagrams with the corresponding transition amplitudes, but this procedure allows us to make the connection to the underlying material

system providing some intuition for their interpretation, and to assess whether a given diagram enters with positive or negative sign.

2.7 Synopsis: Diagrammatics in a Nutshell

This final section briefly summarizes the diagrammatic construction of nonlinear optical signals. We only state the most convenient representations of optical signals in the time and in the frequency domain.

The starting point of our derivations is given by the expectation value of an observable $A(t)$ (for their derivation, see Sect. 2.3),

$$S(t; \Gamma) = \langle A(t) \rangle_{\text{final}}, \quad (2.173)$$

where the expectation value is taken with respect to the final state of the combined matter-field density matrix. We are interested in the change induced by the interaction with the sample system, which is given by Eq. (2.31) [or Eq. (2.57) for the fluorescence signal]. These expressions relate changes of the field measurements to operators of the matter system, and they may be calculated with any of the variety of methods, which have been developed in quantum electrodynamics [Cohen-Tannoudji92], ranging from perturbation theory in the weak interaction limit to the Heisenberg–Langevin equations or the optical Bloch equations in the strong coupling regime. In this dissertation, we work with a perturbative approach, which has been optimized for the description of nonlinear spectroscopic signals. This strong link to nonlinear spectroscopy, as described in Sect. 1.2, facilitates a comparison of nonlinear signals induced by quantum light with conventional spectroscopic signals. Furthermore, its origin in the description of ultrafast optics implies that it is well suited to treat the interaction with broad bandwidth, multimode light fields. On the other hand, this approach comes at the price of not being able to describe strong-field (i.e. nonperturbative) effects, such as Rabi oscillations, due the strong coupling of individual light modes to the sample [Schwartz11], or due to the excitation by strong fields, which may drive multiphoton transitions [Gelin11].

In the following two paragraphs, we review the relevant types of diagrams that will appear throughout this dissertation. The final state in Eq. (2.173) may be obtained by the propagation of a wavefunction, $\varrho_{\text{final}} = |\psi\rangle\langle\psi|$, in which case a perturbative expansion yields the *loop* diagrams (see Sect. 2.5.1), or by a general master equation, which is calculated by *ladder* diagrams (see Sect. 2.5.3). The diagrams represent perturbative expansions of the Dyson series, either Eq. (2.15) in case we are dealing with the propagation of wavefunctions, or Eq. (2.12) in case we propagate the full density matrix. The basic building block of the diagrams are the light-matter interactions as depicted in Fig. 2.10. The evolution of the density matrix is represented by two vertical lines, corresponding to the *bra* or the *ket* side, respectively, and each interaction between light field and matter system is represented by an arrow pointing towards

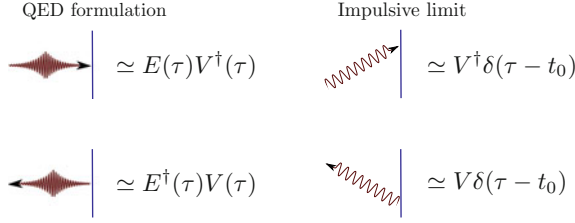


Fig. 2.10 Diagrammatic representation of light-matter interactions: The evolution of the *bra* or the *ket* side of the density matrix is represented by *vertical blue lines*. The light-matter interaction in the QED formulation is represented by *horizontal pulsed arrows*. An *arrow* pointing towards the line corresponds to an excitation of the matter system, and a de-excitation of the light field (and vice versa for an *arrow* pointing away from the line). In the impulsive limit considered in Chap. 7, matter excitations (de-excitations) at time t_0 are represented by *arrows* pointing towards (away from) the line. The explicit field description has been eliminated in this limit

the density matrix (denoting an excitation process) or away from it (indicating a de-excitation).

For the sake of simplicity, we write the interactions as $\mathbb{E}\mathbb{V}$, which may correspond either to a matter excitation ($E V^\dagger$) or a de-excitation ($E^\dagger V$), and represent them by a horizontal pulse without an arrow.

2.7.1 Loop Diagrams

Loop diagrams naturally emerge from the description of optical signals based on the propagation of a wavefunction. The signal after n interactions is given by

$$S^{(n)}(t; \Gamma) = \sum_{k+l=n} \langle \psi^{(l)}(t) | A(t) | \psi^{(k)}(t) \rangle, \quad (2.174)$$

where the k -th order wavefunction is most efficiently evaluated in time domain by using the so-called *loop time* variables, for which the time integrations decouple,

$$\begin{aligned} |\psi^{(k)}(t)\rangle = & \left(-\frac{i}{\hbar}\right)^k \int_0^\infty ds_k \dots \int_0^\infty ds_1 G(s_k) \mathbb{V} G(s_{k-1}) \dots G(s_2) \mathbb{V} G(s_1) \mathbb{V} |g\rangle \\ & \times \mathbb{E}(t - s_k) \dots \mathbb{E}(t - s_k - \dots - s_1) |\psi_{\text{field}}\rangle. \end{aligned} \quad (2.175)$$

Here, we remind the reader that $\mathbb{V}$ denotes either an excitation $V^\dagger$ or a de-excitation V , and $\mathbb{E}$ the complementary field operator. In frequency domain, the state reads

$$|\psi^{(k)}(t)\rangle = \left(-\frac{i}{\hbar}\right)^k \int \frac{d\omega_1}{2\pi} \dots \int \frac{d\omega_k}{2\pi} G(\pm\omega_1 \dots \pm\omega_k) \mathbb{V} \dots \mathbb{V} G(\pm\omega_1) \mathbb{V} |g\rangle \\ \times \mathbb{E}(\omega_k) \dots \mathbb{E}(\omega_1) |\psi_{\text{field}}\rangle e^{-i(\pm\omega_1 + \dots \pm\omega_k)t}. \quad (2.176)$$

This representation simplifies the evaluation of the field part of the wavefunction. The frequency arguments in the matter correlation functions add up from right to left: The first evolution carries the frequency $\pm\omega_1$, where “+” is chosen when the operator $\mathbb{V}$ to its right (i.e. the operator preceding the free evolution) is an exciton excitation operator, and “−” when it is a de-excitation operator. The second free evolution is evaluated at $\pm\omega_1 \pm \omega_2$, and so on.

As a rule of thumb, it is most convenient to evaluate optical signals in a representation in which the more complicated correlation function takes on the simplest possible form. Hence, as one can already guess from Eqs. (2.175) and (2.176), the time representation is better suited to simulate signal, in which the matter system dynamics is more complicated than the field dynamics. Conversely, the frequency domain is best suited to investigate signals in which the field dynamics is more involved than the matter system.

In the diagrammatic representation (Fig. 2.11), both wavefunctions $|\psi^{(k)}(t)\rangle$ and $\langle\psi^{(l)}(t)|$ are represented by vertical lines, and each interaction is represented by a horizontal arrow. The loop times mentioned earlier are indicated. They are given by the time delays s_j between the interactions. Note that there is no time-ordering of the interactions on the *ket* with respect to those on the *bra* side.

Finally, the signal is read out. In the course of this dissertation, the representation of the read-out depends on the specific signal. If it involves the interaction with the same fields as the previous interactions, it is represented by an arrow of the same type. If, however, the signal consists in a fluorescence measurement, it is depicted by blue, horizontal arrows, in order to distinguish this spontaneous emission from the other matter-field interactions.

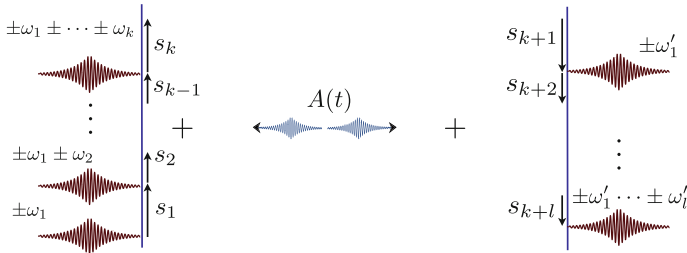


Fig. 2.11 Key ingredients of a loop diagram: the *ket* after k interactions $|\psi^{(k)}(t)\rangle$ (left), the *bra* after l interactions $\langle\psi^{(l)}(t)|$ (right), and the final interaction creating the signal (center). The arguments of the matter Green’s functions during the free evolution between the interactions are indicated in the time and in the frequency domain. $+\omega_i$ indicates an excitation of the matter system, $-\omega_i$ a de-excitation

2.7.2 Ladder Diagrams

Ladder diagrams are used when it is necessary to monitor the evolution of the full density matrix,

$$S^{(n)}(t; \Gamma) = \langle A(t) \rangle_{\text{final}} = \text{tr} \{ A(t) \varrho^{(n)}(t) \}, \quad (2.177)$$

where $\varrho^{(n)}(t)$ denotes the matter-field density matrix after n interactions between the matter and the field. In contrast to the loop diagrams, we obtain full time-ordering of the interactions on the *bra* side with respect to those on the *ket* side: Expansion of the Dyson series (2.12) yields expressions in which an operator acts on one of the two sides of the density matrix. Hence, the time domain signals are given by expressions of the form

$$S^{(n)}(t; \Gamma) = \left(-\frac{i}{\hbar} \right)^n (-1)^{\#(R)} \int_0^\infty dt_n \dots \int_0^\infty dt_1 \text{tr} \{ A(t) \mathcal{G}(t_n) \mathbb{V}_{L/R} \dots \mathcal{G}(t_1) \mathbb{V}_{L/R} \varrho_{\text{matter}} \} \\ \times \text{tr} \{ \mathbb{E}_{L/R}(t - t_n) \dots \mathbb{E}_{L/R}(t - t_n - \dots - t_1) \varrho_{\text{field}} \}. \quad (2.178)$$

Here, the subscripts L/R denote the left-/right-superoperators acting only on the *ket* or *bra* side of the density matrix [see Eqs. (2.19) and (2.20)]. Each interaction $\mathbb{V}_R$ acting on the *bra* side adds a factor (-1) to the overall sign of the diagram, such that the final diagram carries the sign $(-1)^{\#(R)}$, with $\#(R)$ the number of interactions on the *bra* (Fig. 2.12).

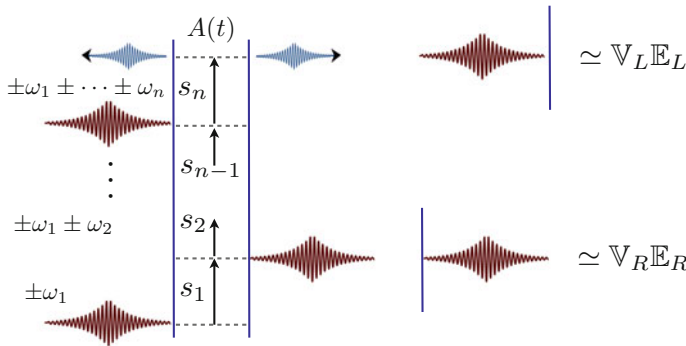


Fig. 2.12 *Left* Representation of a ladder diagram. The evolution of the entire density matrix is monitored, i.e. the interactions on *ket* and *bra* side are fully time-ordered with respect to each other. Time (s_j) and frequency (ω_j) variables used for the evaluation of such signals are indicated. *Right* An interaction acting on the *ket* corresponds to left-superoperators [Eq. (2.19)], and those acting on the *bra* to right-superoperators [Eq. (2.20)]

The frequency domain expression of Eq. (2.178) reads

$$\begin{aligned}
 S^{(n)}(t; \Gamma) = & \left(-\frac{i}{\hbar}\right)^n (-1)^{\#(R)} \int \frac{d\omega_1}{2\pi} \dots \int \frac{d\omega_n}{2\pi} e^{-i(\pm\omega_1 + \dots \pm \omega_n)t} \\
 & \times \text{tr} \left\{ A(t) \mathcal{G}(\pm\omega_1 \dots \pm \omega_n) \mathbb{V}_{L/R} \dots \mathcal{G}(\pm\omega_1) \mathbb{V}_{L/R} \varrho_{\text{matter}} \right\} \\
 & \times \text{tr} \left\{ \mathbb{E}_{L/R}(\omega_n) \dots \mathbb{E}_{L/R}(\omega_1) \varrho_{\text{field}} \right\}, \quad (2.179)
 \end{aligned}$$

where the same rules as before in Eq. (2.176) apply for the sign of the various frequency components.

Impulsive Limit

As described in Sect. 1.2, the multiple frequency dimensions in which conventional nonlinear signals are displayed are created by the Fourier transform of time delays between pulses. In Eqs. (2.175) and (2.178), the time delays are included implicitly in the initial state of the light fields, and hence in the resulting field correlation functions. If the pulse durations are short compared to the scanned time delays, i.e. compared to the relevant time scales of the investigated dynamics, it is possible to apply the *impulsive* approximation: We replace the pulse envelopes in Eq. (2.178)¹⁴ by delta functions. This allows us to carry out the time integrations, and write the impulsive signal as

$$S^{(n)}(t; \Gamma) = \text{tr} \left\{ A(t) \mathcal{G}(t_n^{(0)}) \mathbb{V}_{L/R} \dots \mathcal{G}(t_1^{(0)}) \mathbb{V}_{L/R} \varrho_{\text{matter}} \right\}, \quad (2.180)$$

where the times $t_1^{(0)}, \dots, t_n^{(0)}$ now denote the time delays between subsequent excitation pulses - and not integration variables! The explicit treatment of the field degrees of freedom is thus eliminated.

To distinguish the impulsive signals from the “real” signals given by the convolutions of field and matter correlation functions, we mark the impulsive interactions by wavy lines as shown in Fig. 2.10.

Interpretation

Due to the full time-ordering of all interactions, the ladder diagrams are easier to interpret, as one can always tell in which state the system evolves in between interactions. This is not the case in the description with loop diagrams: Due to the lack of time-ordering between the *ket* and the *bra* side, different fully time-ordered pathways may contribute to a given loop diagram. This greater clarification comes at the price of a much larger number of diagrams that need to be taken into account.

¹⁴We only consider impulsive signals described by ladder diagrams in this dissertation. Of course, the impulsive limit may also be applied to loop diagrams.

2.7.3 Benefits of the Diagrammatic Representation

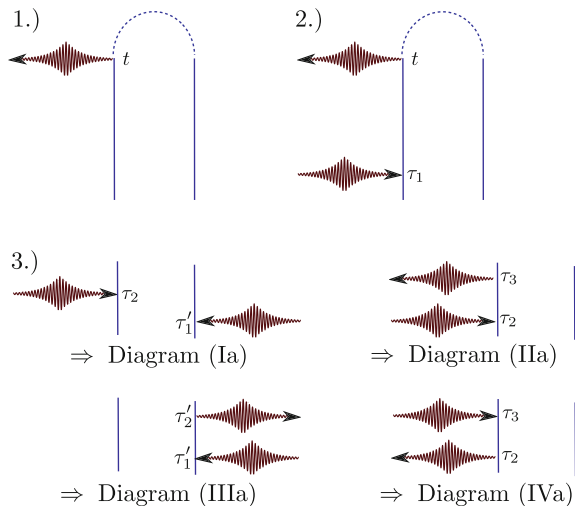
In principle, it is always possible to obtain any perturbative nonlinear signal by straightforward evaluation of all the terms of an expansion of the Dyson series (2.12) to the desired order. For instance, to calculate the fourth-order contribution of a signal, as will be the case in the next chapter, we would obtain four terms for each interaction (two terms from Eq. (2.6) + two possibilities to act either on the *ket* or on the *bra* side of the density matrix), and hence a total of $4^4 = 256$ terms - of which only six finally contribute to the signal (see Fig. 3.13)!

Hence, instead of eliminating these terms by hand, it is a much more economic approach to construct the signal by directly drawing all possible combinations of in- and outgoing arrows that yield nonvanishing contributions, using the following recipe:

- (1) Draw the final interaction creating the signal.
- (2) Add the minimal arrangement of interactions to obtain a nonvanishing signal.
- (3) Distribute the remaining interactions pairwise, such that a) they either create or destroy one excitation on both sides of the density matrix, or b) they create and destroy (or vice versa) one excitation on either side of the density matrix.

Figure 2.13 shows how the third-order contribution to the intensity signal we had discussed in Sect. 2.6, see Fig. 2.9, may be obtained using this approach: The signal is created by a de-excitation at time t [panel (1.)]. The minimal arrangement for a nonvanishing signal (i.e. in this case the linear absorption) is obtained in panel (2.), which consists of an excitation at time τ_1 and the emission creating the signal at time t . To obtain the third-order contribution, we now add pairs of interactions in

Fig. 2.13 Diagram construction of the third-order intensity signal in Fig. 2.9 according to the rules given in Sect. 2.7.3: (1) The de-excitation of the matter at time t creates the signal. (2) To obtain a nonvanishing signal, the *ket* side has to be excited at least once prior to the signal. (3) The two remaining interactions can be added pairwise by either adding an excitation on both sides of the density matrix, or by creating and destroying one on one side of the density matrix, yielding the four diagrams in Fig. 2.9



between this “backbone”.¹⁵ When adding one excitation on each side of the density matrix, we obtain diagram (Ia) of Fig. 2.9. If we add, and then destroy one excitation on the *ket* side, we obtain diagram (IIa). Conversely, creating, and then destroying an excitation on the *bra* side of the density matrix yields diagram (IIIa). And finally, if we destroy, and then recreate the excitation on the *ket*, we obtain diagram (IVa). Any other combination of interactions yields a vanishing field correlation function, either because the excitation pathway along the loop would not end up in the ground state again (to put it differently, such diagrams correspond to terms in Eq. (2.105) in which the *bra* $\langle\psi^{(l)}|$ and the *ket* $V(t)|\psi^{(k)}\rangle$ do not end up in the same state, hence their overlap vanishes), or because a de-excitation acts on the ground state.

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¹⁵Note that our notation of the interaction times is chosen such that each arrow can be identified with its counterpart in Fig. 2.9.

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