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Quantum-enhanced Nonlinear Spectroscopy

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Zusammenfassung

Das Thema der vorliegenden, theoretischen Arbeit liegt an der Schnittstelle zweier ansonsten getrennter Forschungsgebiete - der nichtlinearen Spektroskopie und der Quantenoptik. Einerseits untersucht sie die Nutzung nichtklassischer Lichtquellen aus der Quantenoptik als neue, spektroskopische Werkzeuge. Andererseits verwendet sie Methoden der nichtlinearen Spektroskopie zur Untersuchung von Nichtgleichgewichtsdynamik in typischen Objekten der experimentellen Quantenoptik, wie beispielsweise Ionenketten.

Der erste Teil der Arbeit beschreibt hauptsächlich die Wechselwirkung verschränkter Photonenpaare mit komplexen Quantensystemen. Das Ziel dieses Teils der Arbeit besteht darin, die Verwendung solcher Photonenpaare in der nichtlinearen Spektroskopie zu untersuchen und gegebenenfalls geeignete Experimente vorzuschlagen. Die starken Korrelationen, die zwischen den Photonen herrschen, sollen hierbei genutzt werden, um etwa komplexe spektroskopische Signale zu filtern und gezielt bestimmte Aspekte hervorzuheben oder zu unterdrücken. Bei der Untersuchung der Wellenpakete, die durch die Absorption solcher Photonenpaare erzeugt werden, zeigt sich, dass Mehrphotonenprozesse mit Quantenlicht nicht durch die Fourierungleichung beschränkt sind, welche die gleichzeitige Zeit- und Frequenzauflösung von klassischem Licht limitiert. Wir werden argumentieren, dass dieser Vorteil von Quantenlicht in der Tat eine Konsequenz der sogenannten „Zeit-Energie-Verschränkung“ beider Photonen ist - der Nichtfaktorisierbarkeit der photonischen Wellenfunktion sowohl in der Frequenz- als auch in der Zeitdarstellung: Nur dadurch, dass die Absorption eines Photons die Wellenfunktion des anderen ändert, lässt sich die gleichzeitige Auflösung realisieren. Die derart angeregten Wellenpakete können in Fluoreszenz- und in Absorptionsmessungen nachgewiesen werden. Abschließend zeigen wir noch auf, dass dieser Vorteil in der Zeit- und Frequenzauflösung nicht ausschließlich bei verschränkten Photonenpaaren auftritt, sondern dass die zugrunde liegenden Quantenkorrelationen vielmehr generisch sind, wenn nichtlineare Wellenmischprozesse in einem Regime stattfinden, in dem die elektromagnetische Feldquantisierung relevant wird.

Der zweite Teil der Arbeit präsentiert einen Formalismus zur Beschreibung und Entwicklung nichtlinearer Messprotokolle in einer Ionenkette, die z.B. in einer Quadrupolfalle gefangen sein können. Die zugrunde liegende Motivation besteht darin, die emergente Komplexität der Nichtgleichgewichtsdynamik größerer Ionenketten geeignet zu charakterisieren. Da klarerweise eine direkte Messung des globalen Quantenzustands nur für sehr kleine Systeme möglich ist, sind hierfür notwendigerweise Werkzeuge erforderlich, die gezielt bestimmte Eigenschaften des Systems abfragen. Wir erreichen dies durch die Adaption etablierter Methoden aus dem Bereich der chemischen Physik. In Analogie zu molekularer Spektroskopie „natürlicher Quantensysteme“ schlagen wir Messverfahren vor, um sowohl die elektronischen als auch die phononischen Freiheitsgrade in diesen „künstlichen Quantensystemen“ direkt zu adressieren. Im Gegensatz zu den sehr komplexen Systemen, die traditionell in der nichtlinearen Spektroskopie untersucht werden, ermöglichen gefangene Ionen die Erzeugung sowohl lokaler als auch kollektiver, phononischer Anregungen in der Ionenkette. Diese neuen Kontrollmöglichkeiten eröffnen u. a. die Fähigkeit, kohärenten von inkohärentem Transport phononischer Anregungen zu

unterscheiden. Des weiteren werden Verfahren vorgeschlagen, um kritisches Verhalten nahe eines Phasenübergangs zu beobachten, Anharmonizitäten von Fallenpotentialen zu detektieren und um die Kopplung an dissipative Umgebungen zu charakterisieren.

Abstract

The present dissertation focusses on the interface between two rather disjunct research fields - nonlinear spectroscopy of complex quantum systems and quantum optics. On the one hand, it investigates theoretically the application of nonclassical light sources from quantum optics as novel spectroscopic tools. On the other hand, it adapts methods from nonlinear spectroscopy to probe nonequilibrium physics in engineered quantum optical setups, such as chains of trapped ions.

The first part mostly describes the interaction of entangled photons with complex quantum systems. The main goal of this part of the thesis consists in the discussion of the possible use of such photon pairs in nonlinear spectroscopy, and to propose suitable experimental setups. By investigating the wavepackets created upon their absorption, we show that multi-photon processes with quantum light are not necessarily bounded by the Fourier uncertainty, which restricts the simultaneous time and frequency resolution of classical light. It is argued that this advantage of quantum light is in fact due to the so-called “time-energy entanglement” shared between the two absorbed photons - *i.e.* the nonfactorizability of the photonic wavefunction in, both, the frequency and the time domain: The simultaneous resolution may only be realized, since the absorption of one photon alters the wave function of the other photon. Simulations further reveal how these nonclassically generated wavepackets may be detected in fluorescence as well as in absorption measurements. We further point out that this advantage in the simultaneous time and frequency resolution does not appear exclusively in entangled photon pairs, but that the underlying quantum correlations are rather generic in nonlinear wave-mixing processes, when the quantization of the electromagnetic field becomes relevant.

The second part of this work then develops a novel formalism for nonlinear measurement protocols in a chain of trapped ions. Here, the motivation consists in characterizing the emergent complexity of the nonequilibrium physics of larger ion chains. Since naturally a direct measurement of the global quantum state of a chain is only possible for very small systems, this endeavor requires tools targeting only specific properties of the system. We achieve this goal through the adaption of established methods from chemical physics to such engineered quantum systems. In strong contrast to traditional samples in nonlinear spectroscopy, trapped ions allow for the controlled creation of both local and collective excitation of phononic and electronic degrees of freedom. This greater flexibility in the design of measurement protocols enables us to monitor phonon transport along the ion chain, and to distinguish coherent and incoherent transport. Similar methods can further monitor critical behavior near a phase transition, detect anharmonicities in the trap potential, and the coupling to a decohering environment.

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1. Introduction

Nonlinear optical spectroscopy has emerged as an indispensable tool in semiconductor physics, (physical) chemistry, and even molecular biology, to probe - inter alia - many-body correlations, decoherence or transport processes. Let us start with a definition of this central theme “nonlinear spectroscopy”: As we understand it in the present dissertation, nonlinear spectroscopy employs sequences of short pulses strong enough to stimulate a nonlinear response from the sample, which contains more information than its linear counterpart, since it is connected to higher-order correlation functions of the sample system. This nonlinear response is identified via its (quadratic, cubic, quartic, ..) dependence on the intensity of the incoming pulses. By establishing a connection to quantum optics, this dissertation aims to add a new perspective to the field of nonlinear spectroscopy, and develop new measurement strategies in quantum optical settings.

Historically, it is clear that the development of coherent radiation sources of sufficient intensity poses a natural predicament to extract a nonlinear response from a sample system. Therefore, it should come as no surprise that nonlinear techniques were pioneered in nuclear magnetic resonance in the radio frequency regime [Ernst90], where nuclear spin rotations may be induced to probe, e.g., conformations of complex molecules. Associated with the radio frequency regime, these techniques allowed to access dynamics with characteristic time scales of the order of microseconds. The advent of laser sources in the near infrared optical regime [Maiman60] then triggered the development of sources of sufficient intensity and phase stability to extract nonlinear signals in the optical regime. Experiments were first implemented in the infrared [Hamm11], where they could probe vibrational couplings in molecules or investigate relaxation or transport processes on picosecond time scales. Recent years have seen the development of strong, coherent sources in the visible regime which allow for nonlinear spectroscopic measurements of electronic levels and energy transport [Brixner04], and pushed the time resolution into the femtosecond regime. In the foreseeable future, the maturing of coherent ultraviolet and X-ray sources promises access to the attosecond regime [Bucksbaum07] with “the ability to observe correlated electron dynamics in real time” [Loh13], or the time-resolved study of core-excited states [Hanson95, Biggs13]. Besides accessing ever-higher energies and shorter timescales, new developments continuously refine and improve existing methods. Crudely speaking, it is clear that new developments can only stem from either of two sides: either from the involved electromagnetic fields, where new sources may improve existing measurement schemes, or from the sample systems, where new target systems may require the development of novel methods. In this dissertation, we will touch upon both sides.

On the side of the excitation pulses, possible new methods using classical light sources include the exploitation of strong field effects [Gelin11], where multiphoton processes

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enhance the spectral resolution, and pulse shaping [Herek02, Silberberg09, Shapiro12], where the spectral phase of the pulses is tailored to enhance or suppress certain spectroscopic features. Other approaches aim to overcome the problem that molecular sample systems are typically much smaller than the diffraction limit of optical pulses, thereby inhibiting local excitations and probes in such systems. The use of nanofields [Aeschlimann11, Schlosser13] promises spatial resolution beyond the diffraction limit of optical fields. On the sample side, advances in the fabrication of novel materials on nano- or even molecular scales [Scholes06] call for the constant development and adjustment of nonlinear spectroscopic methods.

Besides these developments relying on a classical description of the light fields, several recent developments necessitate the description of nonlinear optical signals in the framework of quantum electrodynamics. For instance, the strong coupling between molecular excitons and a vacuum cavity mode requires the adaptation of the dressed state picture in chemical physics [Schwartz11]. Even more intuitively, it is quite evident that single molecule spectroscopy [Moerner02, Brinks14] cannot be described using classical fields: Whereas the time-averaged fluorescence may still be treated phenomenologically, the recent observation of photon-antibunching in the fluorescence from a single LH2 complex at ambient temperatures by the group of van Hulst [Wientjes14] clearly requires the adaptation of Glauber’s photon detection theory for such signals to properly account for the photon statistics of the emitted light. Similarly, the recently reported measurement of the absorption of individual photons in retinal rod cells [Phan14] calls for the development of a combined approach, which takes into account the quantum nature of both field and sample. To remedy this situation, and to propose possible alternative, fruitful intersections between these two fields, the present dissertation aims to establish a connection between electronic nonlinear spectroscopy and quantum optics which, surprisingly, has remained largely unexplored to date.

The first step in this endeavor consists in a fully quantum-mechanical derivation of arbitrary nonlinear optical signals. This novel approach to nonlinear spectroscopy not only allows us to recover standard signals, which are commonly derived based on a classical treatment of the light field, but also encompasses possible novel measurement setups such as photon counting.

This in turn enables us to turn to the first focus of our work: to explore the adaptation of nonclassical light sources from quantum optics, which show great promise as novel spectroscopic tools in the optical and near-IR regime. Certain nonlinear signals scale linearly in the pump intensity when induced by entangled photon pairs, whereas they scale quadratically for classical light [Javanainen90, Dayan05]. Hence, optical nonlinearities may be accessed at much lower photon flux compared to the classical regime [Lee06, Harpham09, Guzman10, Upton13], which may help reduce background contributions of linear signals, and minimize damage to photo-sensitive samples. Furthermore, entangled photons feature strong correlations and entanglement in both their frequency and their polarization degree of freedom [Pan12]. It will be the main goal of this thesis to elucidate how these correlations may be used to either control excited state distributions in complex quantum systems, or to enhance the sensitivity of measurements by

employing intricate detection setups inspired from quantum optics. Specifically, we will focus on the time and frequency correlations of entangled photons: Strong correlations in the arrival times of entangled photon pairs can suppress intermediate dynamics between successive absorption events, thereby enabling the excitation of wavepackets that could not be induced with classical light.

The second focus of the present dissertation concerns the adaptation of techniques from nonlinear spectroscopy to quantum optics: Experimentalists in quantum optics have made great progress in the assembly of well-controlled quantum systems [Schneider12]. Ions in quadrupole traps [Leibfried03], ultracold atoms in optical lattices [Bloch08], Rydberg atoms in optical tweezers [Fuhrmanek11, Günter13], and cavity QED systems [Raimond01, Walther06, Cohen-Tannoudji11] all represent - especially in comparison to “traditional” sample systems in nonlinear spectroscopy - unusually clean quantum systems with few, perfectly controlled constituents which can be fully characterized by quantum state tomography [Raymer13, Ramm14]. However, as these constituents are assembled to construct engineered, multipartite systems, it is necessary to develop new tools to interrogate such “quantum-optical” samples, since the experimental overhead of state tomographies increases exponentially with the system size, and is obviously not a viable strategy to characterize larger assemblies of atoms/ions. Hence, the reliable extraction of specific information from a system at the face of ever-increasing complexity poses a fundamental problem in a number of areas in modern physics. For instance, without reliable and fast entanglement certification, quantum computation protocols can no longer be carried out with confidence. As one possible approach to remedy this situation, this dissertation develops a theory of nonlinear signals in such synthetic quantum systems, focussing mainly on the case of trapped ions. Instead of trying to characterize the entire, exponentially growing quantum state, we design measurement protocols to target specific properties of the system. These signals are capable of investigating coherent and incoherent quantum transport, to conveniently monitor excited state dynamics in the vicinity of quantum phase transitions, or to assess the reliability of entanglement creation. In yet another strong contrast to traditional (physical chemistry) sample systems, it is experimentally possible to address the individual ions in a linear trap, providing unique possibilities for the design of novel measurement schemes.

The dissertation is structured as follows: In the following section 2, we will introduce conventional, phase-coherent spectroscopy, and explain its great success - but also point out its limitations. This will lead us to review seminal photonic entanglement effects, insofar as they may be relevant to their spectroscopic application, as well as previous works concerning quantum optical spectroscopy. Finally, we will also introduce the trapped ion crystals, and discuss the need to establish new experimental methods to interrogate them. Chapter 3 will then introduce the Liouville structure, in which our theory is formulated. With this language at hand, we will present the first result of this dissertation - the derivation of nonlinear signals starting from a quantum-mechanical treatment of the field. After further deriving effective interaction operators for the theory of nonlinear signals in trapped ion chains, we will introduce the diagrammatic construction of nonlinear signals, which will form the backbone of our later discussion,

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and also point out the connection between the description in terms of susceptibilities and transition amplitudes.

The chapters 4, 5 and 6 then constitute the main body of the work on quantum spectroscopy. Chapter 4 lays the foundation by examining the excited state distributions created by the absorption of entangled photon pairs, and by simulating the fluorescence signal from these distributions. These insights are further elaborated in chapter 5, where we directly simulate absorption spectra of entangled photons. Chapter 6 finally discusses an interferometric setup, in which one photon does not interact with the sample, but is detected in coincidence with the second photon to exploit their quantum correlations to filter the spectroscopic signal. The last chapter, 7, on quantum spectroscopy puts the previous results into a broader perspective, by investigating quantum correlations in frequency conversion, and pointing out their possible use in spectroscopy. Finally, we develop a theory for nonlinear spectroscopic signals in trapped ion chains in chapter 8, before concluding the work.

2. Background

In this chapter, we review the state of the art of conventional nonlinear optical spectroscopy, of entangled photon experiments insofar as they concern this dissertation, and of trapped ion systems.

Due to the enormous range of time and length scales as well as associated sample systems and investigated physical phenomena, as briefly stated in the introduction above, an exhaustive overview of nonlinear spectroscopic methods would go way beyond the scope of the present dissertation, and can be found in a number of excellent textbooks, such as [Ernst90, Mukamel99, Hamm11]. Therefore, we here restrict our discussion to nonlinear optical spectroscopy and the associated physics which are determined by the time and energy scales set by the optical regime. Most prominently, we focus on exciton dynamics and energy transport processes in molecular aggregates, but also touch upon spectroscopy in solid state (semiconductor) systems. Due to structural similarities between the Hamiltonians of these systems, and those employed in the treatment of trapped ion chains, this discussion already gives us a first impression of the capabilities of nonlinear spectroscopy in the latter part of this dissertation.

Similarly, in the second part of this chapter, we do not intend to give a complete overview of the use of entangled photons in photonic quantum computation (or quantum optics, in general). Instead, we focus on applications which we deem relevant for their possible use in nonlinear optical measurements, and comment on the relevance of photonic entanglement in each application. Specifically, we discuss the interferometric detection of entangled photon pairs and related phenomena, and review previous works on entangled photon spectroscopy.

In the third part of this chapter, we shortly introduce the quadrupole ion trap, its different degrees of freedom, as well as aspects of their experimental control. We will further state the problem, *i.e.* clarify why a theory of nonlinear signals in ion chains is called for.

2.1. Nonlinear optical spectroscopy

This section starts with a brief recollection of the theoretical framework in which nonlinear optical signals are typically formulated [Mukamel99, Boyd03]. Afterwards, we focus on four-wave-mixing signals, and discuss their experimental realization as well as their information content, at hand of the signal created by potassium vapor, a rather simple sample system with only two well-separated transitions, in some detail. The intuition gained this way is used in the final part of this section where we turn to the discussion of four-wave-mixing signals of more complex systems, such as semiconductor devices or

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biomolecular aggregates. The techniques presented here can be found in greater detail in many review papers, see e.g. [Jonas03, Cho08, Milota09, Ginsberg09].

Conventionally, the nonlinear optical response of quantum systems is formulated in a semiclassical description, where the light fields are described by classical Maxwell equations, and the matter system only enters as a source for the polarization. The system response to the excitation by light pulses is connected to the *nonlinear polarization* $P^{NL}(t)$ through its *response function* $R^{(n)}(t_1, \dots, t_n)$. For instance, a particularly important measurement setup is depicted in Fig. 2.1, where three pulses induce a nonlinear response in the sample. The emitted field is then created by the third-order polarization, which may be written as

$$P^{(3)}(t, \Gamma) = \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 R^{(3)}(t_3, t_2, t_1) \epsilon_3(t - t_3) \epsilon_2(t - t_3 - t_2) \epsilon_1(t - t_3 - t_2 - t_1). \quad (2.1)$$

Here, $\epsilon_i(t) = E_i(t) + E_i^\dagger(t)$ denotes the i -th optical pulse interacting with the matter system (and E and $E^\dagger$ its positive (negative) frequency components [Loudon00]), and Γ the set of control parameters such as time delays, center frequencies etc. For the sake of simplicity, we have omitted the vector nature of the light, and the tensorial structure of the response function in non-isotropic media. The response function $R^{(3)}$ is the Fourier transform of a better-known material quantity - the third-order *susceptibility* $\chi^{(3)}$,

$$\chi^{(3)}(\omega; \omega_3, \omega_2, \omega_1) \equiv \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1 R^{(3)}(t_3, t_2, t_1) e^{i(\omega_1(t_1+t_2+t_3) + \omega_2(t_2+t_3) + \omega_3 t_3)}, \quad (2.2)$$

where $\omega = \omega_1 + \omega_2 + \omega_3$. This quantity is conventionally calculated diagrammatically, where each contribution is represented by Feynman diagrams [Mukamel99], and thereby defines an excitation *pathway*, *i.e.* a succession of excitations and de-excitations, thereby providing some intuition into what is going on in the matter system. The diagrammatic theory in a QED formulation forms the basis of this dissertation, and will be introduced in greater detail in chapter 3.

In order to extract the nonlinear susceptibility, sufficient laser power and phase stability is required, which was not achieved in the optical regime until 2004 [Cowan04, Brixner04]. During the last ten years, the field of nonlinear optical spectroscopy has seen an - it is tempting to say - unprecedented growth, and has influenced and connected numerous, previously unrelated research areas [Brańczyk14]. The reason for this boom lies in the tremendous importance of the processes in this energy regime: It provides the time resolution to directly probe the ultrafast energy transport and charge separation processes in photosynthetic systems [Brixner05] as well as in artificial organic solar cells [Rozzi13, Vasa13]. In fact, it was the observation of surprisingly long-lived oscillatory beatings in the former case [Engel07] that created much of the attention nonlinear spectroscopy has received in recent years. But besides this debate, nonlinear optical spectroscopy has also been applied to the study of electronic level dynamics in very diverse systems ranging from nanoscale solid state devices [Dresselhaus05,

Figure 2.1.: Schematic setup of an optical four-wave mixing experiment: Three fields induce the nonlinear response of a sample system in the directions $\vec{k}_4 = \pm\vec{k}_1 \pm \vec{k}_2 \pm \vec{k}_3$, which is combined with a local oscillator field and spectrally dispersed. The time delays τ, T and t may be varied, and their Fourier transform yields the multidimensional spectra.

Li06, Karauskaj10, Dresselhaus10, Kasprzak11, Turner12] over nitrogen vacancy centers [Huxter13] to strongly correlated electron systems [Petersen11, Fausti11].

The basic idea is depicted schematically in Fig. 2.1. Three pulses trigger a nonlinear response in the sample system, which is then combined with a controlled local oscillator field, and detected in a spectrometer. This form of field measurement is typically referred to as *heterodyne detection* [Ginsberg09].¹ The first two time delays between the pulses, τ and T , are controlled, whereas the signal and local oscillator fields are detected over time, and spectrally dispersed in a spectrometer, effectively yielding the Fourier transform of the third time delay [Dai10]. Hence, one obtains the complex-valued signal $\propto P^{(3)}(\tau, T, \Omega_t)$.

The spectacular success of such multi-wave mixing signals stems to a large extent from one important ingredient which has been left unmentioned so far: the ability to disentangle the myriad of possible excitation pathways in the interaction of three laser pulses with a complex matter system using spatial *phase matching*. To describe this effect, we resort - for one of very few occasions in the course of this dissertation - to a vector description of the involved fields. The three pulses which create the nonlinear polarization in the sample are injected into it from different angles (one usually employs the so-called *box geometry* [Brixner04]). The sample consists of a bulk of randomly oriented constituents - be it molecules or quantum dots - which are surrounded by a solvent or trapping matrix. The light pulses trigger a nonlinear response in some of these

¹Note that in quantum optics, the same measurement setup is typically referred to as *homodyne detection* [Lvovsky09], which - in nonlinear spectroscopy terminology - typically refers to the direct intensity measurement of the nonlinear polarization, $\sim |P^{(3)}|^2$ [Mukamel99].

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particles which then emit light in various directions creating a complex (and possibly time-dependent) diffraction pattern in the far field. To see this, we add the spatial dependence of the fields in Eq. (2.1), $\epsilon_i(\vec{r}, t) = E_i(t) \exp(i\vec{k}_i\vec{r}) + E_i^\dagger(t) \exp(-i\vec{k}_i\vec{r})$. For a particle at position $\vec{r}$, the induced nonlinear polarization will then carry the spatial dependence of the involved light pulses, $\sim \exp[i(\pm\vec{k}_4\vec{r} \pm \vec{k}_3\vec{r} \pm \vec{k}_2\vec{r} \pm \vec{k}_1\vec{r})]$, where the “+” (“-”) denotes an interaction with the positive (negative) frequency component of the field. Assuming a uniform distribution of emitters within a macroscopic (*i.e.* much larger than the inverse wavevector mismatch $1/\Delta k$) sample, one can easily see that these phase factors will destroy the coherent signal on average - unless the wavevectors cancel. Hence, the macroscopic nonlinear response will be emitted in the directions

$$\vec{k}_4 = \pm\vec{k}_1 \pm \vec{k}_2 \pm \vec{k}_3. \quad (2.3)$$

Depending on the choice of prefactors in Eq. (2.3), different sets of excitation pathways are selected, as we will see in the following. Note that our discussion, so far, has not taken the level structure of the sample system into account, which may cancel the signal in some directions. One distinguishes the following, seminal optical signals (table 2.1):

Direction	Signal
$-\vec{k}_1 + \vec{k}_2 + \vec{k}_3$	<i>Photon Echo</i> (PE), rephasing
$+\vec{k}_1 - \vec{k}_2 + \vec{k}_3$	<i>Photon Echo</i> (PE), non-rephasing
$+\vec{k}_1 + \vec{k}_2 - \vec{k}_3$	<i>Double Quantum Coherence</i> (DQC)

Table 2.1.: Nomenclature of phase-matched third-order signals. The terminology originates from nuclear magnetic resonance, where the rephasing spin echo may compensate for locally varying precession frequencies of the nuclear spin [Ernst90], *i.e.* eliminate the so-called *inhomogeneous broadening* (static disorder/slow fluctuations). Similarly, the DQC signal may probe interactions between spins.

Besides spatial phase matching, it is also possible to select pathways using *phase cycling* by either pulse shaping [Peifang03, Vaughan07] or acousto-optical modulation [Tekavec07]. These techniques have the additional advantage that they may also be applied to single quantum systems (remember, the spatial phase matching is a constraint imposed by ensemble measurements!), and be used to obtain phase-cycled fluorescence signals from single molecules which contain the same information as stimulated signals from bulk systems [Gerhardt10, Hildner11, Hildner13]. Since our protocol of nonlinear measurements in trapped ion systems is based on this method, phase cycling will be described in greater detail later in chapter 8.

2.1.1. Nonlinear spectroscopy of potassium

We now present examples of PE and DQC signals in potassium vapor [Dai10, Dai12]. This rather simple system allows for a clean interpretation of the signals, and enables

Figure 2.2.: a) Absolute value of the photon echo signals (see Table 2.1) in direction $-\vec{k}_1 + \vec{k}_2 + \vec{k}_3$ (rephasing) and $\vec{k}_1 - \vec{k}_2 + \vec{k}_3$ (non-rephasing). Left panel: Experimental data. Right panel: Simulations. (Figure from Ref. [Dai10] with axis labels adapted)

b) Level scheme of the optically active electronic levels in potassium.

us to develop some intuition for signals from more complex biomolecular samples later in this chapter.

Fig. 2.2 shows the sum of rephasing and non-rephasing PE signals obtained from a vapor cell with potassium [Dai10] - both experimental results and the corresponding theoretical simulations.² To interpret these spectra, let us first inspect the structure of the optically active levels in Fig. 2.2b). Two transitions, D_1 and D_2 , connect the common ground state with two excited states. Both transitions may be clearly read off the photon echo signal along the diagonal [Fig. 2.2a)]. But in addition to this information, which may be obtained with linear spectroscopy as well, we observe strong peaks along the anti-diagonal. These crosspeaks may be traced back to the coupling between the excited states mediated by the common ground state: The photon echo contains a pathway, in which the first two pulses drive the D_1 -transition, for instance, and the final two pulses the D_2 -transition. Due to the common ground state, this creates a signal with the correct phase matching condition $\sim \exp[i(\vec{k}_4 - \vec{k}_3 \pm \vec{k}_2 \pm \vec{k}_1)\vec{r}]$. Were the two diagonal peaks due to two different atomic species within the sample, for instance, we would not observe the crosspeaks [Dai10]. In this situation, crosspeaks could only stem from the collective response of two atoms at $\vec{r}_i$ and $\vec{r}_j$, yielding the phase signature $\sim \exp[i(\vec{k}_4 - \vec{k}_3)\vec{r}_j \pm (\vec{k}_2 \pm \vec{k}_1)\vec{r}_i]$, which does not satisfy the correct phase-matching condition: On average, this signal will be emitted in the direction $\vec{k}_4 = \vec{k}_3$, as the average with respect to the position $\vec{r}_i$ of the other atom is independent of the final two interactions that create the signal (In the next paragraph, we will however discuss the DQC signal, which stems from the collective response in *dense* atomic vapor). Hence, nonlinear spectroscopy is

²The sum of the two directions is employed to obtain absorptive lineshapes, which are easier to interpret [Khalil03]. Each individual signal shows distinct lineshapes with dispersive tails, which complicate their interpretation.

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able to distinguish these two cases by spreading the signal onto two frequency axes. The lineshapes also allow for the measurement of correlation functions of local energy fluctuations [Lorenz08], which can distinguish different environmental influences.

Furthermore, the rephasing part of the PE can suppress inhomogeneous broadening (slow fluctuations) which shows up in the non-rephasing part [Kjellberg06].³ The peaks in Fig. 2.2 are however well-separated, and this property is therefore not vital in our present showcase example. In the later part of this section, we will review more complex spectra where it will become essential.

The second time delay T is kept fixed at 580 fs [Dai10] in Fig. 2.2, but may be varied as well to reveal Raman transitions in the system [Li13], for instance. In more complex systems, the variation of this time delay may also detect environment-induced, irreversible exciton transport [Engel07]. Together with the aforementioned lineshapes, a lot of information on the surrounding environment of the system degrees of freedom may be extracted.

The DQC signal (see table 2.1) of (dense) potassium vapor is depicted in Fig. 2.3, with four pronounced, dispersive resonances at the possible sums of the transition energies, $D_{1,2} + D_{1,2}$. Its most remarkable feature lies in the observation that the signal vanishes for non-interacting systems [Li08], due to destructive interference. Hence, as mentioned before, the resonance structure in Fig. 2.3 stems from the *collective* response of pairs (or larger numbers) of potassium atoms, created by their weak (van-der-Waals) interaction.⁴ Since the main peaks coincide with the three possible sums of the D_1 - and D_2 -lines, we conclude that the interaction is too weak to induce a detectable level shift on the scale of the frequency resolution.

The DQC signal may also be used to reveal interactions between excitons, *i.e.* between bound electron-hole pairs, in more complex samples such as quantum dots [Karaiskaj10], carbon nanotubes [Abramavičius12], or organic molecules [Li08, Kim09a]. We will use similar signals later in chapter 8 to investigate anharmonicities in the confining potential of trapped ions.

2.1.2. Molecular aggregates

Having understood how to read multidimensional plots of nonlinear signals in the “simple” example above, we now turn to an example of those complex quantum systems where nonlinear spectroscopy has been shown to unfold its full potential. It will serve as a case study to explore the unique capabilities of multidimensional spectroscopy - but also to identify its limitations - in the investigation of complex nonequilibrium processes

³Slow fluctuations alter the oscillation frequencies of each individual emitter. The suppression originates from the “rephasing” nature of the signal, where during t_1 and t_3 the signal oscillates with opposite sign, thereby canceling the acquired phase difference between different emitters. It is usually explained with the analogy of having several sprinters run with different speed during a time t_1 . Then their direction is reversed, such that after $2t_1$ they all end up at the same spot again, thus canceling their different velocities.

⁴In the present case, the interaction is caused by fluctuations of the atomic electron densities (as the microscopic cause of the van-der-Waals forces [Buhmann07]). However, the DQC signal may detect *any* interaction that shifts the energy spectrum.

Figure 2.3.: Real part of the double quantum coherence (DQC) signal (see table 2.1) of potassium vapor [see Fig. 2.2b)] in direction $+\vec{k}_1 + \vec{k}_2 - \vec{k}_3$. The dotted vertical lines denote the D_1 and D_2 resonances, and the horizontal lines the two-exciton resonances as indicated.

The resonance at $(D_1, D_1 + D_2)$ is markedly weaker than its counterpart at $\Omega_1 = D_2$, because of the weaker dipole moment of D_1 compared to D_2 . The signal is normalized to the maximal and the minimal peak intensity. (Figure from Ref. [Dai12])

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Figure 2.4.: The PE signal of the reaction center of the $D1 - D2 - cytb559$ complex of Photosystem II, for different delay times T (see Fig. 2.1). The vertical and horizontal lines indicate the energies of exciton states according to the model developed in Ref. [Novoderezhkin07]. The signal intensities at the marked red spots are plotted as functions of the transport time T in the lower panel. Figures taken from Ref. [Myers10], with the axes renamed to account for our present notation.

in nature and technology. The limitations of the present state of the art represent a major motivation for this dissertation.

We chose an experimental PE study on the reaction center of the $D1 - D2 - cytb559$ complex⁵ of *Photosystem II* as our example [Myers10]. Since we will present simulations of another reaction center later in this manuscript, we will not introduce the system at this point in greater detail. Let it suffice here to point out that it is instrumental for photosynthesis of plants, and consists of a pigment-protein compound with six chlorophyll and two pheophytin pigments [Blankenship02], which may absorb light in the optical regime. Its biological function consists in breaking up the bound electron-hole pairs which are created upon photoexcitation. This happens in the so-called *special pair* of two strongly-interacting chlorophylls. Energy is transported to this pair on sub-picosecond timescales, and this transport process may be probed with ultrafast optical spectroscopy.

Some results of Ref. [Myers10] are shown in Fig. 2.4. Four two-dimensional plots depict the signal for different intermediate delay times T (which had been kept fixed in

⁵The complex refers to the protein backbone in which the photosystem is fixed.

our above discussion of potassium vapor). Furthermore, vertical and horizontal white lines indicate the eigenenergies of a model Hamiltonian of the system according to Ref. [Novoderezhkin07]. For small T , the signal is given by a broad resonance which is greatly elongated along the diagonal. It corresponds to overlapping resonances of the various excitons (*i.e.* the eigenstates of the Hamiltonian of the entire compound) forming a broad absorption band. But one may also observe weak off-resonant structures. The temporal evolution of the intensity of such off-diagonal peaks, labelled $CP1$ and $CP2$ in the top left panel of Fig. 2.4, may be attributed to downhill exciton transport, *i.e.* from the higher-energy excitons to the special pair. Peak $CP1$ corresponds to a process where exciton 9 (highest energy) is excited by pulse 1, but the system reemits energy corresponding to the emission from exciton 1 (lowest energy). This analysis is underpinned by the bottom panels of Fig. 2.4, where the evolution of the intensities of the signal at the points marked by the red spots in the third panel ($T = 1504$ fs) is shown as a function of the transport time T , which allows for the extraction of transport timescales between excitons. For very long transport times ($T = 100$ ps) in the right top panel, the entire population has been transferred to low-energy excitons, such that the signal only consists of a horizontally elongated resonance, when Ω_t matches the energy of the low-energy eigenstates.

But even though nonlinear spectroscopy allows for the measurement of these timescales, it is apparent that the interpretation of such plots suffers from many overlapping features due to the large homogeneous broadening (*i.e.* broadening of the resonances induced by fast fluctuations of the chlorophyll environments) of the energy resonances relative to the energy splitting between different exciton states. As stated by the authors, “*energy transfer from excitons 3, 4, and 5 to excitons 1 and 2 is difficult to discern due to the overlapping diagonal feature in this region.*” The reason lies in the large bandwidth that is associated with the ultrashort (few femtoseconds [fs]) pulses. Each pulse always excites wavepackets of all excitons, and the Fourier transform of the time evolution yields the broad distribution of Fig. 2.4 which cannot resolve transport from excitons 3 or 4 to exciton 1.

This lack of control over the excited wavepackets brings about another complication in the *interpretation* of such PE signals: As pointed out in Ref. [Brumer12], the presence of coherence between the excitons in such nonlinear signals need not necessarily be relevant for its biological function. The transport mechanisms taking place after laser excitation may be markedly different from those under natural light conditions, where the excitation is typically transferred (incoherently) from neighboring light harvesting complexes. Hence, the best one can do is to model the system such that it agrees with every spectroscopic measurement, and then simulate natural illumination based on this model. It is therefore imperative to develop complementary spectroscopic techniques which may further restrict the parameter space of model Hamiltonians.

One promising path towards such novel techniques, which we will pursue in this dissertation, lies in the use of quantum light. It features strong frequency-time correlations which may be used to excite non-classical two-exciton distributions in molecular aggregates, creating new “control knobs” for the manipulation of nonlinear signals. A very

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Figure 2.5.: Left panel: Basic scheme of parametric downconversion. A pump beam is injected into a birefringent crystal where a pump photon with frequency ω'_p is split into two daughter photons with frequencies ω'_1 and ω'_2 . Due to energy conservation, we have $\omega'_p = \omega'_1 + \omega'_2$. Right panel: Intensity profiles of a) noncollinear b) collinear and c) spatially separated phase-matching, taken from Ref. [Guzman10].

different approach, which will also be explored, makes use of the great flexibility in system and environment engineering with trapped ions. This opens the possibility to directly test transport theories under well-controlled conditions.

The necessary background for both approaches will be briefly outlined in the following sections.

2.2. Entangled photons

Besides their importance in fundamental tests of quantum mechanics [Pan12], entangled photons have emerged as a prime testbed for the implementation of quantum computation protocols [Kok07]. Driven by these goals, the experimental methods for the creation, manipulation, and detection of entangled pairs have undergone great progress in recent years. In this section, we introduce only one possibility to create such photon pairs - downconversion in a birefringent crystal. Other systems include biexciton decay in semiconductors [Edamatsu04, Stevenson07], four-wave mixing in optical fibers [Garay-Palmett07, Garay-Palmett08], or cold atomic ensembles [Balić05, Cho14], which all create entangled photon pairs with similar properties, such that their description will not add additional insight to our discussion. Afterwards, we will elaborate on some entanglement-related effects in detail, connect the properties responsible for these effects with their possible use as spectroscopic tools, and review previous work in entangled photon spectroscopy. It will become clear that there cannot be a clear demarcation between these two aspects, since any interferometric measurement can also be used - at least in principle - to perform spectroscopy by placing a sample system into one or both of the entangled beams.

2.2.1. Parametric downconversion

Parametric downconversion is illustrated in Fig. 2.5, where a pump photon is downconverted in a birefringent crystal into two daughter photons, denoted here 1 and 2.⁶ A birefringent crystal is characterized by an optical axis along which the group velocity of propagating pulses differs depending on their polarization [Boyd03]. One thus distinguishes two ordinary (*o*) optical axes from this extraordinary one (*e*). Depending on the polarization and the incoming direction of the pump pulse, it is possible to trigger downconversion in the two channels, $e \rightarrow oo$ or $o \rightarrow eo$ [Shih03]. The former process is referred to as *type-I* downconversion, and the latter one as *type-II*. In this dissertation, we will focus on *type-II* downconversion where the photons are created with orthogonal polarization, and travel with different group velocities.

Due to the conservation of energy and momentum, the photon pairs satisfy

$$\begin{aligned}\omega'_p &= \omega'_1 + \omega'_2, \\ \text{and } \vec{k}'_p &= \vec{k}'_1 + \vec{k}'_2.\end{aligned}\tag{2.4}$$

The former equality is the essential cause for what is typically referred to as *time-energy entanglement* [Franson89, Tittel00, Ali Khan06]: If the pump frequency ω'_p is distributed narrowly around a central frequency ω_p , so is the sum of the two downconverted photons. At the same time, the two photons are created almost simultaneously (characterized by the so-called *entanglement time* [Fei97]), and this strong time correlation translates into a very broad bandwidth of each of the two photons (see Fig. 2.6). The frequency of the individual photon is not well-defined, but the measurement of the other photon's frequency will collapse it onto a value such that Eq. (2.4) holds. Note that the notion of time-energy entanglement differs from the regular notion of entanglement of different degrees of freedom, as is the case, for instance, in the polarization entanglement of the photons. Whereas polarization entanglement has a clear definition in terms of perfect correlations in *any* measurement basis [Mintert09], and may be detected in the violation of Bell's inequality, the time does not constitute a quantum-mechanical observable, and hence no such criterion may be derived. We will see, however, later in this dissertation that time-energy entanglement has a well-defined formal definition in terms of the nonseparability of the photonic wavefunction in, either, the time or the frequency domain.

In a similar manner, Eq. (2.5) shows that the photon pairs are also entangled in their wavevectors [Law04]. This property is put to use in several applications such as quantum imaging [Pittman95] or subwavelength diffraction [Boto00, D'Angelo01], where entangled photons may obtain higher contrast than their classical counterparts [Bennink04].⁷

Besides the concrete applications, this relation may also be used to control the central frequencies ω_1 and ω_2 by selecting the wavepackets, e.g., via small slits [Peřina98,

⁶Historically, the two photons are often referred to as *signal* and *idler*. This nomenclature originates from the use of PDC as a single photon source (the signal), when the second photon was not recorded (*i.e.* remained idle).

⁷A similar effect will be shown in the two-photon absorption of entangled photons in complex quantum systems later in this manuscript.

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Figure 2.6.: Frequency and time correlations between entangled photons for realistic parameters in a BBO crystal [Jennewein09]. a) Frequency anti-correlations due to a narrow pump pulse. Each of the two photons has a very large bandwidth (marginal along one of the axes), but once the first photon is measured, the wavefunction of its counterpart collapses onto a very narrow frequency window. b) Time correlations of the same entangled pair. Once the first photon arrives, the other one follows within a very short time delay. However, the arrival time of the first one is determined by the time resolution of the pump pulse, and therefore the distribution is very broad. The frequencies are given in wavenumbers (cm^{-1}), and the times in femtoseconds (fs). Note that this so-called *two-photon joint spectral density* may be measured explicitly [Kim05, Mosley08].

Joobeur94, Grice97]. Different possibilities for spatial phase matching are shown in Fig. 2.5, as reported in Ref. [Guzman10]: Depending on the orientation of the pump pulse with respect to the optical axes of the birefringent crystal, Eq. (2.5) may be fulfilled by different geometries. In the course of this dissertation, we will focus on *collinear* downconversion which somewhat simplifies the notation since it allows for a one-dimensional treatment of the fields, but captures all the essential physics, *i.e.* the time-energy correlations as well as the polarization entanglement (the latter is however not discussed in the present dissertation).

2.2.2. Entangled-photon interferometry

Having introduced the main concepts for (time-energy) entanglement of photon pairs, let us now turn to the most important experimental signatures thereof. Their first and most famous application was undoubtedly the violation of Bell's inequality in the polarization degree of freedom [Aspect81, Aspect82a, Aspect82b, Ou88]. Notwithstanding the importance of these experiments, we will be only concerned with the frequency degrees of freedom in the course of this dissertation, and we will therefore focus on effects which directly relate to time-frequency entanglement (or correlations).

Hong-Ou-Mandel (HOM) effect The first and most important manifestation in two-photon interferometry was described by Hong, Ou and Mandel in their seminal experiment [Hong87] which demonstrated the measurement of subpicosecond time delays in the coincidence count rate of entangled photons: Two-photon wavepackets created by parametric downconversion are mixed on a balanced beamsplitter, and then detected in coincidence.

But even though it employs photon pairs from a downconversion source, it is easy to see that this experiment measures the indistinguishability of the two photons rather than their entanglement. In a very crude picture, the effect is explained in a simple input-output relation of the beamsplitter [Cohen-Tannoudji11]. The quantum state of two indistinguishable photons impinging onto the input modes of the beamsplitter may then be written as $|1, 1\rangle$. This state is transformed into $(|2, 0\rangle \pm |0, 2\rangle)/\sqrt{2}$, which implies that coincidence measurements $\propto |\langle 0, 0|E_2 E_1|2, 0\rangle|^2$ vanish. It is clear that this simple argument only holds for perfectly indistinguishable photons. Any short time delay will induce a possible element to distinguish the two, which is what enabled Hong, Ou and Mandel to measure the subpicosecond time delays mentioned above.

Here, downconversion is merely a means to create photon pairs, but the time-energy entanglement is neither necessary nor beneficial for the effect. In fact, strong time-energy entanglement is tantamount to large bandwidths of the individual photon wavepackets [see Fig. 2.6a)]. Perfect interference requires the two wave packets to be identical, which becomes more cumbersome with increasing bandwidth. Imbalances due to a finite pump bandwidth and the different propagation speeds inside the nonlinear crystal quickly degrade the signal.

Dispersion cancellation Dispersion cancellation has been proposed and demonstrated by Steinberg et al. in [Steinberg92a, Steinberg92b]. It relies on the same setup as the HOM effect. When a dispersive medium is placed into the beam of one of the two photons, the photon wavepacket will be delayed due to the different group velocity inside the medium (compared to the vacuum), but it will also be spread out in time (this is referred to as group velocity dispersion). Surprisingly, the effect of leading-order dispersion is cancelled in the coincidence detection of the two photons. As discussed nicely in [Erdmann00], this phenomenon may be understood by the destructive interference between the pathways where both photons are transmitted, and both are reflected. In contrast to the HOM effect, the strong frequency correlations associated with the time-energy entanglement are essential for the cancellation [Grice97].

A conceptually very similar proposal was given by Franson - nonlocal dispersion cancellation [Franson92, Larchuk95] (even predating the Steinberg proposal in the HOM setup). Here, each photon is sent through a dispersive medium, with the two media causing group velocity dispersion of equal strength but opposite sign. Again, it turns out that due to the frequency correlations the dispersion of both media is cancelled.

Is dispersion cancellation a quantum effect? Originally believed to be a hallmark of entanglement, it was shown by Resch and co-workers in a series of papers that these effects may be reproduced by frequency correlations in classical light combined with post-

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Figure 2.7.: a) Two-photon absorption signal vs. time delay between the two photons with on-resonant (circles) and off-resonant (squares) pump pulse. The solid line shows the theoretical prediction for the case of a resonant pump pulse. b) Same resonance vs. the pump wavelength ω_p (see Fig. 2.5). The circles denote the measured signal at zero time delay, and the squares at 100 fs delay. The solid line indicates the pump pulse spectrum, for comparison. c) Level scheme in Rubidium: The two photons excite the degenerate D -levels which decay non-radiatively to $5P_{1/2}$. Fluorescence of the $P_{1/2} \rightarrow S_{1/2}$ transition is collected. The results are taken from Ref. [Dayan04].

selection of the signal [Resch07, Kaltenbaek08, Lavoie09, Kaltenbaek09]. Similar results have been obtained for other degrees of freedom as well (see, e.g., quantum imaging with thermal light [Valencia05]). In this sense, the situation is similar to quantum computation [Nielsen10] - of course, any result of a quantum computation could also be obtained with a classical computer, it may just take exponentially more time to accomplish the task.

2.2.3. Entangled-photon spectroscopy

The distinction between the previous section and this one is somewhat arbitrary: Even though effects such as dispersion cancellation have been mostly explored due to a fundamental interest in the nonlocality of quantum physics rather than in a spectroscopic tool, we may clearly turn the question around, and ask what we can learn from the coincidence measurements about the medium. In this sense, our distinction of the following effects lies in the intention rather than in any fundamental difference: We now consider the entangled photons as a given, and aim to learn about a sample system through their interaction with it.

Linear biphoton spectroscopy We first briefly discuss linear optical measurements with entangled photons. Spectroscopy with squeezed light was first demonstrated in

Ref. [Polzik92], but has not found widespread application. Very recent experiments [Phan14] also use downconversion sources for the controlled excitation of retinal rod cells by single photons. A more successful approach is often termed *biphoton spectroscopy*, which denotes an experimental setup where only one photon is directed onto the sample, and the other one serves as a reference in coincidence measurements [Yabushita04, Kalachev07, Kalachev08, Slattery13, Kalashnikov14]. Such setups are most interesting in very noisy environments since the coincidence detection greatly reduces the number of accidental “clicks”. As stated in [Kalashnikov14], the “*detection of a refractive-index change is demonstrated with a noise level 70 times higher than the signal, which is shown to be inaccessible with the conventional transmission spectroscopy*”. So far, these measurements were all restricted to the linear regime. However, we will explore in chapter 6 how they may be straightforwardly generalized to measure nonlinear optical signals.

Two-photon absorption (TPA) is in some sense the most obvious application of entangled photons: Since they arrive in pairs, the first photon may excite to a far off-resonant or to a virtual state, and the second photon then completes the absorption process [Dayan05]. A clean example of such a process is given in Ref. [Dayan04], and the main results are reproduced in Fig. 2.7. Panel a) shows the two-photon resonance as a function of the time delay between the two photons, demonstrating the strong time correlation necessary for TPA.⁸ Only when the two photons arrive within a time window of approximately 20 fs, TPA is possible.⁹ By itself, this is a feature that could be achieved by ultrafast laser pulses as well. But Fig. 2.7b), which shows the dependence on the pump wavelength, demonstrates that the TPA resonance is also spectrally very narrow, and that its width is comparable to the pump bandwidth. Hence, TPA is both well resolved in the time delay and in the pump frequency. As expressed by the authors in Ref. [Dayan04], “*the coherent TPA signal appears only when the pump is on-resonance with the $5S \rightarrow 4D$ transition, and exhibits a sharp dependence on the signal-idler delay, exactly as if the interaction was induced by a pair of coherent,¹⁰ 23 fs pulses with the same spectra as the signal and idler beams.*” In contrast to classical light, one can obtain both high time *and* frequency resolution [Ali Khan06] - a central result which will appear repeatedly in the course of this dissertation.

Similar experiments have already been carried out in much more complex sample systems such as organic molecules [Lee06, Harpham09, Guzman10, Upton13]. We present some of these results in Fig. 2.8 to illustrate another peculiar feature of TPA of entangled photons: its *scaling behavior* with intensity. As predicted theoretically in Ref. [Javanainen90] and also measured in [Dayan05], the quasi-simultaneous arrival of

⁸Strictly speaking, we would call the optical signal *two-photon induced fluorescence* (TPIF) since fluorescence from the $P_{1/2} \rightarrow S_{1/2}$ transition is collected [see Fig. 2.7c)]. However, TPA and TPIF are often used interchangeably in the literature, and the underlying physics is the same [see chapters 4 and 5].

⁹The entanglement time in the cited paper [Dayan04] is on the order of 20 fs. TPA can only take place when the two photon wavepackets overlap temporally at the sample. Hence, the width of the resonance is determined by the entanglement time.

¹⁰*i.e.* pulses, in which the field is in a coherent state.

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Figure 2.8.: a) Two-photon absorption signal vs. the entangled photon flux. b) Same for two-photon induced fluorescence (see text). The results are taken from Ref. [Guzman10].

photon pairs stemming from the downconversion process is reflected in a *linear* scaling of the TPA signal, whereas classically induced TPA scales *quadratically*. This scaling is clearly seen in Fig. 2.8 for both two-photon absorption (*i.e.* depletion of the absorption field intensity) and two-photon induced fluorescence (*i.e.* measurement of an associated molecular decay). As mentioned before, both measurements yield very similar information content (see also our discussion of transition amplitudes vs. susceptibilities in section 3.6, as well as in chapter 4). With increasing intensity, different uncorrelated photon pairs start to overlap in time, and the classical, quadratic scaling is recovered.

The investigation of TPA measurements have not been restricted to the two scenarios of Figs. 2.7 and 2.8. Theoretical works have investigated TPA in quantum wells [Salazar12], and the control of vibronic states in molecular systems using quantum-correlated photon pairs [Oka11a, Oka11b, Oka12].

Once again, we may ask whether the characteristic TPA features represent a bona fide entanglement effect. The linear scaling may be directly traced back to the shared dependence of the two-photon wavefunction on the pump intensity: Since each pump photon creates two downconverted photons, optical signals that depend on one such pair must scale linearly in the destroyed pump photons' flux. As such, it clearly constitutes a *quantum effect*: By splitting one field quantum of the pump pulse into two, the created pair can drive two-photon transitions that are not coupled by direct dipole transitions, while retaining the linear scaling of a single-photon process. The question about the relevance of entanglement however is more involved, and subject of ongoing discussion in the literature: It had been shown already that TPA may also be enhanced significantly by shaped classical pulses [Dudovich01]. So, from this point of view, the spectral features in Fig. 2.7 may well be related to details of the photons' spectral envelope. In a similar spirit, we have already seen how photon-correlation effects that were initially attributed

to entanglement may be reproduced by classical correlations in combination with post-selection of the signals [Resch07, Kaltenbaek08, Lavoie09].

On the other hand, it has been shown that entangled photons may induce collective transitions between noninteracting (and possibly spatially separate) two-level atoms [Muthukrishnan04], emphasizing the nonlocal nature of the process. Later investigations clarified that the resulting entanglement between the two-level atoms may not be observed in single-particle measurements due to destructive interference between pathways [Richter11]. Furthermore, similar collective resonances may be obtained with separable correlated states, as shown very recently [Zheng13]. The authors of this last paper express their main finding that they *“have shown that what is necessary for the enhancement of the transition probability is neither quantum entanglement nor temporal correlations, but rather frequency anticorrelation, which can be due to the presence of entanglement in the state, but also to correlations that are not related to entanglement.”* This view will turn out to be consistent with our finding that one needs irreversible dynamics to obtain an advantage due to entanglement (entanglement in this context is tantamount to simultaneous strong frequency and time correlations, see section 2.2.1).

Entanglement-induced transparency is a peculiar effect in the TPA process, and bears its name from a similarity to electromagnetically induced transparency [Fei97]. It is based on the variation of the TPA cross section as a function of the entanglement time. As mentioned in the previous section, the entanglement time, which is given by the maximal time delay between the two photons which emerge from the downconversion process, characterizes the time correlations between the photons, and may be controlled by changing the length of the birefringent crystal in propagation direction. As reported in [Fei97], the TPA cross section shows strongly oscillatory behavior with variable entanglement time, which may be explained by the interference between excitation pathways via different intermediate states. Such interference is clearly not specific to entangled photons, since the interference between excitation pathways forms the very basis of any coherent control scheme [Shapiro12], and not least of electromagnetically induced transparency. The peculiar feature of “entanglement-induced” transparency lies in the fact that the destructive interference, which is responsible for the transparency, takes place due to the shared wavefunction of the entangled photon pair, and not between distinct laser pulses.

So far, this interference effect is not directly related to the topic of this section. By introducing an additional delay stage into one of the photon beams, one may use this behavior to perform *entangled virtual-state spectroscopy* [Saleh98]. In principle, this method should allow to measure the energy of strongly off-resonant states. This was already simulated in a molecular system [Kojima04]. It was also shown, however, that, since the transitions involved are far off-resonant, the method strongly depends on the high- and low-frequency tails of the wavepacket frequency distribution [deJ Leon-Montiel13], thus rendering the proposal inapplicable under realistic conditions.

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And so, even though these schemes are not directly applicable to more complex quantum systems since they depend strongly on small changes in the spectral profiles of the photons [deJ Leon-Montiel13], they demonstrate one important distinction of quantum spectroscopy: the availability of control parameters such as the entanglement time which have no classical counterpart - at least no one-to-one analogon. We will make use of these control parameters repeatedly in the course of this dissertation. In fact, we will mostly be concerned with the dependence of signals on these new parameters, and not with “classical” time delays.

“Schrödinger cat” spectroscopy is considered in Ref. [Kira11], where the authors discuss quantum spectroscopy with a single-mode “Schrödinger cat state” - a superposition of two coherent wavepackets. In contrast to the previous examples of entangled-photon spectroscopy, this approach does not pertain to the multimode nature of entangled photon pairs obtained from downconversion, but from a superposition state of the light field, which shows different fluctuation properties compared to a “classical” coherent state. The authors demonstrate that the system’s classical response (*i.e.* response to classical laser light, see Eq. (2.1)) may be mapped onto its response to quantum light. The suppressed fluctuations of the cat states along certain frequency axes are then reflected in reduced fluctuations of the signal, allowing the authors to enhance their spectral resolution. This sort of data processing was used to investigate biexciton coherences [Mootz14], and was crucial in the revelation of a new type of quasi-particle, termed *quantum droplet* (featuring a spatial correlation function similar to that of a water droplet) [Almand-Hunter14]. These results seem to suggest that any sample response may always be obtained by an appropriate superposition of responses to classical light. However, despite these impressive results, all results were obtained in single-mode regimes. The present dissertation will be mostly concerned with highly entangled regimes (in terms of Schmidt modes) where the number of relevant modes may easily exceed fifty or more. Even if it were possible to disentangle the response of the different modes, which may not always be possible, a mapping onto classical responses would require the acquisition of response functions pertaining to each mode, which consist of strongly oscillatory ultrafast pulses, thus rendering any mapping onto classical response functions completely unfeasible - both in practice and in simulations.

Nonlinear spectroscopic schemes Let us finally review approaches in the literature which propose concrete setups for nonlinear spectroscopic measurements with entangled photons. Proposals by the Mukamel group [Roslyak09a, Roslyak09b, Rahav10, Richter10, Dorfman14a] and by Raymer and co-workers [Raymer13] follow in spirit developments of coherent nonlinear spectroscopy as they were discussed in the previous section. In [Roslyak09a], the intensity dependence of different excitation pathways was examined, and frequency-domain response functions [similar to Eq. (2.2)] were discussed. Ref. [Roslyak09b] demonstrated the use of novel control parameters of entangled light to obtain multidimensional signals - in that sense, it constitutes the first multidimensional generalization of entanglement-induced transparency. Rahav and Mukamel also

Figure 2.9.: a) Observation of quantum jumps of a single Ba^+ ion, taken from Ref. [Nagourney86]. b) Geometry of a linear radio frequency trap [Leibfried03]: The electric potential of two opposing, wedge-shaped electrodes is varied rapidly, while the other two electrodes are kept at constant potential. This creates an effective harmonic confinement potential for the ions in x/y -direction. The ions are also confined along the z -direction (not depicted).

considered photoelectron spectroscopy induced by the interaction with both classical and quantum light fields [Rahav10], and in [Richter10] DQC-signals induced by entangled photons were simulated, and their control by the mentioned control parameters discussed. Raymer and co-workers recently further proposed phase cycling for the selection of pathways [Raymer13], and propose photon counting as an additional means to select pathways and suppress single photon events. By subtracting events, in which one of the photons passes through the sample, they resolve fluorescence events that stem solely from the absorption of entangled pairs (We will discuss similar approaches in chapter 5).

2.3. Trapped ions

Trapped ions have become an essential workhorse of modern quantum physics [Leibfried03]. They constitute one of the oldest, and most developed schemes for measurements on single quantum systems. For instance, the first direct observation of quantum jumps [Nagourney86, Sauter86, Bergquist86] between two electronic levels in a single Ba^+ ion, as shown in Fig. 2.9a), constituted a major paradigm shift in quantum physics, famously contradicting Schrödinger's statement that *"we never experiment with just one electron or atom or (small) molecule. In thought-experiments we sometimes assume that we do; this invariably entails ridiculous consequences... we are not experimenting with single particles, any more than we can raise Ichthyosauria in the zoo"* [Schrödinger52]. Since then, their controlled assembly and manipulation has seen great progress, with applications ranging from precision measurements [Gill05, Madej12] to quantum computing

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[Häffner08]. Most importantly for our purposes, trapped ion chains are considered as promising prototypes of quantum simulators [Barreiro11, Blatt12, Schneider12, Yung14]. Here, the idea consists in the implementation of complex Hamiltonians in trapped ion crystals, using the laser fields to induce and control interactions between the ions.

The general setup which we will consider in this dissertation is sketched in Fig. 2.9b), where a rapidly oscillating electric field creates an effectively harmonic trapping potential. A number of positively charged ions is placed in between four electrodes, and the voltage of two of them is modulated at radio frequency (RF), while the other two electrodes are kept at constant voltage. The electrodes thereby create at any moment in time an unstable equilibrium point (or actually an unstable line along the z -direction), where the stable and unstable (transverse) directions alternate with the RF [Leibfried03]. Hence, as long as the oscillation is fast compared to the motion of the ions, one effectively obtains a transverse harmonic trapping potential for the ions. To confine the ions also along the z -direction, a much weaker positive potential is applied from both sides of the trap. Due to their Coulomb repulsion, the ions then form a linear chain along the z -direction.¹¹ This ground state geometry has two important consequences for us: First, the Coulomb repulsion is much stronger than, for instance, the dipole-dipole interaction between molecules. Thus, whereas the size of molecular aggregates or other traditional sample systems in nonlinear spectroscopy may fall well below the diffraction limit in the optical regime, ions in a linear trap may be resolved and addressed individually (see, e.g., the inset in Fig. 2.10, which clearly resolves the different ions). Second, the Coulomb repulsion couples the ions, such that their motion within the trapping potential is correlated. This has already been applied to create effective interactions between the (non-interacting) electronic states of the ions [Cirac95, Monroe95]. Typical equilibrium distances between the ions are on the order of $5\mu\text{m}$ [Häffner05], and trap frequencies (*i.e.* eigenfrequencies of vibrations around the equilibrium positions) on the order of $2\pi \times 3$ MHz [Gessner14b].

Ion traps are well-controlled systems, accessible to full quantum state tomography. But already for the comparatively small 8-ion chain of Fig. 2.10 [Häffner05] it took the authors 650,000 measurements, or approximately ten hours, to obtain their result. It is clear that due to the exponential scaling of the size of the Hilbert space with the number of ions, state tomography is only feasible for rather small systems.¹² Besides, in many situations such as quantum simulations one is not necessarily interested in the huge information contained in the full density matrix. Consider quantum energy transport along an ion chain, for instance, which for phononic transport has been considered in [Bermudez13, Ramm14] (and in more general settings in, e.g., Refs. [Casati06, Zheng11, Asadian13]). The creation of local phonons has been achieved recently [Harlander11, Brown11, Haze12, Mizrahi13], enabling the excitation of nonequilibrium wavepackets, and the investigation of their spreading along the chain. To exam-

¹¹However, if the ions are packed too densely, their mutual repulsion will eventually force the ions to leave the linear configuration, and form three-dimensional ion crystals [Shimshoni11, Pyka13, Ulm13].

¹²Even worse, the general validity of tomography protocol has been questioned [Hradil06], since the truncation of the system Hamiltonian or experimental noise may greatly affect the “(re)constructed” state.

2.4. Time and Energy scales in this dissertation

Figure 2.10.: Quantum state tomography of an 8-ion “W”-state in the electronic degrees of freedom, taken from Ref. [Häffner05]. See also footnote 12. The inset shows the fluorescence collected from the ion chain.

ine such a process, one full quantum state tomography is not even sufficient, instead one would have to carry out quantum *process* tomographies, which are even more expensive. Hence, it is clearly necessary to develop new, specialized tools to monitor such transport processes. The characterization of complex systems is naturally encountered in many fields of modern physics, and consequently a wealth of approaches has been developed, ranging from level statistics [Beenakker97] to Loschmidt echoes [Gorin06]. To make full use of the experimental capabilities available in trapped ion crystals, here, we aim to make explicit use of the ability to excite and read out local excitations. First steps in this direction employ Ramsey interference schemes to probe quantum phase transitions [Knap13]. However, as we shall see in chapter 8, coherent multidimensional spectroscopy offers much greater flexibility in the design of measurement protocols specific to a given question.

2.4. Time and Energy scales in this dissertation

As a final section of this background chapter, we would like to remark on the time and energy units that will be used throughout this dissertation. During the larger part, we will be concerned with the interaction of quantum light with excitonic systems. In the spirit of spectroscopy, we will measure frequencies in wavenumbers (cm^{-1}), which - for historic reasons - are defined as the inverse wavelength λ [Hamm11]. Thus, it relates to the “regular” angular frequency $\omega[\text{rad/s}]$ as

$$\omega[\text{rad/s}] = 2\pi \frac{c}{\lambda} t \equiv \omega[\text{cm}^{-1}] 2\pi c t. \quad (2.6)$$

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Hence,

$$\begin{aligned}
\omega[\text{cm}^{-1}] &= \frac{\omega[\text{rad/s}]}{2\pi c} \\
&\approx \left(\frac{1}{18} 10^{-10} \frac{\text{s}}{\text{cm}} \right) \omega[\text{rad/s}] \\
&= 5.6 \times 10^{-12} \frac{\text{s}}{\text{cm}} \omega[\text{rad/s}].
\end{aligned} \tag{2.7}$$

Time scales, on the other hand, will be presented in femtoseconds (fs). To convert time into “inverse wavenumbers”, we write the argument of the time evolution as $\omega(2\pi ct) \equiv \omega\tilde{t}$, where $\tilde{t}$ denotes the time in inverse wavenumber units. Using Eq. (2.7), we obtain

$$\tilde{t}[\text{cm}] = 1.8 \times 10^{-4} t[\text{fs}]. \tag{2.8}$$

Note that the time $\tilde{t}$ in Eq. (2.8) includes the factor 2π , such that $\omega\tilde{t}$ oscillates with the correct angular frequency. In this sense $\tilde{t}$ may be thought of as a “angular time”. To obtain the real time, Eq. (2.8) has to be divided by 2π . Nevertheless, Eq. (2.8) may be used to convert a bandwidth σ given in wavenumber into the time duration of a pulse, since for a Gaussian pulse envelope in the frequency domain, we obtain the Fourier transform

$$\int d\omega e^{-\omega^2/(2\sigma^2)} e^{i2\pi c\omega t} \sim e^{-t^2/(2\sigma_t^2)}, \tag{2.9}$$

with the pulse duration $\sigma_t = 2\pi c/\sigma$.

Finally, in chapter 8, we will work with trapped ion systems where the relevant time and energy scales may be adjusted externally, e.g. via control of trap frequencies through the applied field strength. We then normalize the relevant Hamiltonians with respect to these external parameters.

3. 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.

3.1. Motivation & 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 section 3.2.

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

3. Nonlinear optical signals

- that the field creating the signal has to be connected to the de-excitation of the sample system,

$$E_{\text{signal}}^\dagger \sim V. \quad (3.1)$$

Measuring the intensity of this field is then given by

$$\langle E_{\text{signal}}^\dagger E_{\text{signal}} \rangle \sim \langle V V^\dagger \rangle. \quad (3.2)$$

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 section 3.3.

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. (3.2). 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 section 3.5, where we also introduce the diagrammatic representation of the perturbative expansions, which may provide intuition for the construction of measurement protocols.

3.2. Light-matter Hamiltonian & Liouville Space notation

3.2.1. Light-matter interaction

We consider a system described by the total Hamiltonian

$$H_{\text{tot}} = H_{\text{matter}} + H_{\text{field}} + H_{\text{int}}, \quad (3.3)$$

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. 3.1; 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.

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.

3.2. Light-matter Hamiltonian & Liouville Space notation

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

$$H_{\text{int}} = \vec{\epsilon} \vec{\mathcal{V}}, \quad (3.4)$$

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. 3.1, $\vec{V}$ 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]

$$\vec{E}(t) = i\hat{e}\sqrt{\frac{\pi\hbar\omega}{\epsilon_0 c A_0}} \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} a(\omega') e^{-i\omega' t}, \quad (3.5)$$

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. (3.5), 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. (3.5) allows to extend the frequency integration over the entire real axis [remember, Eq. (3.5) 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).

3. Nonlinear optical signals

Figure 3.1.: 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.

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. (3.5)], 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

$$H_{\text{int}} = E(t)V^\dagger(t) + E^\dagger(t)V(t), \quad (3.6)$$

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. 3.1: 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

$$V = \sum_{g,e} \mu_{eg} |g\rangle \langle e| + \sum_{e,f} \mu_{fe} |e\rangle \langle f|, \quad (3.7)$$

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

3.2.2. 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]

$$\langle\langle A|B\rangle\rangle \equiv \text{tr} \left\{ A^\dagger B \right\}, \quad (3.8)$$

$\mathcal{L}$ 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

$$\frac{d}{dt}\varrho(t) = -\frac{i}{\hbar} [H_{\text{int}}(t), \varrho(t)]. \quad (3.9)$$

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

$$H_{\text{int},-}X \equiv H_{\text{int}}X - XH_{\text{int}}, \quad (3.10)$$

we write the formal solution of Eq. (3.9) as a Dyson series in Liouville space. Hence, we obtain the density matrix

$$\varrho(t) = \mathcal{G}(t, t_0)\varrho(t_0), \quad (3.11)$$

with the Liouville space Green's function

$$\mathcal{G}(t, t_0) = \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int},-} \right], \quad (3.12)$$

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

$$\mathcal{T}A(t_1)B(t_2) \equiv \Theta(t_1 - t_2)A(t_1)B(t_2) + \Theta(t_2 - t_1)B(t_2)A(t_1), \quad (3.13)$$

where

$$\Theta(t) = \begin{cases} 1 & t \geq 0 \\ 0 & t < 0 \end{cases} \quad (3.14)$$

is the Heaviside function. To contrast the Liouville space Green's function (3.12) from its Hilbert space counterpart, we will denote the latter one by

$$G(t - t_0) = \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int}}(\tau) \right]. \quad (3.15)$$

As initial conditions in (3.9), we always assume factorizing initial conditions, *i.e.*

$$\varrho(t_0) = \varrho_{\text{matter}}(t_0) \otimes \varrho_{\text{field}}(t_0), \quad (3.16)$$

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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,

$$\varrho_{\text{matter}}(t_0) = |g\rangle\langle g|, \quad (3.17)$$

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. 3.1, 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

$$A_+X \equiv \frac{1}{2} (AX + XA), \quad (3.18)$$

and the left-/right-superoperators via

$$A_L \equiv 2A_+ + A_-, \quad (3.19)$$

$$A_R \equiv 2A_+ - A_-. \quad (3.20)$$

3.3. 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. (3.11)] by

$$\langle A(t) \rangle_{\text{final}} \equiv \text{tr}\{A(t)\varrho(t)\}, \quad (3.21)$$

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

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.

respect to the initial state by

$$\langle A(t) \rangle \equiv \text{tr}\{A(t)\varrho(t_0)\}. \quad (3.22)$$

Using Eq. (3.11), we can relate the two as

$$\langle A(t) \rangle_{\text{final}} = \langle \mathcal{T} A(t) \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int},-} \right] \rangle. \quad (3.23)$$

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 (3.13) - all the interactions in the exponential are placed to the right of the measured quantity. By expanding the exponential in Eq. (3.23), we will later in section 3.5 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 (3.16), 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 (3.4), 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]

$$H_{\text{int},-}(t) = \epsilon_+(t)\mathcal{V}_-(t) + \epsilon_-(t)\mathcal{V}_+(t), \quad (3.24)$$

where $\epsilon_{\pm}$ and $\mathcal{V}_{\pm}$ are defined by Eqs. (3.10) and (3.18), respectively.³ This identity will be regularly employed in the subsequent derivations.

3.3.1. 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

$$S = \langle A_+(t) \rangle_{\text{final}} = \langle \mathcal{T} A_+(t) \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int},-}(\tau) \right] \rangle \quad (3.25)$$

$$= S_0 - \frac{i}{\hbar} \int_{t_0}^t d\tau \langle \mathcal{T} A_+(t) H_{\text{int},-}(\tau) \exp \left[-\frac{i}{\hbar} \int_{t_0}^{\tau} d\tau' H_{\text{int},-}(\tau') \right] \rangle, \quad (3.26)$$

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 A acts

³This identity can be verified by straightforward calculation.

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Figure 3.2.: 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.

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, $\langle \mathcal{V}_- \rangle = \text{tr}\{\mathcal{V} \varrho\} - \text{tr}\{\varrho \mathcal{V}\} = 0$). Thus, we obtain

$$S = -\frac{i}{\hbar} \int_{t_0}^t d\tau \langle \mathcal{T} A_+(t) \epsilon_-(\tau) \mathcal{V}_+(\tau) \exp \left[-\frac{i}{\hbar} \int_{t_0}^{\tau} d\tau' H_{\text{int},-}(\tau') \right] \rangle. \quad (3.27)$$

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

$$\text{tr}\{A_+ \epsilon_- \varrho\} = \frac{1}{2} \text{tr}\{A \epsilon \varrho + \epsilon \varrho A - A \varrho \epsilon - \varrho \epsilon A\} \quad (3.28)$$

$$= \text{tr}\{(A \epsilon - \epsilon A) \varrho\} \quad (3.29)$$

$$= \text{tr}\{[A, \epsilon] \varrho\} = \text{tr}\{[A, \epsilon]_+ \varrho\}. \quad (3.30)$$

Note that $[A, \epsilon]_+$ denotes the “+” superoperator of the operator $[A, \epsilon]$ as defined in Eq. (3.18). Therefore, we obtain the leading-order interaction-induced contribution in the number of matter-field interactions to the observable’s expectation value,

$$S = -\frac{i}{\hbar} \int_{t_0}^t d\tau \langle [A(t), \epsilon(\tau)]_+ \mathcal{V}_+(\tau) \rangle_{\text{final}}. \quad (3.31)$$

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 $A(t)$,

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as sketched in Fig. 3.2. First, we discuss transmission measurements, where 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. 3.2a): 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

$$a(t) = \int \frac{d\omega}{\sqrt{2\pi}} a(\omega) e^{-i\omega t}, \quad (3.32)$$

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. (3.31) [recall the definition of ϵ through E and $E^\dagger$ on page 33]

$$\begin{aligned} & [A(t), \epsilon(\tau)] \\ &= \sqrt{\frac{\pi\hbar\omega}{\epsilon_0 c A_0}} \int \frac{d\omega}{\sqrt{2\pi}} \int \frac{d\omega'}{\sqrt{2\pi}} \int \frac{d\omega''}{2\pi} e^{i(\omega-\omega')t} \left[a^\dagger(\omega) a(\omega'), i a(\omega'') e^{-i\omega''\tau} + (-i) a^\dagger(\omega'') e^{i\omega''\tau} \right] \end{aligned} \quad (3.33)$$

$$= \frac{1}{(2\pi)^2} \sqrt{\frac{\pi\hbar\omega}{\epsilon_0 c A_0}} \int d\omega \int d\omega' e^{i(\omega-\omega')t} \left(-i a(\omega') e^{-i\omega\tau} + (-i) a^\dagger(\omega) e^{-i\omega'\tau} \right) \quad (3.34)$$

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

$$[A(t), \epsilon(\tau)] = \left(-E(t) + E^\dagger(t) \right) \delta(t-\tau). \quad (3.35)$$

This yields, in Eq. (3.31),

$$S = -\frac{i}{\hbar} \left\langle \left(-E_+(t) + E_+^\dagger(t) \right) \mathcal{V}_+(t) \right\rangle_{\text{final}}, \quad (3.36)$$

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),

⁴Our choice of normalization with $1/\sqrt{2\pi}$ - as well as $1/(2\pi)$ in Eq. (3.5) - 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.

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we recover the known result [Rahav10]

$$\begin{aligned} S &= -\frac{i}{\hbar} \left(\langle -E_+(t)V_+^\dagger(t) \rangle_{\text{final}} + \langle E_+^\dagger(t)V_+(t) \rangle_{\text{final}} \right) \\ &= \frac{2}{\hbar} \Im \langle E_+^\dagger(t)V_+(t) \rangle_{\text{final}}. \end{aligned} \quad (3.37)$$

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

$$S' = \frac{2}{\hbar} \int_{-\infty}^{\infty} dt \Im \langle E_+^\dagger(t)V_+(t) \rangle_{\text{final}}, \quad (3.38)$$

as we will employ at the beginning of chapter 5.

Note that we encounter an apparent ambiguity in the derivation of Eq. (3.37): We could have also picked the signal

$$S' = -\frac{2}{\hbar} \Im \langle E_+(t)V_+^\dagger(t) \rangle_{\text{final}}. \quad (3.39)$$

Both definitions are mathematically equivalent, since $\Im \langle EV^\dagger \rangle = -\Im \langle E^\dagger V \rangle$. However, their physical interpretation in terms of the underlying process in the sample differs: In Eq. (3.37), the last interaction corresponds to a de-excitation, and the creation of a photon which yields the signal, whereas in Eq. (3.39) 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 section 3.6 for quantum light.

Frequency-dispersed intensity measurement

We still discuss the setup depicted in Fig. 3.2a), 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. (3.25), by

$$S = \langle \mathcal{T} \left(a^\dagger(\omega)a(\omega) \right)_+ \exp \left[-\frac{i}{\hbar} \int_{t_0}^{\infty} d\tau H_{\text{int},-}(\tau) \right] \rangle, \quad (3.40)$$

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. (3.31). The commutator is calculated just like in our previous calculation, Eq. (3.34), and we obtain

$$[A(\omega), \epsilon(\tau)] = -E(\omega)e^{-i\omega\tau} + E^\dagger(\omega)e^{i\omega\tau}, \quad (3.41)$$

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and Eq. (3.31) then reads

$$S = -\frac{i}{\hbar} \int_{t_0}^{\infty} d\tau \langle \left(-E(\omega)e^{-i\omega\tau} + E^\dagger(\omega)e^{i\omega\tau} \right)_+ \mathcal{V}_+(\tau) \rangle. \quad (3.42)$$

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

$$S = \frac{2}{\hbar} \Im \langle E^\dagger(\omega) V(\omega) \rangle_{\text{final}}. \quad (3.43)$$

Here, we have of course the same ambiguity as in the time-resolved signal above. Note also that Eq. (3.43) is not simply the Fourier transform of Eq. (3.37): In the time domain, Eq. (3.43) must be written as

$$S = \frac{2}{\hbar} \Im \int dt_1 \int dt_2 e^{i\omega(t_1-t_2)} \langle E^\dagger(t_1) V(t_2) \rangle_{\text{final}}. \quad (3.44)$$

It contains contributions from two different times t_1 and t_2 , and may therefore not be obtained from Eq. (3.37) 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 section 4.6, as well as in chapters 5 and 6.

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 chapter 2). The signal is superimposed with a local oscillator field, and then detected [see Fig. 3.2b)]. 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. (3.31) yields

$$[a(t), \epsilon(\tau)] = \sqrt{\frac{\hbar\omega}{2\epsilon_0 c A_0}} \delta(t - \tau). \quad (3.45)$$

The result (3.31) then takes the form

$$S = \frac{2}{\hbar} \sqrt{\frac{\hbar\omega}{2\epsilon_0 c A_0}} \Im \langle V_+(t) \rangle_{\text{final}}. \quad (3.46)$$

Apart from the field normalization, Eq. (3.46) coincides with the semiclassical expression [Mukamel99], where the matter dipole operator is the source of the nonlinear polarization, as does the intensity signal we have derived above. We will not discuss heterodyne-detected signals in this dissertation.

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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. 3.2c). We assume that only field E_2 interacts with the matter system [and thus enters solely in the field $\epsilon_{\pm}(t)$ in Eq. (3.6)], 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. (3.35)

$$[A(t, t'), \epsilon_2(\tau)] = a_1^\dagger(t') \left(-E_2(t) + E_2^\dagger(t) \right) a_1(t') \delta(t - \tau). \quad (3.47)$$

Therefore, the signal reads

$$S = \frac{2}{\hbar} \Im \langle \left(a_1^\dagger(t')a_1(t')E_2^\dagger(t) \right)_+ V_+(t) \rangle_{\text{final}}. \quad (3.48)$$

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. (3.43) yields

$$S = \frac{2}{\hbar} \Im \langle \left(a_1^\dagger(\omega')a_1(\omega')E^\dagger(\omega) \right)_+ V_+(\omega) \rangle_{\text{final}}. \quad (3.49)$$

This signal will be discussed in chapter 6.

3.3.2. 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. (3.37). 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. 3.2d)]. 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. (3.37) 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. (3.37) is still formally correct, it is misleading, since the linear term vanishes. We need to expand Eq. (3.25) to second order in the interaction Hamiltonian with the vacuum field,

$$S = \left(-\frac{i}{\hbar} \right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \langle A_+(t) H_{\text{int},-}(\tau_2) H_{\text{int},-}(\tau_1) \rangle_{\text{final}} \quad (3.50)$$

$$= \left(-\frac{i}{\hbar} \right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \langle [A(t), \epsilon(\tau_2)]_+ \mathcal{V}_+(\tau_2) H_{\text{int},-}(\tau_1) \rangle_{\text{final}} \quad (3.51)$$

$$= \left(-\frac{i}{\hbar} \right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \langle [A(t), \epsilon(\tau_2)]_+ \mathcal{V}_+(\tau_2) (\epsilon_-(\tau_1)\mathcal{V}_+(\tau_1) + \epsilon_+(\tau_1)\mathcal{V}_-(\tau_1)) \rangle_{\text{final}}. \quad (3.52)$$

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To obtain Eq.(3.52), we have used our previous result, Eq. (3.31) in the second line. Here, in contrast to the derivation of Eq. (3.37), both terms $\sim \epsilon_- \mathcal{V}_+$ and $\sim \epsilon_+ \mathcal{V}_-$ in Eq. (3.52) 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 (3.10) and (3.18) as well as the result (3.41), the superoperator expression reads

$$\begin{aligned} & \langle [A(t), \epsilon(\tau_2)]_+ \epsilon_+(\tau_1) \rangle \\ &= \delta(t - \tau_2) \langle 0 | \left(-E(t) + E^\dagger(t) \right) \left(E(\tau_1) + E^\dagger(\tau_1) \right) \\ &+ \left(E(\tau_1) + E^\dagger(\tau_1) \right) \left(-E(t) + E^\dagger(t) \right) | 0 \rangle \end{aligned} \quad (3.53)$$

$$= \delta(t - \tau_2) \langle 0 | -E(t)E^\dagger(\tau_1) + E(\tau_1)E^\dagger(t) | 0 \rangle \quad (3.54)$$

Within the slowly-varying envelope approximation [see Eq. (3.5)] employed in this dissertation, the two terms yield identical results,

$$\langle 0 | E(t)E^\dagger(\tau_1) | 0 \rangle = \langle 0 | E(\tau_1)E^\dagger(t) | 0 \rangle = \frac{\hbar\omega}{2\epsilon_0 c A_0} \delta(t - \tau_1), \quad (3.55)$$

such that their difference vanishes. It is important to keep in mind that the simplification between Eqs. (3.53) and (3.54) rests on the fact that the field is in the vacuum state, and normally-order correlation functions vanish. In transmission measurements (3.37), additional terms need to be taken into account.

The second field correlation function in Eq. (3.52) evaluates to

$$\begin{aligned} & \langle [A(t), \epsilon(\tau_2)]_+ \epsilon_-(\tau_1) \rangle \\ &= \delta(t - \tau_2) \langle 0 | -E(t)E^\dagger(\tau_1) - E(\tau_1)E^\dagger(t) | 0 \rangle, \end{aligned} \quad (3.56)$$

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

$$S = - \left(-\frac{i}{\hbar} \right)^2 \frac{\hbar\omega}{2\epsilon_0 c A_0} \langle \mathcal{V}_+(t) \mathcal{V}_+(t) \rangle_{\text{final}}. \quad (3.57)$$

As discussed following Eq. (3.37), since the photodetectors collecting the fluorescence often possess insufficient time resolution to obtain time-resolved signals, it may be more appropriate to integrate Eq. (3.57) over time,

$$S' = \frac{\omega}{2\hbar\epsilon_0 c A_0} \int dt \langle \mathcal{V}_+(t) \mathcal{V}_+(t) \rangle_{\text{final}}. \quad (3.58)$$

Employing the interaction Hamiltonian (3.6) in the RWA again, we note that the non-vanishing contributions to the field correlation function (3.56) 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 $V^\dagger(t)V(\tau_1)$)

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in the first term, and $V^\dagger(\tau_1)V(t)$ in the second term). This reasoning means, we may write the signal as

$$S = \frac{\omega}{2\hbar\epsilon_0 c A_0} \langle V_L(t)V_R^\dagger(t) \rangle_{\text{final}}. \quad (3.59)$$

This result also justifies one further simplification which we will use in chapters 4 and 8: Consider the expression for the excitation annihilation operator (3.7), 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 section 4.6.

3.3.3. Classical vs. 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 chapter 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. (3.6) 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. (3.24), the semiclassical interaction Hamiltonian is simply given by

$$H_{\text{semiclassical}}(t) = \epsilon_+(t)\mathcal{V}_-(t), \quad (3.60)$$

and the matter correlation functions therefore read [Mukamel11]

$$R^{(n)}(t, \dots, \tau_1) \propto \langle \mathcal{V}_+(t)\mathcal{V}_-(\tau_n) \cdots \mathcal{V}_-(\tau_1) \rangle, \quad (3.61)$$

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

⁵The left-most operator $\mathcal{V}_+$ stems from the signal, and the other operators $\mathcal{V}_-$ from the expansion of the Dyson series (3.12) with the semiclassical Hamiltonian (3.60).

Figure 3.3.: 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. (3.101), which will be described by a single wavy line.

fully quantum mechanical treatment presented here is able to capture all of these effects in one consistent approach.

Except for chapter 5, Eq. (5.18), 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.

3.4. 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 (3.4), 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 chapter 8: 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

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the Hamiltonian has an enormous dimension, we derive a set of effective interaction operators that suffice to calculate nonlinear signals with manageable overhead.⁶

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.

3.4.1. 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. 3.3a). 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,

$$E_i(t) = E_i e^{i(\vec{k}\vec{x} - i\omega_i t)} + c.c. \quad (3.62)$$

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 $a^\dagger(a)$.

⁶A notable example of such effective interactions from the literature includes the Mølmer-Sørensen Hamiltonian, which will be discussed in chapter 8 [see Eq. (8.8)]. 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.

3.4. Effective interactions in ion chains

This allows us to write the Hamiltonian (in the interaction picture with respect to the electromagnetic field Hamiltonian) as

$$\begin{aligned} H_{\text{int}}(t) = & \hbar\omega_e\sigma_+\sigma_- + \hbar\nu_x a^\dagger a \\ & + \sigma_+ \left(\hbar\Omega_1 e^{i(\vec{k}_1\vec{r}-\omega_1 t+\phi_1)} + \hbar\Omega_2 e^{i(\vec{k}_2\vec{r}-\omega_2 t+\phi_2)} \right) \\ & + \sigma_- \left(\hbar\Omega_1 e^{-i(\vec{k}_1\vec{r}-\omega_1 t+\phi_1)} + \hbar\Omega_2 e^{-i(\vec{k}_2\vec{r}-\omega_2 t+\phi_2)} \right), \end{aligned} \quad (3.63)$$

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]

$$e^{i\vec{k}_j\vec{r}} = e^{i\eta_j(a+a^\dagger)}, \quad (3.64)$$

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 (3.64) by its linear contribution

$$e^{i\eta_j(a+a^\dagger)} \approx 1 + i\eta_j(a + a^\dagger), \quad (3.65)$$

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

The Hamiltonian (3.63) 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

$$U_{\text{field}}(t) = \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_0^t d\tau H_{\text{int}}(\tau) \right]. \quad (3.66)$$

A similar derivation can be found in Ref. [Roos08]. Our goal in this derivation is to replace the time-ordered integrations in Eq. (3.66) by an effective interaction,

$$U_{\text{field}}(t) \simeq \exp \left[-\frac{i}{\hbar} V_{\text{phonon}} t \right]. \quad (3.67)$$

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We will proceed in two steps: First, we change to a rotating frame, in which the interaction Hamiltonian (3.63) oscillates rapidly. Second, by employing the Magnus expansion, we identify non-oscillatory terms, from which we obtain the result (3.67).

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

$$U_0(t) = e^{-i(\omega_e \sigma_+ \sigma_- + \nu_x a^\dagger a)t}, \quad (3.68)$$

such that we obtain

$$H'(t) = U_0^\dagger(t) H_{\text{int}}(t) U_0(t) - \hbar \omega_e \sigma_+ \sigma_- - \hbar \nu_x a^\dagger a \quad (3.69)$$

$$= \sigma_+ \left(\frac{\hbar \Omega_1}{2} e^{-i\Delta t} e^{i(\eta_1 (a e^{-i\nu_x t} + a^\dagger e^{i\nu_x t}) + \phi_1)} + \frac{\hbar \Omega_2}{2} e^{-i(\Delta - \nu_x)t} e^{i(\eta_2 (a e^{-i\nu_x t} + a^\dagger e^{i\nu_x t}) + \phi_2)} \right) + H.c. \quad (3.70)$$

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. (3.70) oscillate very rapidly, and only products of two interactions can contribute significantly to Eq. (3.66). This hand-waving argument is made precise by the *Magnus* series [Magnus54], which replaces the time-ordered exponential in Eq. (3.66) by the exponential of a series expansion,

$$\mathcal{T} \exp \left[-\frac{i}{\hbar} \int_0^t d\tau H'(\tau) \right] = \exp \left[\sum_{n=1}^{\infty} F_n(t) \right], \quad (3.71)$$

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

$$F_1(t) = -\frac{i}{\hbar} \int_0^t d\tau_1 H'(\tau_1), \quad (3.72)$$

and

$$F_2(t) = \frac{1}{2} \left(-\frac{i}{\hbar} \right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 [H'(\tau_2), H'(\tau_1)]. \quad (3.73)$$

The integrand of Eq. (3.72) oscillates rapidly between the initial time 0 and the final time t . As we will see, Eq. (3.73) on the other hand contains terms, which only oscillate rapidly between the first and the second interaction [see also Fig. 3.3b)], thus yielding the dominant contribution to the Magnus series. The evaluation of Eq. (3.73) will result in the effective interaction operator we wish to obtain. Before evaluating the commutator,

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we carry out the time integrals first. Inserting Eq. (3.70) in Eq. (3.73), we note that it is sufficient to evaluate integrals of the form

$$h_{k,l}(t) = \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 e^{-i\Delta(\tau_2-\tau_1)} e^{ik\nu_x\tau_2} e^{-il\nu_x\tau_1}, \quad (3.74)$$

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. (3.70), 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

$$h_{k,l}(t) = \int_0^t d\tau_2 e^{-i(\Delta-l\nu_x)s} \int_0^t ds e^{i(k-l)\nu_x\tau_2}. \quad (3.75)$$

The τ_2 -integration yields

$$\int_0^t d\tau_2 e^{-i(\Delta-l\nu_x)s} = \frac{e^{-i(\Delta-l\nu_x)t} - 1}{-i(\Delta-l\nu_x)} \approx \frac{-i}{\Delta}, \quad (3.76)$$

where we assumed again that the laser fields are far off-resonant, hence $\Delta \gg |\nu_x|$. 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

$$h_{k,l}(t) \approx \frac{1}{\Delta} [-i\delta_{k,l}t + \mathcal{O}(1/\nu_x)]. \quad (3.77)$$

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.*

$$F_2(t) \approx -iV_{\text{eff}}t/\hbar, \quad (3.78)$$

as discussed in Eq. (3.67).

The evaluation of the commutator terms in Eq. (3.73) is now straightforward: Inserting the Hamiltonian (3.70) in Eq. (3.73), we obtain four different terms,

$$F_2(t) = F_2^{(1,1)}(t) + F_2^{(2,2)}(t) + F_2^{(1,2)}(t) + F_2^{(2,1)}(t) \quad (3.79)$$

Here, the brackets indicate the light fields involved, *i.e.* $F^{(2,2)}$ corresponds to two interactions 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

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phonons in the system. The first phase-independent term in the Lamb-Dicke limit (3.65) is given by

$$F_2^{(1,1)}(t) = \frac{1}{2} \left(-\frac{i}{\hbar} \right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 e^{-i\Delta(\tau_2-\tau_1)} \times \left[\sigma_+ \left(1 + i\eta_1(ae^{-i\nu_x\tau_2} + a^\dagger e^{i\nu_x\tau_2}) \right), \sigma_- \left(1 - i\eta_1(ae^{-i\nu_x\tau_1} + a^\dagger e^{i\nu_x\tau_1}) \right) \right] + H.c., \quad (3.80)$$

which yields in total eighteen different terms. According to Eq. (3.77), only those terms dominate in the final propagator, in which the frequency in the left argument of the commutator (3.67), $k\nu_x$, and in the right argument, $-\nu_x$, cancel one another. Hence, we obtain

$$F_2^{(1,1)}(t) = \frac{1}{2} \left(-\frac{i}{\hbar} \frac{\hbar\Omega_1}{2} \right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 e^{-i\Delta(\tau_2-\tau_1)} \times \left([\sigma_+, \sigma_-] + \eta_1^2 [\sigma_+ a, \sigma_- a^\dagger] e^{-i\nu_x(\tau_2-\tau_1)} + \eta_1^2 [\sigma_+ a^\dagger, \sigma_- a] e^{i\nu_x(\tau_2-\tau_1)} \right) + H.c. \quad (3.81)$$

$$= \left(-\frac{i\Omega_1}{2} \right)^2 \frac{-it}{\Delta} 2\sigma_z \left(1 + \eta_1^2 (2a^\dagger a + 1) \right) - H.c. \quad (3.82)$$

$$= i \frac{\Omega_1^2 t}{2\Delta} \sigma_z \left(1 + \eta_1^2 (2a^\dagger a + 1) \right) \simeq i \frac{\Omega_1^2 t}{2\Delta} \sigma_z, \quad (3.83)$$

where we neglected corrections to the Lamb-Dicke limit (3.65) 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. (3.83) 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,

$$F_2^{(2,2)}(t) = i \frac{\Omega_2^2 t}{2\Delta} \sigma_z \left(1 + \eta_1^2 (2a^\dagger a + 1) \right) \simeq i \frac{\Omega_2^2 t}{2\Delta} \sigma_z. \quad (3.84)$$

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

$$F_2^{(1,2)}(t) = \frac{1}{2} \left(-\frac{i}{\hbar} \right)^2 \frac{\hbar\Omega_1}{2} \frac{\hbar\Omega_2}{2} \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 e^{-i\Delta(\tau_2-\tau_1)} e^{i(\phi_1-\phi_2)} \times e^{-i\nu_x\tau_1} \left[\sigma_+ \left(1 + i\eta_1(ae^{-i\nu_x\tau_2} + a^\dagger e^{i\nu_x\tau_2}) \right), \sigma_- \left(1 - i\eta_2(ae^{-i\nu_x\tau_1} + a^\dagger e^{i\nu_x\tau_1}) \right) \right] + H.c. \quad (3.85)$$

The only relevant difference (apart from the different Lamb-Dicke parameter η_2 and Rabi frequency Ω_2) with respect to Eq. (3.80) consists in the additional factor $\exp(-i\nu_x\tau_1)$ in

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the second line of Eq. (3.85), which stems from the frequency difference between the two laser fields E_1 and E_2 [see Eq. (3.70)]. This factor changes the dominant contributions to $F^{1,2}(t)$. Using Eq. (3.77), we again only retain those commutator terms satisfying $k = l$,

$$F_2^{(1,2)}(t) = -\frac{\Omega_1\Omega_2}{8} \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 e^{-i\Delta(\tau_2-\tau_1)} e^{i(\phi_1-\phi_2)} \times \left([\sigma_+, -i\eta_2\sigma_-a^\dagger] + [i\eta_1\sigma_+a^\dagger, \sigma_-] e^{i\nu_x(\tau_2-\tau_1)} \right) + H.c. \quad (3.86)$$

$$= \frac{\Omega_1\Omega_2(\eta_1 - \eta_2)t}{4\Delta} \sigma_z \left(ae^{-i(\phi_1-\phi_2)} - a^\dagger e^{i(\phi_1-\phi_2)} \right). \quad (3.87)$$

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

$$F_2^{(1,2)}(t) + F_2^{(2,1)}(t) = -\frac{i}{\hbar} \left(i \frac{\hbar\Omega_1\Omega_2(\eta_1 - \eta_2)t}{2\Delta} \sigma_z (ae^{-i\phi} - a^\dagger e^{i\phi}) \right) t, \quad (3.88)$$

where

$$\phi = \phi_1 - \phi_2. \quad (3.89)$$

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 (3.67), we arrive at

$$V_{\text{phonon}} = i \frac{\hbar\Omega_1\Omega_2(\eta_1 - \eta_2)}{2\Delta} \left(ae^{-i\phi} - a^\dagger e^{i\phi} \right). \quad (3.90)$$

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. (3.97), 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 chapter 8, 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 (3.67), 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,

$$H_{\text{int},i}(t) = E_i(t) \sum_n \mu_n |\chi\rangle \langle \downarrow, n| e^{i\omega_{\chi n} t} + h.c. \quad i \in 1, 2, \quad (3.91)$$

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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. (3.62), 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 ,

$$\begin{aligned} |\psi_{\text{final}}(t)\rangle &= \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 H_{\text{int},2}(\tau_2) H_{\text{int},1}(\tau_1) |\downarrow, n-1\rangle + \dots \\ &= \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 E_2^*(\tau_2) E_1(\tau_1) \mu_{n-1} \mu_n e^{-i\omega_{\chi n}\tau_2} e^{i\omega_{\chi n-1}\tau_1} |\downarrow, n\rangle + \dots \end{aligned} \quad (3.92)$$

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. (3.83) and (3.84), and whose derivation we will not repeat. The other relevant term is the phonon annihilation, which is simply the inverse process of Eq. (3.92), in which the system ends in the state $|\downarrow, n-2\rangle$. Our process of interest is represented diagrammatically in Fig. 3.3b): 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,

$$E_i(t) = \int \frac{d\omega}{2\pi} A_i(\omega) e^{-i\omega(t-t_i^{(0)})-i\phi_i}, \quad (3.93)$$

where we introduce the central time of the pulse $t_i^{(0)}$, and an additional phase ϕ_i . We further introduced the pulse amplitude $A_i(\omega)$. Furthermore, we will denote the pulse's center frequency ω_i . Both control parameters will be used in chapter 8 to design measurement protocols.

To simplify Eq. (3.92), 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

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substitution to the integration variable $s = \tau_2 - \tau_1$, we obtain

$$|\psi_{\text{final}}\rangle = \left(-\frac{i}{\hbar}\right)^2 \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} \mu_{n-1}\mu_n A_1(\omega) A_2^*(\omega') e^{i(\phi_2 - \phi_1)} \\ \times 2\pi\delta(\omega - \omega' - \nu_x) \frac{ie^{i(\omega - \omega')t_1^{(0)}}}{\omega - \omega_{\chi n-1} + i\eta} |\downarrow, n\rangle + \dots \quad (3.94)$$

$$= \left(-\frac{i}{\hbar}\right)^2 \int \frac{d\omega}{2\pi} \mu_{n-1}\mu_n A_1(\omega) A_2^*(\omega - \nu_x) e^{i(\phi_2 - \phi_1)} \\ \times \frac{ie^{i\nu_x t_1^{(0)}}}{\omega - \omega_{\chi n-1} + i\eta} |\downarrow, n\rangle + \dots \quad (3.95)$$

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. 3.3) to combine the exponentials $\exp(-i\omega_{\chi n}\tau_2)$ and $\exp(i\omega_{\chi n-1}\tau_1)$ in Eq. (3.92).

To further simplify Eq. (3.95), 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. (3.95) 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,

$$|\psi_{\text{final}}\rangle = -i \frac{\mu_n \mu_{n-1}}{\hbar^2 \Delta} e^{i(\phi_2 - \phi_1) + i\nu_x t_1^{(0)}} \delta(t - t_1^{(0)}) \int \frac{d\omega}{2\pi} A_1(\omega) A_2^*(\omega - \nu_x) |\downarrow, n\rangle + \dots \quad (3.96)$$

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 chapter 8 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. (3.96) (which, in molecular spectroscopy would be called a *polarizability* [Mukamel09]) as

$$\alpha_{n, n-1}(t) = i\tilde{\kappa} e^{i\phi} \delta(t - t_1^{(0)}) |\downarrow, n\rangle \langle \downarrow, n-1| \quad (3.97)$$

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

$$\alpha_{n, n-1}(t) = i \frac{\tilde{\kappa}}{\sqrt{n}} e^{i\phi} \delta(t - t_1^{(0)}) a^\dagger |\downarrow, n-1\rangle \langle \downarrow, n-1| \quad (3.98)$$

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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. (3.98) 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

$$\mu_{n-1} \propto \langle\downarrow, n-1|\sigma_+|\chi, n-1\rangle = \mu \propto \langle\downarrow|\sigma_+|\chi\rangle\langle n-1|n-1\rangle, \quad (3.99)$$

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

$$\mu_n \propto \langle\chi, n-1|\sigma^- a|\downarrow, n\rangle = \langle\chi|\sigma^-|\downarrow\rangle\langle n-1|a|n\rangle \sim \sqrt{n}, \quad (3.100)$$

which is thus proportional to $\sqrt{n}$. Taken together, this factor cancels the contribution from the factor $1/\sqrt{n}$ in Eq. (3.98), 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. (3.97), such that we obtain the effective interaction operator

$$\tilde{V}_{\text{Phonon}}(t) = \kappa \left(a^\dagger e^{i\phi} - a e^{-i\phi} \right) \delta(t - t_1^{(0)}), \quad (3.101)$$

where $\kappa = i\tilde{\kappa}/\sqrt{n}$, a denotes the phonon annihilation operator, and we recall the phase ϕ is defined in Eq. (3.89).

Our above derivation of the excitation of phonons was carried out for an individual trapped ion. As we will see in chapter 8, when several ions are trapped in a linear chain, their individual vibrational modes are coupled [see, e.g., Eq. (8.1)], *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. (3.90). The other derivation explicitly takes the finite bandwidths into account, and by following similar derivations in chemical physics [Mukamel09], we obtained Eq. (3.101). Both approaches yielded the same functional dependence on the phonon operators.

The first derivation offers some clear advantages: By explicit evaluation of the propagator (3.66), we obtain the effective Hamiltonian (3.90), whose validity is only limited by the Lamb-Dicke limit (3.65). 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. (3.65) 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. (3.90) 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 chapter 8, 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. (3.96), and an evaluation of the Franck-Condon factor in Eqs. (3.99) and (3.100) 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.

3.4.2. 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. 3.4. 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

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Figure 3.4.: 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.

populations may be assessed: As described at the end of section 3.3.2 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

$$V_{\text{el}} = \frac{1}{\sqrt{2}} \left(\sigma^+ e^{i\phi} - \sigma^- e^{-i\phi} \right), \quad (3.102)$$

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 (3.90) - take the excitation (3.102) to be instantaneous, *i.e.* that the excitation takes place at a well-defined moment during the system's evolution. In contrast to Eq. (3.90), however, the present interaction need not be weak.

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

3.5. Diagram construction

We now turn to the final step of our approach sketched in section 3.1: 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. (3.37), or of fluorescence signals, Eq. (3.57). 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.

3.5.1. Loop diagrams

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

$$|\psi(t)\rangle = \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int}}(\tau) \right] |\psi(t_0)\rangle. \quad (3.103)$$

Note that in contrast to the superoperator Dyson series, Eq. (3.12), here we deal with the Dyson series (3.15) of the Hamiltonian operator in the lower-dimensional Hilbert space. As we have seen before, the absorption signal is given by Eq. (3.37), 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

$$S(t, \Gamma) = \frac{2}{\hbar} \Im \langle \psi(t) | E^\dagger(t) V(t) | \psi(t) \rangle, \quad (3.104)$$

where Γ summarizes the set of external control parameters. Expansion of the exponential in Eq. (3.103) to the desired order in H_{int} generates approximate expressions for the signal S . Hence, the n -th order signal reads

$$S^{(n)}(\Gamma) = \frac{2}{\hbar} \Im \sum_{k+l=n} \langle \psi^{(k)}(t) | E^\dagger(t) V(t) | \psi^{(l)}(t) \rangle, \quad (3.105)$$

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

$$|\psi^{(k)}(t)\rangle = \left(-\frac{i}{\hbar} \right)^k \int_{t_0}^t d\tau_k \int_{t_0}^{\tau_k} d\tau_{k-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 H_{\text{int}}(\tau_k) \cdots H_{\text{int}}(\tau_1) |\psi(t_0)\rangle. \quad (3.106)$$

Using the definition of the interaction Hamiltonian in the rotating wave approximation (3.6), and the initial condition (3.16), 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

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

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the “+1” is due to the interaction creating the signal in Eq. (3.104)],

$$\begin{aligned}
S^{(k,l)}(\Gamma) &= \langle \psi^{(k)}(t) | E^\dagger(t) V(t) | \psi^{(l)}(t) \rangle \\
&= (-1)^k \left(-\frac{i}{\hbar} \right)^n \int_{t_0}^t d\tau'_k \cdots \int_{t_0}^{\tau'_2} d\tau'_1 \int_{t_0}^t d\tau_l \cdots \int_{t_0}^{\tau_2} d\tau_1 \\
&\quad \times \langle \mathcal{V}(\tau'_1) \cdots \mathcal{V}(\tau'_k) V(t) \mathcal{V}(\tau_l) \cdots \mathcal{V}(\tau_1) \rangle \\
&\quad \times \langle \epsilon(\tau'_1) \cdots \epsilon(\tau'_k) E^\dagger(t) \epsilon(\tau_l) \cdots \epsilon(\tau_1) \rangle.
\end{aligned} \tag{3.107}$$

Note that, for simplicity of notation, we have not yet employed the rotating wave approximation in Eq. (3.107), such that we work with the quantities $\epsilon = E + E^\dagger$ and $\mathcal{V} = V + V^\dagger$ [recall Eq. (3.24)]. The signal contribution (3.107) 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. (3.95)]. Rewriting the signal in the Schrödinger picture with respect to the matter Hamiltonian,

$$\mathcal{V}_{\text{interaction}}(t) = G^\dagger(t) \mathcal{V}_{\text{Schrödinger}} G(t), \tag{3.108}$$

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 $G(\tau_{j+1} - \tau_j)$,

$$\begin{aligned}
S^{(k,l)}(\Gamma) &= (-1)^k \left(-\frac{i}{\hbar} \right)^n \int_0^\infty ds_n \cdots \int_0^\infty ds_1 \\
&\quad \times \langle \mathcal{V} G^\dagger(s_n) \mathcal{V} \cdots G^\dagger(s_{l+1}) V G(s_l) \mathcal{V} \cdots G(s_1) \mathcal{V} \rangle \\
&\quad \times \langle \epsilon(t - s_{l+1} \cdots - s_n) \epsilon(t - \cdots s_{n-1}) \cdots E^\dagger(t) \epsilon(t - s_l) \cdots \epsilon(t - \cdots - s_1) \rangle.
\end{aligned} \tag{3.109}$$

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 $t - s_l - \cdots - s_1$, and τ'_1 into $t - s_{l+1} - \cdots - s_n$. 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 chapter 2 we simply need to replace the field correlation function in Eq. (3.109) by classical field amplitudes $\mathcal{A} = A + A^*$,

$$\begin{aligned}
&\langle \epsilon(t - s_{l+1} \cdots - s_n) \epsilon(t - \cdots s_{n-1}) \cdots E^\dagger(t) \epsilon(t - s_l) \cdots \epsilon(t - \cdots - s_1) \rangle_{\text{semiclassical}} \\
&= \mathcal{A}(t - s_{l+1} \cdots - s_n) \mathcal{A}(t - \cdots s_{n-1}) \cdots A^*(t) \mathcal{A}(t - s_l) \cdots \mathcal{A}(t - \cdots - s_1).
\end{aligned} \tag{3.110}$$

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Figure 3.5.: Construction of the third-order loop diagram pertaining to Eq. (3.116): a) The evolution of the wavefunction according to Eq. (3.103) 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 (3.113) is obtained from the evolution of two wavefunctions $|\psi^{(2)}\rangle$ and $\langle\psi^{(1)}|$, see Eqs. (3.114) and (3.115), 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.

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. (3.104). However, a straightforward evaluation of Eq. (3.109) quickly runs into problems, since - by definition $\mathcal{V} = V + V^\dagger$ - we have 2^n possible terms [even using the RWA (3.6)], which may contribute to Eq. (3.109). 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 section 3.6).

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. (3.105), $S^{(3,0)}$, $S^{(2,1)}$, $S^{(1,2)}$, and $S^{(0,3)}$, which read, for instance,

$$S^{(3,0)} = (-1)^3 \left(-\frac{i}{\hbar}\right)^3 \int_0^\infty ds_3 \int_0^\infty ds_2 \int_0^\infty ds_1 \langle \mathcal{V} G^\dagger(s_3) \mathcal{V} G^\dagger(s_2) \mathcal{V} G^\dagger(s_1) V \rangle \\ \times \langle \epsilon(t - s_1 - s_2 - s_3) \epsilon(t - s_1 - s_2) \epsilon(t - s_1) E^\dagger(t) \rangle, \quad (3.111)$$

$$S^{(1,2)} = (-1)^1 \left(-\frac{i}{\hbar}\right)^3 \int_0^\infty ds_3 \int_0^\infty ds_2 \int_0^\infty ds_1 \langle \mathcal{V} G^\dagger(s_3) \mathcal{V} G(s_2) V G(s_1) \mathcal{V} \rangle \\ \times \langle \epsilon(t - s_3) E^\dagger(t) \epsilon(t - s_2) \epsilon(t - s_2 - s_1) \rangle, \quad (3.112)$$

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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. 3.1) 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 (3.112),

$$S_{\text{example}} = \langle \psi^{(1)}(t) | E^\dagger(t) V(t) | \psi^{(2)}(t) \rangle, \quad (3.113)$$

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. (3.106). We recall that ψ lives in the combined field-matter Hilbert space, such that - using the factorizing initial conditions (3.16) 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

$$\begin{aligned} |\psi^{(2)}(t)\rangle = & \left(-\frac{i}{\hbar}\right)^2 \int_0^\infty ds_2 \int_0^\infty ds_1 G(s_2) V^\dagger G(s_1) V^\dagger |\psi_{\text{matter}}(t_0)\rangle \\ & \times E(t - s_2) E(t - s_2 - s_1) |\psi_{\text{field}}(t_0)\rangle. \end{aligned} \quad (3.114)$$

It is easy to realize that the only contribution to $|\psi^{(2)}(t)\rangle$ consists of the two excitations in Eq. (3.114): 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. 3.5a), 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

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

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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

$$\begin{aligned} \langle \psi^{(1)}(t) | = & - \left(-\frac{i}{\hbar} \right) \int_0^\infty ds_3 \langle \psi_{\text{matter}}(t_0) | V G^\dagger(s_3) \\ & \times \langle \psi_{\text{field}}(t_0) | E^\dagger(t - s_3), \end{aligned} \quad (3.115)$$

and represented by the right transition amplitude in Fig. 3.5b). The minus-sign in Eq. (3.115) stems from taking the Hermitian conjugate of $|\psi^{(1)}\rangle$.

The final signal $E^\dagger V$ (which is time-independent in the Schrödinger picture), see Eq. (3.113), is sandwiched between these two expressions to yield

$$\begin{aligned} S_{\text{example}} = & - \left(-\frac{i}{\hbar} \right)^3 \int_0^\infty ds_3 \int_0^\infty ds_2 \int_0^\infty ds_1 \langle V G^\dagger(s_3) V G(s_2) V^\dagger G(s_1) V^\dagger \rangle \\ & \times \langle E^\dagger(t - s_3) E^\dagger(t) E(t - s_2) E(t - s_2 - s_1) \rangle. \end{aligned} \quad (3.116)$$

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 (3.113).

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.

3.5.2. Unrestricted loop diagrams

One is not always interested solely in the evaluation of specific nonlinear signals, *i.e.* of specific observables. For instance, in chapter 4, we mostly simulate excited state population distributions, without reference to a specific measurement setup. Furthermore, as discussed at hand of Eq. (3.37) on page 40, 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

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 section 3.6.

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Figure 3.6.: Splitting of an unrestricted loop diagram, *i.e.* of a process that does not end with a measurement, pertaining to Eq. (3.120) as the sum of two loop diagrams, according to Eq. (3.123). The loop times s_j and the interaction times τ_j are indicated.

the matrix elements with respect to the matter degree of freedom, one is left with transition operators acting on the field space,

$$\begin{aligned} T_{fi}(t) &= \langle f(t) | \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int}}(\tau) \right] | i(t_0) \rangle \\ &= T_{fi}^{(1)}(t) + T_{fi}^{(2)}(t) + T_{fi}^{(3)}(t) \cdots \end{aligned} \quad (3.117)$$

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

$$T_{fi}^{(1)}(t) = -\frac{i}{\hbar} \int_{t_0}^t d\tau \langle f(t) | \mathcal{V}(\tau) | i(t_0) \rangle \epsilon(\tau). \quad (3.118)$$

The probability for the transition between the state $|i\rangle$ and $|f\rangle$ will be the modulus square of Eq. (3.117), when averaged with respect to the initial state of the electromagnetic fields,

$$p_{fi}(t) = \langle T_{fi}^\dagger(t) T_{fi}(t) \rangle \equiv \text{tr} \left\{ T_{fi}^\dagger(t) T_{fi}(t) \varrho_{\text{field}}(t_0) \right\}, \quad (3.119)$$

where ϱ_{field} denotes the initial state of the electromagnetic field. Expansion of Eq. (3.119) in the form of Eq. (3.117), and evaluation thereof will lead to expressions of the form

$$\begin{aligned} p_{fi,\text{example}}(t) &= \langle T_{fi}^{\dagger(1)}(t) T_{fi}^{(3)}(t) \rangle \\ &= \left(-\frac{i}{\hbar} \right)^3 \left(\frac{i}{\hbar} \right) \int_{t_0}^t d\tau_3 \int_{t_0}^{\tau_3} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^{\tau_1} d\tau_1' \\ &\quad \times \langle i(t_0) | V(\tau_1') P_f(t) V(\tau_3) V^\dagger(\tau_2) V^\dagger(\tau_1) | i(t_0) \rangle \\ &\quad \times \langle E^\dagger(\tau_1') E^\dagger(\tau_3) E(\tau_2) E(\tau_1) \rangle, \end{aligned} \quad (3.120)$$

¹¹Note 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.

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where we introduce the projector onto the final state $P_f(t) = |f(t)\rangle\langle f(t)|$. In loop times, Eq. (3.120) reads

$$\begin{aligned} p_{fi,\text{example}}(t) = & - \left(-\frac{i}{\hbar} \right)^4 \int_0^\infty ds_4 \int_0^\infty ds_3 \int_0^\infty ds_2 \int_0^\infty ds_1 \\ & \times \langle VG^\dagger(s_4)P_f G(s_3)VG(s_2)V^\dagger G(s_1)V^\dagger \rangle \\ & \times \langle E^\dagger(t-s_4)E^\dagger(t-s_3)E(t-s_3-s_2)E(t-s_3-s_2-s_1) \rangle, \end{aligned} \quad (3.121)$$

which looks indeed very similar to the integral expressions of our previous example of a loop diagram, Eq. (3.116), except that the two transition amplitudes are no longer connected by a final matter-field interaction creating the signal. The diagrammatic representation in Fig. 3.6 of the above expression is straightforward, using our derivation of the loop diagram (3.112): Each (k -th order) transition amplitude $T_{fi}^{(k)}$ is represented by a vertical blue line, in analogy to Fig. 3.5a), in which each of the k interactions is represented by an arrow. The two transition amplitudes are finally 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. (3.120), 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

$$\int_{t_0}^t d\tau_3 \int_{t_0}^t d\tau'_1 = \int_{t_0}^t d\tau_3 \int_{t_0}^{\tau_3} d\tau'_1 + \int_{t_0}^t d\tau'_1 \int_{t_0}^{\tau'_1} d\tau_3. \quad (3.122)$$

This procedure splits Eq. (3.120) in two terms

$$p_{fi,\text{example}}(t) = \left(-\frac{i}{\hbar} \right) \int_{t_0}^t d\tau_3 \tilde{p}_{(a)}(\tau_3) + \left(\frac{i}{\hbar} \right) \int_{t_0}^t d\tau'_1 \tilde{p}_{(b)}(\tau'_1), \quad (3.123)$$

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

$$\begin{aligned} \tilde{p}_{(a)}(\tau_3) = & - \left(-\frac{i}{\hbar} \right)^3 \int_{t_0}^{\tau_3} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^{\tau_3} d\tau'_1 \\ & \times \langle i(t_0)|V(\tau'_1)P_f(t)V(\tau_3)V^\dagger(\tau_2)V^\dagger(\tau_1)|i(t_0)\rangle \\ & \times \langle E^\dagger(\tau'_1)E^\dagger(\tau_3)E(\tau_2)E(\tau_1) \rangle, \end{aligned} \quad (3.124)$$

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Figure 3.7.: The loop diagram, Eq. (3.116), may be written as the sum (3.129) 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.

and

$$\begin{aligned} \tilde{p}_{(b)}(\tau'_1) &= \left(-\frac{i}{\hbar}\right)^3 \int_{t_0}^{\tau'_1} d\tau_3 \int_{t_0}^{\tau_3} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \\ &\times \langle i(t_0) | V(\tau'_1) P_f(t) V(\tau_3) V^\dagger(\tau_2) V^\dagger(\tau_1) | i(t_0) \rangle \\ &\times \langle E^\dagger(\tau'_1) E^\dagger(\tau_3) E(\tau_2) E(\tau_1) \rangle, \end{aligned} \quad (3.125)$$

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 section 3.5.1. One small difference between the two still remains: Since we only considered a single final state f , the resulting loops (3.124) and (3.125) 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. (3.124) and (3.125), 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 section 3.6, we will follow the derivation in the opposite direction to express optical signals in terms of transition amplitudes.

3.5.3. 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 section 3.2. When we expand the entire density matrix (3.12), 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

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loop is no longer possible ($\mathcal{G}^\dagger$ as defined in Eq. (3.12) 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. (3.116) as time-ordered Liouville space expressions,

$$S_{\text{example}} = (-1) \left(-\frac{i}{\hbar} \right)^3 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^{\tau_1} d\tau'_1 \langle V_R(\tau'_1) V_L(t) V_L^\dagger(\tau_2) V_L^\dagger(\tau_1) \rangle \\ \times \langle E_R^\dagger(\tau'_1) E_L^\dagger(t) E_L(\tau_2) E_L(\tau_1) \rangle, \quad (3.126)$$

where we have adopted the “left” and “right” Liouville superoperators, Eqs. (3.19) and (3.20), 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 (3.116) may be obtained again from Eq. (3.126) 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

$$\langle V_R(\tau'_1) V_L(t) V_L^\dagger(\tau_2) V_L^\dagger(\tau_1) \rangle = \text{tr} \left\{ V(t) V^\dagger(\tau_2) V^\dagger(\tau_1) \varrho(t_0) V(\tau'_1) \right\} \quad (3.127)$$

$$= \text{tr} \left\{ V(\tau'_1) V(t) V^\dagger(\tau_2) V^\dagger(\tau_1) \varrho(t_0) \right\}, \quad (3.128)$$

which coincides with the matter correlation function in Eq. (3.116), 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,

$$S_{\text{example}} = (-1) \left(-\frac{i}{\hbar} \right)^3 \\ \times \left(\int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^{\tau_1} d\tau'_1 + \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau'_1 \int_{t_0}^{\tau'_1} d\tau_1 + \int_{t_0}^t d\tau'_1 \int_{t_0}^{\tau'_1} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \right) \\ \times \langle V_R(\tau'_1) V_L(t) V_L^\dagger(\tau_2) V_L^\dagger(\tau_1) \rangle \langle E_R^\dagger(\tau'_1) E_L^\dagger(t) E_L(\tau_2) E_L(\tau_1) \rangle. \quad (3.129)$$

One usually relabels the time integrations to $\tau_1, \dots, \tau_3$ in ascending chronological order

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as depicted in Fig. 3.7,

$$S_{\text{example}} = (-1) \left(-\frac{i}{\hbar} \right)^3 \int_{t_0}^t d\tau_3 \int_{t_0}^{\tau_3} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1$$

$$\times \left(\langle V_L(t) V_L^\dagger(\tau_3) V_L^\dagger(\tau_2) V_R(\tau_1) \rangle \langle E_L^\dagger(t) E_L(\tau_3) E_L(\tau_2) E_R^\dagger(\tau_1) \rangle \right. \quad (3.130)$$

$$+ \langle V_L(t) V_L^\dagger(\tau_3) V_R(\tau_2) V_L^\dagger(\tau_1) \rangle \langle E_L^\dagger(t) E_L(\tau_3) E_R^\dagger(\tau_2) E_L(\tau_1) \rangle \quad (3.131)$$

$$\left. + \langle V_L(t) V_R(\tau_3) V_L^\dagger(\tau_2) V_L^\dagger(\tau_1) \rangle \langle E_L^\dagger(t) E_R^\dagger(\tau_3) E_L(\tau_2) E_L(\tau_1) \rangle \right). \quad (3.132)$$

In analogy to the loop times [see their introduction following Eq. (3.107)], we may also simplify the evaluation of these nested integrals by changing to the time delays between interactions (now in physical time),

$$t_j \equiv \tau_{j+1} - \tau_j, \quad (3.133)$$

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

$$S_{\text{example}} = (-1) \left(-\frac{i}{\hbar} \right)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \times$$

$$\left(\langle V_L \mathcal{G}(t_3) V_L^\dagger \mathcal{G}(t) V_L^\dagger \mathcal{G}(t_1) V_R \rangle \langle E^\dagger(t - t_3 - t_2 - t_1) E^\dagger(t) E(t - t_4) E(t - t_3 - t_2) \rangle + \right.$$

$$\langle V_L \mathcal{G}(t_3) V_L^\dagger \mathcal{G}(t_2) V_R \mathcal{G}(t_1) V_L^\dagger \rangle \langle E^\dagger(t - t_3 - t_2) E^\dagger(t) E(t - t_3) E(t - t_3 - t_2 - t_1) \rangle +$$

$$\left. \langle V_L \mathcal{G}(t_3) V_R \mathcal{G}(t_2) V_L^\dagger \mathcal{G}(t_1) V_L^\dagger \rangle \langle E^\dagger(t - t_3) E^\dagger(t) E(t - t_3 - t_2) E(t - t_3 - t_2 - t_1) \rangle \right). \quad (3.134)$$

Even though the expressions in Eq. (3.134) look rather deterrently, they may be easily visualized by their Feynman diagrams. To that end, let us discuss the second line of Eq. (3.134) in more detail, which is represented by the left-most ladder diagram in Fig. 3.7. 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

3.5. Diagram construction

of quantum correlations of the light onto optical signals, which are not degraded by fluctuations. Hence, the field correlation functions in Eq. (3.134) may still be evaluated in Hilbert space, yielding the same correlation functions as in Eq. (3.116), 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. (3.132)

$$\begin{aligned} & \text{tr} \left\{ E_L^\dagger(t) E_L(t - t_3) E_L(t - t_3 - t_2) E_R^\dagger(t - t_3 - t_2 - t_1) \varrho_{\text{field}} \right\} \\ &= \text{tr} \left\{ E^\dagger(t - t_3 - t_2 - t_1) E^\dagger(t) E(t - t_4) E(t - t_3 - t_2) \varrho_{\text{field}} \right\}. \end{aligned} \quad (3.135)$$

This is the reason all the field correlation functions in Eq. (3.134) may be written in normally ordered form.

Despite their apparent greater complexity, ladder diagrams of the type (3.134), depicted in Fig. 3.7, 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. (3.12) 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.

3.5.4. Time vs. 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. (3.116) as a concrete example. To obtain the frequency domain expression, we decompose the field correlation into its Fourier components

$$\begin{aligned} & \langle E^\dagger(t - s_3) E^\dagger(t) E(t - s_2) E(t - s_2 - s_1) \rangle \\ &= \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} e^{i(\omega'_a + \omega'_b - \omega_a - \omega_b)t} e^{i\omega_a s_1} e^{i(\omega_a + \omega_b)s_2} e^{-i\omega'_a s_3} \\ & \times \langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle, \end{aligned} \quad (3.136)$$

which allows us to carry out the time integrations in Eq. (3.116), and replace the time-dependent propagators $G(s_1)$, $G(s_2)$, and $G^\dagger(s_3)$ by the frequency domain Green's functions

$$G(\omega) \equiv \int_0^\infty ds e^{i\omega s} G(s) \quad (3.137)$$

$$= \frac{i}{\omega - H_{\text{matter}}/\hbar + i\eta}. \quad (3.138)$$

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Eq. (3.116) then takes the form

$$\begin{aligned}
S_{\text{example}} &= \left(-\frac{i}{\hbar}\right)^3 \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} e^{i(\omega'_a + \omega'_b - \omega_a - \omega_b)t} \\
&\quad \times \langle V G^\dagger(\omega'_a) V G(\omega_a + \omega_b) V^\dagger G(\omega_a) V^\dagger \rangle \\
&\quad \times \langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle.
\end{aligned} \tag{3.139}$$

As one can see from Eq. (3.139), the frequency domain representation may be beneficial in the case of time-integrated signals such as Eq. (3.38): Integrating over t in Eq. (3.139) 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.

3.5.5. 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,

$$E_i(t) \simeq \delta(t - (t_i^{(0)} - t_{i-1}^{(0)})). \tag{3.140}$$

We may then carry out the time integrations in any perturbative signal. For instance, we obtain for Eq. (3.134)

$$\begin{aligned}
S_{\text{example}} &= (-1) \left(-\frac{i}{\hbar}\right)^3 \left(\langle V_L \mathcal{G}(t_3^{(0)}) V_L^\dagger \mathcal{G}(t_2^{(0)}) V_L^\dagger \mathcal{G}(t_1^{(0)}) V_R \rangle \right. \\
&\quad \left. + \langle V_L \mathcal{G}(t_3^{(0)}) V_L^\dagger \mathcal{G}(t_2^{(0)}) V_R \mathcal{G}(t_1^{(0)}) V_L^\dagger \rangle + \langle V_L \mathcal{G}(t_3^{(0)}) V_R \mathcal{G}(t_2^{(0)}) V_L^\dagger \mathcal{G}(t_1^{(0)}) V_L^\dagger \rangle \right)
\end{aligned} \tag{3.141}$$

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.

3.6. Susceptibilities vs. 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*

3.6. Susceptibilities vs. transition amplitudes in the quantum domain

Figure 3.8.: The loop diagrams comprising the symmetrized linear absorption signal (3.142). Diagram (a) is obtained from the expansion (3.145) of $\langle E^\dagger V \rangle$, and diagram (b) from the expansion of $\langle EV^\dagger \rangle$.

[Boyd03]. As mentioned in the derivation of Eq. (3.37), 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. (3.37). 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. 3.1). 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. (3.37) over time. We further aim to address the described ambiguity in the representation of optical signals, which we had noted in section 3.3. To this end, we symmetrize the signal with respect to the two possible representations, Eqs. (3.37) and (3.39), of the final interaction,

$$S(\Gamma) = \frac{1}{2} \int_{-\infty}^{\infty} dt \left(\frac{2}{\hbar} \Im \langle E_+^\dagger(t) V_+(t) \rangle_{\text{final}} - \frac{2}{\hbar} \Im \langle E_+(t) V_+^\dagger(t) \rangle_{\text{final}} \right). \quad (3.142)$$

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

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(i.e. we simply replace $E_+ \rightarrow E$ etc.), and obtain the result in terms of loop diagrams.

3.6.1. Linear absorption

We first analyze the first term in Eq. (3.142), $\langle E^\dagger(t)V(t) \rangle$. The linear absorption signal is obtained by expanding the exponential (3.15) to first order, which leaves us with two possible contributions,

$$S^{(1,0)}(\Gamma) = \frac{1}{\hbar} \int_{-\infty}^{\infty} dt \Im \langle \psi^{(1)}(t) | E^\dagger(t) V(t) | \psi^{(0)}(t) \rangle, \quad (3.143)$$

$$S^{(0,1)}(\Gamma) = \frac{1}{\hbar} \int_{-\infty}^{\infty} dt \Im \langle \psi^{(0)}(t) | E^\dagger(t) V(t) | \psi^{(1)}(t) \rangle, \quad (3.144)$$

where we recall our definition (3.106) of the k -th wavefunction. In Eq. (3.143), the de-excitation operator $V(t)$ acts on the ground state, and this contribution therefore vanishes.¹² To avoid this situation in Eq. (3.144), 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

$$S^{(0,1)}(\Gamma) = \frac{1}{\hbar} \int_{-\infty}^{\infty} dt \int_{t_0}^t d\tau_1 \Im \left(-\frac{i}{\hbar} \right) \langle \psi^{(0)}(t_0) | E^\dagger(t) V(t) E(\tau_1) V^\dagger(\tau_1) | \psi^{(0)}(t_0) \rangle. \quad (3.145)$$

This expression may be represented by diagram (a) in Fig. 3.8. 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

$$S^{(0,1)}(\Gamma) = \frac{1}{\hbar} \int_{-\infty}^{\infty} dt \int_{t_0}^t d\tau_1 \Im \left(-\frac{i}{\hbar} \right) \langle g | V G(t - \tau_1) V^\dagger | g \rangle \langle E^\dagger(t) E(\tau_1) \rangle, \quad (3.146)$$

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. 3.1, Eq. (3.7), the matter correlation function is given by the sum-over-states expression

$$\langle g | V G(t - \tau_1) V^\dagger | g \rangle = \sum_e |\mu_{ge}|^2 e^{-i\omega_e(t-\tau_1)}, \quad (3.147)$$

where the sum e runs over all the single exciton states in the associated manifold in Fig. 3.1.¹³ To evaluate the signal, we now change to the loop time $s = t - \tau_1$, and decompose the field correlation function as

$$\langle E^\dagger(t) E(t - s) \rangle = \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} e^{i\omega t - i\omega'(t-s)} \langle E^\dagger(\omega) E(\omega') \rangle, \quad (3.148)$$

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.

¹³Similarly, we will denote summations over the other state manifolds in Fig. 3.1 by summation indices g, f , etc. in the following.

3.6. Susceptibilities vs. transition amplitudes in the quantum domain

and, after inserting Eqs. (3.147) and (3.148) in (3.146), we can carry out the time integrations, and obtain

$$S^{(0,1)}(\Gamma) = \frac{1}{\hbar^2} \Im \int \frac{d\omega}{2\pi} \frac{|\mu_{ge}|^2}{\omega - \omega_e + i\eta} \langle E^\dagger(\omega) E(\omega) \rangle. \quad (3.149)$$

Here, we have added the infinitesimal complex factor $i\eta$ to evaluate the s -integration in Eq. (3.146), after the substitution $s = t - \tau_1$. The t -integration yielded a delta function $2\pi\delta(\omega - \omega')$.

To rewrite Eq. (3.149) as the modulus square of a transition amplitude, we now define the first-order transition amplitude operator acting on the field Hilbert space,

$$T_{eg}^{(1)}(\omega) = \sum_e \frac{\mu_{eg}}{\hbar} E(\omega). \quad (3.150)$$

This allows us to write the signal as

$$S^{(0,1)}(\Gamma) = \sum_e \Im \int \frac{d\omega}{2\pi} \frac{1}{\omega - \omega_e + i\eta} \langle T_{eg}^{(1)\dagger}(\omega) T_{eg}^{(1)}(\omega) \rangle. \quad (3.151)$$

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

$$\frac{1}{\omega + i\eta} = \text{PP} \frac{1}{\omega} - i\pi\delta(\omega), \quad (3.152)$$

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

$$S^{(0,1)}(\Gamma) = -\frac{1}{2} \sum_e \langle |T_{eg}^{(1)}(\omega_e)|^2 \rangle, \quad (3.153)$$

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

In an identical derivation, we can express the second term in Eq. (3.142) by the single Feynman diagram (b) in Fig. 3.8. In contrast to Eqs. (3.143) and (3.143), 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.(3.153). Hence, the full linear absorption signal is given by

$$S^{(1)}(\Gamma) = - \sum_e \langle |T_{eg}^{(1)}(\omega_e)|^2 \rangle. \quad (3.154)$$

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

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Figure 3.9.: The loop diagrams comprising the symmetrized third-order absorption signal contributing to Eq. (3.142). 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.

example, in which we could derive the diagrammatic representation of the signal in detail - we can already draw some useful conclusions from Eq. (3.154): The sign of the linear absorption is negative due to our definition (3.31) 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 (3.37) is negative. We have also seen that, in fact, both terms in Eq. (3.142) yield the same transition amplitude $\langle |T_{eg}^{(1)}(\omega_e)|^2 \rangle$, even though their diagrammatic representation in Fig. 3.8 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.

3.6.2. 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 section 2.2, and therefore this is the lowest order where we can expect to see entanglement effects in optical signals. Expanding the time evolution operator (3.15) to third order, we obtain the loop diagrams depicted in Fig. 3.9. Diagrams (Ia)-(IVa) are obtained by expanding the first term in Eq. (3.142), and the convention that the final interaction happens on the *ket*-side. Similarly, the second line, diagrams

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(Ib)-(IVb), stem from the expansion of the second term in Eq. (3.142). Diagrams (I) & (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) & (IV) will be called *Raman* pathways, since they show a succession of excitations and de-excitations, $\langle VV^\dagger VV^\dagger \rangle$. 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. (3.90), the polarizability consisted of a succession of electronic excitation and de-excitation, *i.e.* $VV^\dagger$, and we will later encounter this quantity in chapter 7. It is in this spirit that the four-point correlation functions $\langle VV^\dagger VV^\dagger \rangle$ 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. 3.9 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),

$$S_{(\text{Ia})}^{(3)} = -\frac{1}{\hbar} \Im \left[\left(-\frac{i}{\hbar} \right)^3 \int_{-\infty}^{\infty} dt \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^{\tau_1} d\tau'_1 \langle V(\tau'_1) V(t) V^\dagger(\tau_2) V^\dagger(\tau_1) \rangle \right. \\ \left. \times \langle E^\dagger(\tau'_1) E^\dagger(t) E(\tau_2) E(\tau_1) \rangle \right] \quad (3.155)$$

(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,

$$\langle E^\dagger(\tau'_1) E^\dagger(t) E(\tau_2) E(\tau_1) \rangle = \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} e^{i\omega'_a \tau'_1 + i\omega'_b t - i\omega_b \tau_2 - i\omega_a \tau_1} \\ \times \langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle. \quad (3.156)$$

By changing to the loop times defined in section 3.5, and evaluating the matter correlation function in a sum-over-states expression, using Eq. (3.7),

$$\langle VG^\dagger(s_3) VG(s_2) V^\dagger G(s_1) V^\dagger \rangle = \sum_{g,e,f,e'} \mu_{ge} e^{-i\omega_e s_1} \mu_{ef} e^{-i\omega_f s_2} \mu_{fe'} e^{i\omega_{e'} s_3} \mu_{e'g}, \quad (3.157)$$

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we may carry out the time integrations,

$$\begin{aligned}
S_{(\text{Ia})}^{(3)} = & -\frac{1}{\hbar} \Im \left[\left(-\frac{i}{\hbar} \right)^3 \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} 2\pi \delta(\omega_a + \omega_b - \omega'_a - \omega'_b) \right. \\
& \times \langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle \frac{i\mu_{ge}}{\omega_a - \omega_e + i\eta} \frac{i\mu_{ef}}{\omega_a + \omega_b - \omega_f + i\eta} \\
& \left. \times \frac{-i\mu_{fe'}}{\omega'_a - \omega_{e'} - i\eta} \mu_{e'g} \right], \tag{3.158}
\end{aligned}$$

where we again introduced the usual infinitesimal factor η to write the matter propagators in frequency domain [see Eq. (3.138)]. 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

$$T_{fg}^{(2)}(\omega_{\text{sum}}) = \frac{1}{\hbar^2} \sum_e \int \frac{d\omega_a}{2\pi} \frac{\mu_{ge}\mu_{ef}}{\omega_a - \omega_e + i\eta} E(\omega_{\text{sum}} - \omega_a) E(\omega_a), \tag{3.159}$$

we may rewrite the signal as

$$S_{(\text{Ia})}^{(3)}(\Gamma) = \Im \left[\sum_f \int \frac{d\omega_{\text{sum}}}{2\pi} \langle T_{fg}^{(2)\dagger}(\omega_{\text{sum}}) T_{fg}^{(2)}(\omega_{\text{sum}}) \rangle \frac{1}{\omega_{\text{sum}} - \omega_f + i\eta} \right]. \tag{3.160}$$

Finally, as in our derivation of Eq. (3.154), we use the identity (3.152) to express Eq. (3.160) as the modulus square of transition amplitude operators acting on the initial quantum state of the light,

$$S_{(\text{Ia})}^{(3)}(\Gamma) = -\frac{1}{2} \sum_f \langle |T_{fg}^{(2)}(\omega_f)|^2 \rangle. \tag{3.161}$$

In an identical calculation, we obtain

$$S_{(\text{Ib})}^{(3)} = -\frac{1}{2} \sum_f \langle |T_{fg}^{(2)}(\omega_f)|^2 \rangle. \tag{3.162}$$

Hence, the final third-order contribution to the signal (3.142), 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

$$S_{(\text{IIa})}^{(3)}(\Gamma) = \Im \left[\sum_{e'} \int \frac{d\omega}{2\pi} \langle T_{e'g}^{(1)\dagger}(\omega) T_{e'g}^{(3)}(\omega) \rangle \frac{1}{\omega - \omega_{e'} + i\eta} \right], \tag{3.163}$$

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and

$$S_{(\text{IIb})}^{(3)}(\Gamma) = -\Im \left[\sum_{e'} \int \frac{d\omega}{2\pi} \langle T_{e'g}^{(3)\dagger}(\omega) T_{e'g}^{(1)}(\omega) \rangle \frac{1}{\omega - \omega_{e'} - i\eta} \right], \quad (3.164)$$

with the first- and third-order transition amplitude operators

$$T_{e'g}^{(1)}(\omega) = \frac{\mu_{e'g}}{\hbar} E(\omega), \quad (3.165)$$

$$T_{e'g}^{(3)}(\omega) = \frac{1}{\hbar^3} \sum_{e,f} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_x}{2\pi} \frac{\mu_{ge}}{\omega_a - \omega_e + i\eta} \frac{\mu_{ef}\mu_{fe'}}{\omega_x - \omega_f + i\eta} \\ \times E^\dagger(\omega_x - \omega) E(\omega_x - \omega_a) E(\omega_a). \quad (3.166)$$

Thus, employing Eq. (3.152), the sum of the these two diagrams may be written as,

$$S_{(\text{IIa})}^{(3)}(\Gamma) + S_{(\text{IIb})}^{(3)}(\Gamma) \\ = \Im \sum_{e'} \int \frac{d\omega}{2\pi} \left[-i\pi \delta(\omega - \omega_{e'}) \langle T_{e'g}^{(1)\dagger}(\omega) T_{e'g}^{(3)}(\omega) + T_{e'g}^{(3)\dagger}(\omega) T_{e'g}^{(1)}(\omega) \rangle \right. \\ \left. \text{PP} \frac{1}{\omega - \omega_{e'}} \langle T_{e'g}^{(1)\dagger}(\omega) T_{e'g}^{(3)}(\omega) - T_{e'g}^{(3)\dagger}(\omega) T_{e'g}^{(1)}(\omega) \rangle \right] \quad (3.167)$$

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

$$S_{(\text{IIa})}^{(3)}(\Gamma) + S_{(\text{IIb})}^{(3)}(\Gamma) = -2\Re \sum_{e'} \langle T_{e'g}^{(1)\dagger}(\omega_{e'}) T_{e'g}^{(3)}(\omega_{e'}) \rangle, \quad (3.168)$$

and the sum of the TPA pathways yields

$$S_{\text{TPA}}^{(3)}(\Gamma) = - \sum_f \langle |T_{fg}^{(2)}(\omega_f)|^2 \rangle - 2\Re \sum_{e'} \langle T_{e'g}^{(1)\dagger}(\omega_{e'}) T_{e'g}^{(3)}(\omega_{e'}) \rangle. \quad (3.169)$$

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 chapter 5.

Raman pathways

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

$$T_{g'g}^{(2)}(\omega) = \frac{1}{\hbar^2} \sum_e \int \frac{d\omega_a}{2\pi} \frac{\mu_{ge}\mu_{eg'}}{\omega_a - \omega_e + i\eta} E^\dagger(\omega_a - \omega) E(\omega_a), \quad (3.170)$$

$$T_{e'g}^{(3)}(\omega) = \frac{1}{\hbar^3} \sum_{e,g'} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_-}{2\pi} \frac{\mu_{ge}}{\omega_a - \omega_e + i\eta} \frac{\mu_{eg'}\mu_{g'e'}}{\omega_- - \omega_{g'} + i\eta} \\ \times E(\omega - \omega_-) E^\dagger(\omega_a - \omega_-) E(\omega_a). \quad (3.171)$$

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$T_{g'g}^{(2)}$ describes a generalization of the Raman process we described in the derivation of the effective interaction operators earlier in section 3.4. 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. (3.97). $T'^{(3)}$ corresponds to a Raman process where the system evolves in the ground state after the first two interactions, whereas $T^{(3)}$ defined in Eq. (3.166) describes the two-photon absorption (TPA) process. After similar calculations as before, we obtain the final result

$$S_{\text{Raman}}^{(3)}(\Gamma) = \sum_{g'} \langle |T_{g'g}^{(2)}(\omega_{g'})|^2 \rangle - 2\Re \sum_{e'} \langle T_{e'g}^{(1)\dagger}(\omega_{e'}) T_{e'g}'^{(3)}(\omega_{e'}) \rangle. \quad (3.172)$$

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 $T^{(1)\dagger}T'^{(3)}$ -contribution has the same sign as its TPA analog in Eq. (3.168). However, note that the $T^{(3)}$ amplitude (3.166) has a photon creation operator as leftmost operator. Hence, it finishes with a photon emission. The $T'^{(3)}$ -pathway in the Raman signals finishes with a photon annihilation. As we will show in chapter 5, this difference causes the two contributions to have opposite signs after all.

In conclusion, Eqs. (3.169) and (3.172) 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.

3.7. 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 section 3.3),

$$S(t; \Gamma) = \langle A(t) \rangle_{\text{final}}, \quad (3.173)$$

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. (3.31) [or Eq. (3.57) 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

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Figure 3.10.: 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 chapter 8, 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.

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 chapter 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 to 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. (3.173) 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 section 3.5.1), or by a general master equation, which is calculated by *ladder* diagrams (see section 3.5.3). The diagrams represent perturbative expansions of the Dyson series, either Eq. (3.15) in case we are dealing with the propagation of wavefunctions, or Eq. (3.12) in case we propagate the full density matrix. The basic building block of the diagrams are the light-matter interactions as depicted in Fig. 3.10. 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 the density matrix (denoting an excitation process) or away from it (indicating a de-excitation).

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Figure 3.11.: 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.

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

3.7.1. 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

$$S^{(n)}(t; \Gamma) = \sum_{k+l=n} \langle\psi^{(l)}(t)|A(t)|\psi^{(k)}(t)\rangle, \quad (3.174)$$

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,

$$|\psi^{(k)}(t)\rangle = \left(-\frac{i}{\hbar}\right)^k \int_0^\infty ds_k \cdots \int_0^\infty ds_1 G(s_k) \mathbb{V} G(s_{k-1}) \cdots G(s_2) \mathbb{V} G(s_1) \mathbb{V} |g\rangle \\ \times \mathbb{E}(t - s_k) \cdots \mathbb{E}(t - s_k - \cdots - s_1) |\psi_{\text{field}}\rangle. \quad (3.175)$$

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

$$|\psi^{(k)}(t)\rangle = \left(-\frac{i}{\hbar}\right)^k \int \frac{d\omega_1}{2\pi} \cdots \int \frac{d\omega_k}{2\pi} G(\pm\omega_1 \cdots \pm\omega_k) \mathbb{V} \cdots \mathbb{V} G(\pm\omega_1) \mathbb{V} |g\rangle \\ \times \mathbb{E}(\omega_k) \cdots \mathbb{E}(\omega_1) |\psi_{\text{field}}\rangle e^{-i(\pm\omega_1 + \cdots \pm\omega_k)t}. \quad (3.176)$$

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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. (3.175) and (3.176), 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. 3.11), 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.

3.7.2. Ladder diagrams

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

$$S^{(n)}(t; \Gamma) = \langle A(t) \rangle_{\text{final}} = \text{tr} \left\{ A(t) \varrho^{(n)}(t) \right\}, \quad (3.177)$$

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 (3.12) 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

$$\begin{aligned} S^{(n)}(t; \Gamma) &= \left(-\frac{i}{\hbar} \right)^n (-1)^{\#(R)} \int_0^\infty dt_n \cdots \int_0^\infty dt_1 \text{tr} \left\{ A(t) \mathcal{G}(t_n) \mathbb{V}_{L/R} \cdots \mathcal{G}(t_1) \mathbb{V}_{L/R} \varrho_{\text{matter}} \right\} \\ &\quad \times \text{tr} \left\{ \mathbb{E}_{L/R}(t - t_n) \cdots \mathbb{E}_{L/R}(t - t_n - \cdots - t_1) \varrho_{\text{field}} \right\}. \end{aligned} \quad (3.178)$$

Here, the subscripts L/R denote the left-/right-superoperators acting only on the *ket* or *bra* side of the density matrix [see Eqs. (3.19) and (3.20)]. Each interaction $\mathbb{V}_R$ acting

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Figure 3.12.: 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. (3.19)], and those acting on the *bra* to right-superoperators [Eq. (3.20)].

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*.

The frequency domain expression of Eq. (3.178) reads

$$\begin{aligned}
 S^{(n)}(t; \Gamma) = & \left(-\frac{i}{\hbar} \right)^n (-1)^{\#(R)} \int \frac{d\omega_1}{2\pi} \dots \int \frac{d\omega_n}{2\pi} e^{-i(\pm\omega_1 + \dots \pm \omega_n)t} \\
 & \times \text{tr} \left\{ A(t) \mathcal{G}(\pm\omega_1 \dots \pm \omega_n) \mathbb{V}_{L/R} \dots \mathcal{G}(\pm\omega_1) \mathbb{V}_{L/R} \varrho_{\text{matter}} \right\} \\
 & \times \text{tr} \left\{ \mathbb{E}_{L/R}(\omega_n) \dots \mathbb{E}_{L/R}(\omega_1) \varrho_{\text{field}} \right\}, \quad (3.179)
 \end{aligned}$$

where the same rules as before in Eq. (3.176) apply for the sign of the various frequency components.

Impulsive limit

As described in chapter 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. (3.175) and (3.178), 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. (3.178)¹⁴ by delta functions. This

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

allows us to carry out the time integrations, and write the impulsive signal as

$$S^{(n)}(t; \Gamma) = \text{tr} \left\{ A(t) \mathcal{G}(t_n^{(0)}) \mathbb{V}_{L/R} \cdots \mathcal{G}(t_1^{(0)}) \mathbb{V}_{L/R} \varrho_{\text{matter}} \right\}, \quad (3.180)$$

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. 3.10.

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.

3.7.3. 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 (3.12) 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. (3.6) + 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. 4.13)!

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.

Fig. 3.13 shows how the third-order contribution to the intensity signal we had discussed in section 3.6, see Fig. 3.9, 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

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Figure 3.13.: Diagram construction of the third-order intensity signal in Fig. 3.9 according to the rules given in section 3.7.3: 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. 3.9.

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 between this “backbone”.¹⁵ When adding one excitation on each side of the density matrix, we obtain diagram (Ia) of Fig. 3.9. 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. (3.105) 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.

¹⁵Note that our notation of the interaction times is chosen such that each arrow can be identified with its counterpart in Fig. 3.9.

4. Excited state distributions and fluorescence signals

It is clear by its very construction that any nonlinear optical signal will strongly depend on the excited state wavepackets created by the absorption of photons from the excitation pulses. However, these wavepackets are seldom discussed, since in the case of classical laser light they are fairly straightforward to characterize: As we will show in section 4.1 below, the factorization of laser field correlation functions directly translates into the factorization of the induced excited state distributions (in the absence of exciton interactions) [Schlawin14b].¹ In other words, any correlation function of two “classical” laser pulses factorizes into products of field amplitudes, *i.e.* $\langle E^\dagger(t_1)E(t_2) \rangle = A^*(t_1)A(t_2)$, such that there are no correlations between the fields at the two times t_1 and t_2 . This lack of correlations implies that no correlations can be induced in a sample system by multiphoton absorptions from this classical light field.

Quantum light, and in particular entangled photons, feature much more complicated correlation functions, and the wavepackets induced by such fields are far from obvious. Since we aim to investigate nonlinear spectroscopy using such light sources in a systematic way, we will simulate wavepacket dynamics (excited state distributions) induced by the coupling to either entangled photons or classical laser pulses. We will calculate the excited state distributions at a time t after the light pulses have passed through the sample. To simplify our discussion, we neglect energy dissipation after the photon absorption. This will also allow us to compare the wavepackets induced by pulses with the steady-state distribution induced by continuous-wave (cw) excitation.

We will first introduce the *two-photon induced fluorescence* signal which is most closely related to the wavepacket distributions we are interested in. To set the stage, we will then consider the simplest possible toy model - a three-level system, in which resonantly enhanced as well as far off-resonant two-photon absorption events are possible. Its discussion will allow us to develop some intuition for the dependence of the entangled photon correlation function on the external control parameters, and to discuss the intensity crossover with increasing pump intensity, when different entangled pairs start to overlap temporally (see our discussion in section 2.2.3). In a subsequent step, we will turn to the wavepackets induced in a quantum system with more complex level structure - the bacterial reaction center (RC) of *Blastochloris viridis*. We will compare these wavepackets with those induced by classical light, or by separable, unentangled - yet correlated - two-photon states.

¹Furthermore, the broad bandwidth of ultrashort pulses often leads to an almost uniform excitation of all the accessible electronic states in a molecule. In such a situation, the Fourier transform with respect to the time delays as discussed in chapter 2 will reveal all the states, see, e.g., Fig. 2.2.

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Afterwards, we will give the full picture: the wavepackets induced in the RC *in the presence of dissipation*, which induces irreversible energy transport towards lower-energy states. This will clarify the importance of simultaneous time and frequency correlations in entangled photon pairs. We will trace back the peculiar excited state distributions induced by strongly entangled photons to the violation of a classical time-energy uncertainty.

In the final section, we will simulate the two-photon induced fluorescence signal of the RC, and show how signatures of the induced wavepackets may be detected in this optical signal.

4.1. Excursion: Matter correlations induced by coupling to quantum light

Before we discuss the interaction of quantum light with multi-level systems, we will first give a simple argument to clarify the statement made in the introduction: that classical light does not induce correlations within a sample system, while quantum light does.

To this end, we first consider an ensemble of noninteracting two-level atoms (with different transition frequencies $\{\omega_{e_i}\}$) coupled to the electromagnetic field. The full density matrix of the combined light-matter system is given by the Dyson series (3.12),

$$\varrho(t) = \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_{\text{int},-}(\tau) \right] |g(t_0)\rangle \langle g(t_0)| \otimes \varrho_{\text{field}}(t_0), \quad (4.1)$$

where, as before, $|g\rangle$ denotes the ground state the matter system is initially prepared in, and ϱ_{field} the initial state of the light field. From this expression, it is straightforward to extract the matrix elements with respect to single- and two exciton states (which constitute the e - and f -manifolds in Fig. 3.1) after interaction with the fields,

$$\varrho_{e_i, e_{i'}}(t) = \text{tr} \{ |e_{i'}(t)\rangle \langle e_i(t)| \varrho(t) \}. \quad (4.2)$$

Expanding the exponential in Eq. (4.1) with the interaction Hamiltonian (3.6), we obtain the leading-order contribution [Schlawin14b]

$$\begin{aligned} \varrho_{e_i, e_{i'}}(t) &= \left(-\frac{i}{\hbar} \right)^2 \int_{t_0}^t d\tau_1 \int_{t_0}^{\tau_1} d\tau'_1 \\ &\times \langle g(t_0) | V(\tau'_1) | e_{i'}(t) \rangle \langle e_i(t) | V^\dagger(\tau_1) | g(t_0) \rangle \\ &\times \langle E^\dagger(\tau'_1) E(\tau_1) \rangle, \end{aligned} \quad (4.3)$$

with $\langle E^\dagger(\tau'_1) E(\tau_1) \rangle \equiv \text{tr} \{ E^\dagger(\tau'_1) E(\tau_1) \varrho_{\text{field}}(t_0) \}$. Similarly, we obtain for doubly excited states $|e_i, e_j\rangle$,

$$\varrho_{e_i e_j, e_{i'} e_{j'}}(t) = \text{tr} \{ \mathcal{T} |e_{i'}(t), e_{j'}(t)\rangle \langle e_i(t), e_j(t)| \varrho(t) \}, \quad (4.4)$$

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the leading-order contribution

$$\begin{aligned} \varrho_{e_i e_j, e_{i'} e_{j'}}(t) &= \left(-\frac{i}{\hbar}\right)^4 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^t d\tau'_2 \int_{t_0}^{\tau'_2} d\tau'_1 \\ &\times \langle g(t_0) | V(\tau'_1) V(\tau'_2) | e_{i'}(t), e_{j'}(t) \rangle \langle e_i(t), e_j(t) | V^\dagger(\tau_2) V^\dagger(\tau_1) | g(t_0) \rangle \\ &\times \langle E^\dagger(\tau'_1) E^\dagger(\tau'_2) E(\tau_2) E(\tau_1) \rangle, \end{aligned} \quad (4.5)$$

where four-point correlation functions of matter- and field-systems appear. Note that our “observables” $|e_{i'}(t)\rangle\langle e_i(t)|$ and $|e_{i'}(t), e_{j'}(t)\rangle\langle e_i(t), e_j(t)|$ do not constitute field-matter interactions. In analogy to our derivation of nonlinear optical signals in the previous chapter, the resulting expressions can therefore be represented by unrestricted loop diagrams (see section 3.5.2), where the pathway ends up in a coherence at time t . It is those kinds of diagrams that we will have to evaluate in this chapter in order to obtain excited state distributions in a complex sample system.

In the frequency domain, the above expressions (4.3) and (4.5) read

$$\begin{aligned} \varrho_{e_i, e_{i'}}(t) &= \left(-\frac{i}{\hbar}\right)^2 \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \mu_{ge_{i'}} \mu_{ge_i} \frac{\langle E^\dagger(\omega_a) E(\omega_b) \rangle e^{i(\omega_a - \omega_b)t}}{(\omega_b - \omega_{e_i} + i\eta)(\omega_a - \omega_{e_{i'}} - i\eta)} \quad (4.6) \\ \varrho_{e_i e_j, e_{i'} e_{j'}}(t) &= \left(-\frac{i}{\hbar}\right)^4 \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} \mu_{ge_{i'}} \mu_{ge_{j'}} \mu_{ge_i} \mu_{ge_j} \\ &\times \sum_{\omega_i = \{\omega_{e_i}, \omega_{e_j}\}} \frac{\langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle e^{-i(\omega_a + \omega_b)t}}{(\omega_a - \omega_i + i\eta)(\omega_a + \omega_b - \omega_{e_i g} - \omega_{e_j g} + i\eta)} \\ &\times \sum_{\omega_j = \{\omega_{e_{i'}}, \omega_{e_{j'}}\}} \frac{e^{i(\omega'_a + \omega'_b)t}}{(\omega'_a - \omega_j - i\eta)(\omega'_a + \omega'_b - \omega_{e_{i'}} - \omega_{e_{j'}} - i\eta)}, \end{aligned} \quad (4.7)$$

where we introduced the complex factor $i\eta$ to write the e -state component of the frequency domain Green's function (3.138), $G_e(\omega) = i/(\omega - \omega_e + i\eta)$. In deriving Eqs. (4.6) and (4.7), we have changed to the loop time variables, and extended their integration to ∞ (see our discussion in chapter 3, page 58). The latter step is only valid if the time t is set after the interaction of the light pulses with the sample: For instance, to obtain Eq. (4.6), we change to the loop time variable $s_1 = t - \tau_1$, and obtain the integration boundaries $(0, t - t_0)$. To arrive at the frequency domain representation (4.6), we have to send the integration boundary $t - t_0 \rightarrow \infty$, which has been argued to be justified when t_0 predates the interaction. But if t also predates the interaction time, one could also argue to send $t \rightarrow -\infty$, rendering the difference $t - t_0$ undefined. Hence, the frequency expressions above require the time t to succeed the interaction between the light pulses and the sample.

To evaluate Eqs. (4.6) and (4.7), we use relation (3.152), which we recall is given by

$$\frac{1}{\omega + i\eta} = \text{PP} \frac{1}{\omega} - i\pi\delta(\omega). \quad (4.8)$$

4. Excited state distributions and fluorescence signals

In section 3.6, this relation was used to show that nonlinear signals - given by the imaginary part of nonlinear susceptibilities - can be connected to transition amplitudes in the matter system. This result was true for pulsed as well as continuous light (cw) illumination. Here, we will use the relation in a less stringent way by restricting our discussion to the interaction with pulsed light. Note that, in Eq. (3.152), the delta part yields resonant contributions at frequency zero. The Cauchy principal value $\text{PP } 1/\omega$ gives positive and negative contributions outside the resonance, and it can be thought of as a measure of the “skewdness” of the test function: Its action on a (well-behaved) test function is defined by

$$\text{PP} \frac{1}{\omega} [f_{\text{test}}(\omega)] \equiv \int d\omega \frac{1}{\omega} f_{\text{test}}(\omega). \quad (4.9)$$

If $f_{\text{test}}(\omega)$ is symmetric - or, more importantly for our case, is nearly constant - around $\omega = 0$, the integral vanishes exactly. In the present dissertation, we are mostly interested in the interaction of short laser pulses with matter systems. These pulses typically have bandwidths on the order of $\geq 100 \text{ cm}^{-1}$, whereas the principal value (4.9) measures asymmetries on the single wavenumber level. Hence, we can assume that the pulse envelopes we discuss here are almost flat in the single wavenumber regime, and therefore their principal value can be neglected. We thus obtain from Eqs. (4.6) and (4.7) the (unnormalized) density matrix elements

$$\varrho_{e_i e_{i'}}(t) = \left(-\frac{i}{2\hbar}\right)^2 \mu_{ge_{i'}} \mu_{ge_i} e^{i(\omega_{e_{i'}} - \omega_{e_i})t} \langle E^\dagger(\omega_{e_{i'}}) E(\omega_{e_i}) \rangle \quad (4.10)$$

$$\begin{aligned} \varrho_{e_i e_j, e_{i'} e_{j'}}(t) &= \frac{1}{4} \left(-\frac{i}{\hbar}\right)^4 \mu_{ge_{i'}} \mu_{ge_{j'}} \mu_{ge_i} \mu_{ge_j} e^{-i(\omega_{e_i} + \omega_{e_j} - \omega_{e_{i'}} - \omega_{e_{j'}})t} \\ &\times \langle E^\dagger(\omega_{e_{i'}}) E^\dagger(\omega_{e_{j'}}) E(\omega_{e_i}) E(\omega_{e_j}) \rangle. \end{aligned} \quad (4.11)$$

Note that the four terms from the summations ω_i and ω_j in Eq. (4.7) all yield the same results: For instance, if the first interaction excites $|e_i\rangle$, the second one has to excite $|e_j\rangle$, yielding the field operators $E(\omega_{e_j})E(\omega_{e_i})$ (in this order). If, on the other hand, we first excite $|e_j\rangle$ and then $|e_i\rangle$, we arrive at $E(\omega_{e_i})E(\omega_{e_j})$. But since the field operators commute, they both yield the same field correlation function. The prefactor in Eq. (4.11) is therefore obtained from the frequency normalization $1/(2\pi)^4$, the factor π^4 from Eq. (4.9), and the four identical terms from the summations in Eq. (4.7) [a similar derivation applies, of course, also for the prefactor in Eq. (4.10)].

It is necessary to reiterate that Eqs. (4.10) and (4.11) are obtained by perturbative expansion of the Dyson series. Hence, any property we derive from these expressions refers to these leading-order contributions. Higher-order effects are not captured by this approach, but may nevertheless be relevant in some situations, such as saturation effects [Shatokhin05] or multiple scattering [Akkermans07].

Having derived the density matrices after the absorption of one or two light quanta, we still need to find a measure for the correlations induced between the noninteracting two-level atoms of the irradiated sample; if possible, one that constitutes an actual

4.1. Excursion: Matter correlations induced by coupling to quantum light

observable. Naturally, these correlations may not be detected in single-particle measurements [Richter11]. Hence, we need to define an observable that depends on the signal from at least two atoms. We therefore define the (time-resolved) two-photon counting signal as

$$S_{ij}(\Gamma) = \frac{\langle B_i(t)B_j(t) \rangle}{4\langle B_i(t) \rangle \langle B_j(t) \rangle}, \quad (4.12)$$

where we assume that $i \neq j$, $B_i(t) = |e_i(t)\rangle\langle e_i(t)|$, and Γ denotes the set of control parameters, such as the center frequencies of optical pulses, and their bandwidth. The factor 4 is inserted to account for the four different excitation pathways to excite $|e_i, e_j\rangle\langle e_j, e_i|$ [see our discussion following Eq. (4.11)]. We collect photons from the two-level atoms, which we assume to be distinguishable by their frequency.² In this situation the fluorescence is proportional to the population in the excited state i , hence to $B_i(t)$. A non-unity S_{ij} implies that the two-level atoms are correlated; the probability of the system i and j being excited differs from the product of probabilities. Note also that Eq. (4.12) is actually time-independent - even though we consider excitation by pulsed light - since our signal may only probe populations in the density matrix, which - once excited - remain constant in time in the framework of our model, until their photon emission is detected. The photon coincidence results can be obtained directly from Eq. (4.11),

$$S_{ij}(\Gamma) = \frac{\langle E^\dagger(\omega_{e_i})E^\dagger(\omega_{e_j})E(\omega_{e_i})E(\omega_{e_j}) \rangle}{\langle E^\dagger(\omega_{e_i})E(\omega_{e_i}) \rangle \langle E^\dagger(\omega_{e_j})E(\omega_{e_j}) \rangle} \quad (4.13)$$

Finally, we remark that Eq. (4.13) is similar - but not identical - to the Fourier transform of the g_2 -function of the incoming fields [Glauber07]

$$g_2(t, \tau) \equiv \frac{\langle E^\dagger(t)E^\dagger(t+\tau)E(t+\tau)E(t) \rangle}{\langle E^\dagger(t)E(t) \rangle^2}, \quad (4.14)$$

For instance, the Fourier transform of the nominator in Eq. (4.14) contains four frequencies

$$G_2(t, \tau) = \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} e^{i(\omega'_a + \omega'_b - \omega_b - \omega_a)t} \\ \times e^{i(\omega'_b - \omega_b)\tau} \langle E^\dagger(\omega'_a)E^\dagger(\omega'_b)E(\omega_b)E(\omega_a) \rangle, \quad (4.15)$$

and cannot be brought into a form resembling Eq. (4.12). Despite this difference, the dependence of Eq. (4.13) on the four-point correlation function of the field already gives us a hint that correlations between the two-level atoms induced by nonclassical light might be related to nonclassical photon statistics of the light field.

²Of course, Eq. (4.12) is a great simplification, assuming perfect detection probability and time resolution. In principle, however, it may be measured as stated: To measure the nominator $\langle B_i(t)B_j(t) \rangle$, we collect coincident counts at time t at frequencies ω_{e_i} and ω_{e_j} [Shatokhin00] (which, of course, is only possible if the Fourier uncertainty restricting time and energy resolution is not violated, see section 4.5.4 later in this chapter). The denominator is obtained similarly by measuring individual counts at either frequency.

4. Excited state distributions and fluorescence signals

4.1.1. Classical coherent light

For classical coherent light, the electric field operators of the field correlation functions in Eqs. (4.10) and (4.11) may be replaced by field amplitudes $A(\omega)$. The density matrix (4.11) then factorizes into products of single-photon transition amplitudes

$$\varrho_{e_i e_j, e_{i'} e_{j'}}(t) = 4T_{e_{i'} g}^*(t) T_{e_j g}^*(t) T_{e_i g}(t) T_{e_{j'} g}(t), \quad (4.16)$$

with the definition

$$T_{eg}(t) = \left(-\frac{i}{\hbar} \right) \mu_{eg} A(\omega_e) e^{-i\omega_e t}. \quad (4.17)$$

This is a product state, and indeed all many-body observables will factorize, signifying the absence of correlations. Due to this factorization, we obtain for the coincidence rate (4.12)

$$S_{ij}(\Gamma) = 1. \quad (4.18)$$

Thus, to leading order in the matter-field interaction, classical light does not create correlations between non-interacting two-level atoms. Higher-order multiple scattering effects, which are responsible for interference effects such as coherent backscattering [Kuga84, Albada85, Wolf85] (also termed weak localization) and Anderson (strong) localization [Anderson58], are not captured by this approach. Such effects establish interactions between different atoms, and could potentially create correlations in the final state [Shatokhin12].

4.1.2. Superpositions of two-photon Fock states

A general two-photon state may be written as³

$$|\psi\rangle = \int d\omega_a \int d\omega_b \Phi(\omega_a, \omega_b) a^\dagger(\omega_a) a^\dagger(\omega_b) |0\rangle. \quad (4.19)$$

Its four-point field correlation function factorizes as

$$\begin{aligned} & \langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle \\ &= \langle \psi | E^\dagger(\omega'_a) E^\dagger(\omega'_b) | 0 \rangle \langle 0 | E(\omega_b) E(\omega_a) | \psi \rangle \end{aligned} \quad (4.20)$$

$$= \Phi^*(\omega'_a, \omega'_b) \Phi(\omega_a, \omega_b), \quad (4.21)$$

where - for ease of notation - we have absorbed the field normalization (see our definition (3.5) of the field operator in section 3.2) into the two-photon amplitude $\Phi(\omega_a, \omega_b)$. Consequently, Eq. (4.7) factorizes into two-photon transition amplitudes

$$\varrho_{e_i e_j, e_{i'} e_{j'}}(t) = T_{e_i, e_j g}^*(t) T_{e_{i'}, e_{j'} g}(t), \quad (4.22)$$

³If the spectral two-photon amplitude $\Phi(\omega_a, \omega_b)$ can be factorized into two single-photon wavepackets, *i.e.* $\Phi(\omega_a, \omega_b) = \Phi_1(\omega_a) \Phi_2(\omega_b)$, the state is separable, otherwise it is called “time-frequency” entangled [Grice97, Law00] (see also our discussion in appendix A and later in this chapter).

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with

$$T_{e_i, e_j g}(t) = \mu_{ge_i} \mu_{ge_j} e^{-i(\omega_{e_i g} + \omega_{e_j g})t} \times [\Phi(\omega_{e_i g}, \omega_{e_j g}) + \Phi(\omega_{e_j g}, \omega_{e_i g})]. \quad (4.23)$$

Here, the two terms stem from the absorption of, either, atom i first [by the interaction with $E(\omega_a)$] and then atom j [$E(\omega_b)$], or vice versa, atom j by $E(\omega_a)$ and i by $E(\omega_b)$. In our previous discussion of classical light (4.16), this sum did not show up explicitly, since in this case both terms were identical. Instead, the factor 4 in Eq. (4.12) was introduced to account for the number of possible excitation pathways.

Eq. (4.23) implies that two-photon states prepare pure doubly-excited states, just like classical coherent light, Eq. (4.16). However, even if the two-photon state is separable, $\Phi(\omega_a, \omega_b) = \Phi_1(\omega_a)\Phi_2(\omega_b)$, we obtain

$$T_{e_i, e_j g}(t) = \mu_{ge_i} \mu_{ge_j} e^{-i(\omega_{e_i g} + \omega_{e_j g})t} \times [\Phi_1(\omega_{e_i g})\Phi_2(\omega_{e_j g}) + \Phi_1(\omega_{e_j g})\Phi_2(\omega_{e_i g})]. \quad (4.24)$$

Thus, even though the photon wavefunction is separable, it can establish a phase relation between the two excited two-level atoms, $\Phi_1(\omega_{e_i g})\Phi_2(\omega_{e_j g}) + \Phi_1(\omega_{e_j g})\Phi_2(\omega_{e_i g})$, which may be regarded as an entangled doubly-excited state of the matter. On a formal level, this means that we may not factorize (4.23) into a product as before, $T_{e_i, e_j g} \neq T_{e_i g} T_{e_j g}$. The absorption of a photon from beam 1 by molecule i depletes this field, leaving only beam 2 to excite molecule j . It is this back-action of the matter system onto the electromagnetic field (remember, in contrast, in the case of Eq. (4.17) the coherent state of the field remains unaffected by the interaction with the two-level atoms) that is the key difference between classical and quantum fields, and this back-action is responsible for the creation of phase coherence between different two-level atoms.

These simple considerations motivate us to examine more closely the wavepackets after excitation by nonclassical light, in the following.

4.2. Excited state distributions and fluorescence

Intuitively, one might guess that - to observe the impact of entanglement between photons in optical signals - it is most natural to study absorption signals (*i.e.* to measure the depletion of a light field) of sample systems created by the absorption of several photons. In section 3.6 of the previous chapter, we had investigated such an example - the third-order contributions to intensity measurements of arbitrary light beams, and had shown that they may be written in terms of transition amplitudes between the ground and various excited states [see Eqs. (3.169) and (3.172)]. The interference between two-photon absorption and Raman pathways in this signal complicates their analysis tremendously. We will therefore postpone its interpretation to the next chapter 5, and here discuss only excited state distributions in the doubly excited manifold, and more directly related fluorescence signals. We will first discuss the relation between excited

4. Excited state distributions and fluorescence signals

state population distributions and their fluorescence yield, where the level scheme is the same as before, sketched in Fig. 3.1.

Our discussion is mainly aimed at the description of the interaction of entangled photon pairs with complex quantum systems. It is therefore suggestive to investigate signals created by the absorption of pairs of photons, where the sample system ends up in a doubly-excited f -state (see Fig. 3.1). One possibility consists in collecting the spectrally-dispersed fluorescence from the decay of the f -states. For a complete microscopic description of a fluorescence signal in combination with the absorption of photon pairs, one would have to expand the fluorescence signal in Eq. (3.57) to fourth order (for absorption to promote the sample system into the f -manifold), resulting in a six-point correlation function of the matter system, which is very expensive to calculate.⁴ However, we may use the fact that, since electronic coherences decay very fast (on fs timescales [Engel07]) compared to electronic populations (typically in the ns regime [Blankenship02]), the fluorescence signal is essentially created by pathways going through an f -population after the interaction with the excitation pulses. Hence, to calculate the signal, it is sufficient in many situations to determine the f -state population $p_f(t)$ after the interaction (see, e.g., Ref. [Tekavec07, Lott11]), where typically one sends $t \rightarrow \infty$. In a situation where many f -states contribute to the fluorescence signal at different frequencies, one has to add additional information on the oscillator strength of different decay pathways [Mukamel99].

This approach culminates in the *two-photon induced fluorescence* (TPIF) signal,

$$\tilde{S}_{\text{TPIF}}(\omega; \Gamma) = \sum_{e,f} |\mu_{ef}|^2 \delta(\omega - \omega_f + \omega_e) \int dt p_f(t; \Gamma), \quad (4.25)$$

where the summations run over all doubly excited states f and all single excited states e . We recall that μ_{ef} denotes the dipole moment connecting the states e and f , and ω denotes the detected frequency. $p_f(t; \Gamma)$ denotes the population in state f at time t , and Γ denotes the set of control parameters of the excitation pulses. We consider photon detectors which are very slow compared to the decay dynamics in the sample, such that the fluorescence signal is obtained from the time-integrated f -population.

We may also be only interested in the total fluorescence obtained from the sample after photoexcitation. It is obtained by integration of Eq. (4.25) over the detection frequency,

$$S_{\text{TPIF}}(\Gamma) = \int d\omega \tilde{S}_{\text{TPIF}}(\omega; \Gamma), \quad (4.26)$$

and is often called the *fluorescence action spectrum* (or *fluorescence excitation spectrum*, see e.g. Refs. [Mukamel99, Blankenship02]). The name originates from the fact that the “spectrum” is typically obtained by measuring the fluorescence yield as a function of the

⁴Consider, for instance, a sample system consisting of twelve states in each relevant manifold. To evaluate a six-point correlation function in a sum-over-states expansion would then require us to evaluate on the order of $12^6 \sim 3 \times 10^6$ possible excitation pathways.

4.3. Two-photon induced fluorescence (TPIF)

center frequency of a narrow-band excitation pulse (hence, by measuring its “action” onto the sample) - and not by dispersing the emitted light.

To calculate the TPIF signal (4.25), we need to obtain the population in the f -manifold after the absorption of a pair of photons. A perturbative expansion of the Dyson series as in section 4.1, yields the leading-order contribution

$$p_f(t; \Gamma) = \left(-\frac{i}{\hbar}\right)^4 \int_{t_0}^t d\tau_4 \int_{t_0}^{\tau_4} d\tau_3 \int_{t_0}^{\tau_3} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \\ \times \langle P_f(t) H_{\text{int},-}(\tau_4) H_{\text{int},-}(\tau_3) H_{\text{int},-}(\tau_2) H_{\text{int},-}(\tau_1) \varrho(t_0) \rangle, \quad (4.27)$$

where we defined the projector onto an f -state, $P_f = |f\rangle\langle f|$. In the absence of dissipation, we may rewrite Eq. (4.27) as a single unrestricted loop diagram (see section 3.5.2), where interactions on the *ket* (*i.e.* τ_1 and τ_2) and *bra* side (τ'_1 and τ'_2) are no longer time-ordered,⁵

$$p_f(t; \Gamma) = \left(-\frac{i}{\hbar}\right)^4 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \int_{t_0}^t d\tau'_2 \int_{t_0}^{\tau'_2} d\tau'_1 \\ \times \langle V G^\dagger(\tau'_2 - \tau'_1) V G^\dagger(t - \tau'_2) P_f G(t - \tau_2) V^\dagger G(\tau_2 - \tau_1) V^\dagger \rangle \\ \times \langle E^\dagger(\tau'_1) E^\dagger(\tau'_2) E(\tau_2) E(\tau_1) \rangle. \quad (4.28)$$

Eq. (4.28) is represented diagrammatically in Fig. 4.1. Note that in Eq. (4.27) we expanded the Dyson series (3.12) to fourth order. In contrast, in our derivation of the TPA signal, Eq. (3.168), in the previous chapter we only take the third order into account. The TPA signal is given by a matter-field interaction, whereas in our current definition of the TPIF signal, the final signal is not treated explicitly. Therefore, the final correlation functions in both signals will both be fourth-order correlation functions, and their information content is essentially the same, as we will elaborate in the following two chapters.

4.3. Two-photon induced fluorescence (TPIF)

We first discuss the TPIF signal induced by a classical laser pulse with Gaussian envelope,

$$A(\omega) = \frac{1}{\pi^{1/4} \sqrt{\sigma}} \exp [-(\omega - \omega_0)^2 / 2\sigma^2], \quad (4.29)$$

which is normalized, such that

$$\int d\omega |A(\omega)|^2 \equiv 1. \quad (4.30)$$

We neglected the intensity of the excitation pulse in Eq. (4.29), since for our purposes it only represents a constant prefactor that does not affect the spectral structure of our

⁵In section 4.5, we will take dissipation into account, and expand Eq. (4.27) into six fully time-ordered expressions.

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Figure 4.1.: a) The f -state population as defined in Eq. (4.27) is given by a single unrestricted loop diagram. b) The toy model we discuss at first consists of a three-level system, where the intermediate state is either close to resonance (11,000 cm^{-1}), or far off-resonant (17,000 cm^{-1}), with respect to single-photon transitions.

signal. Our toy model depicted in Fig. 4.1b) only features one two-photon transition $g \rightarrow e \rightarrow f$, such that the detected frequency ω in Eq. (4.25) only yields a resonance at the $f \rightarrow e$ transition.⁶ Therefore, the dispersed frequency does not provide us with information on interfering excitation pathways, as opposed to the discussions later in section 4.6 and chapter 5. Hence, we simulate the fluorescence action spectrum (4.26), which we write as⁷

$$S_{\text{TPIF}}(\omega_0, \sigma) = \sum_e |\mu_{ef}|^2 \int d\omega_{\text{sum}} |T_{fg}(\omega_{\text{sum}}; \omega_0, \sigma)|^2, \quad (4.31)$$

with the transition amplitude defined as

$$T_{fg}(\omega_{\text{sum}}; \omega_0, \sigma) = \left(-\frac{i}{\hbar}\right)^2 \int \frac{d\omega_a}{2\pi} \sum_e \frac{\mu_{ge}}{\omega_a - \omega_e + i\gamma_e} \frac{\mu_{ef}}{\omega_{\text{sum}} - \omega_f + i\gamma_f} A(\omega_a) A(\omega_{\text{sum}} - \omega_a). \quad (4.32)$$

Even though we currently only consider the simple toy model in Fig. 4.1, we include a summation over several intermediate states e for later reference. The integrand in

⁶In principle, the direct decay $f \rightarrow g$ is also possible. However, such dipole coupling only occurs in systems with broken centrosymmetry (*i.e.* a nonvanishing second-order susceptibility $\chi^{(2)}$) [Boyd03]. This is typically not the case in molecular aggregate systems considered here, where only adjacent manifolds are dipole-coupled (see Fig. 3.1).

⁷The population in state f may be written in terms of the transition amplitude $T_{fg}(t)$, see section (3.5.2), and the time integration in Eq. (4.25) yields a delta-function in the frequency domain [Mukamel10b].

4.3. Two-photon induced fluorescence (TPIF)

Eq. (4.32) describes a process, in which the system is first excited from its ground state $|g\rangle$ to the first excited state $|e\rangle$ by the absorption of a photon with frequency ω_a , followed by the excitation from $|e\rangle$ to $|f\rangle$ by a photon with frequency $\omega_{\text{sum}} - \omega_a$. To obtain the full transition amplitude, we need to sum up all such amplitudes, *i.e.* integrate over ω_a [twice, since the modulus square of Eq. (4.32) enters in Eq. (4.31)] and ω_{sum} ,

$$S_{\text{TPIF}}(\omega_0, \sigma) = \sum_e \frac{|\mu_{ef}|^2}{\hbar^4} \int d\omega_{\text{sum}} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega'_a}{2\pi} \sum_{e', e''} \frac{\mu_{ge'} A(\omega_a)}{\omega_a - \omega_{e'} + i\gamma_{e'}} \times \frac{\mu_{ge''} A^*(\omega'_a)}{\omega_{a'} - \omega_{e''} - i\gamma_{e'}} \frac{\mu_{e'f} \mu_{e''f} A(\omega_{\text{sum}} - \omega_a) A^*(\omega_{\text{sum}} - \omega'_a)}{(\omega_{\text{sum}} - \omega_f)^2 + \gamma_f^2}. \quad (4.33)$$

Both dipole moments μ_{ge} and μ_{ef} are assumed to be real (which can always be achieved by absorbing any complex phase into the states $|g\rangle$ and $|f\rangle$), and set to the same strength. We employed the phenomenological inverse lifetimes $\gamma_e = \gamma_f = 200 \text{ cm}^{-1}$. To evaluate the integrals in Eq. (4.31) numerically, each integration was sampled in the area $\pm 30 \times \gamma_{\text{max}}$ (where γ_{max} denotes the largest of the three broadening constants γ_e, γ_f and σ) around the center frequency ω_0 [see Eq. (4.29)].

Using these parameters, we depict the simulated signal as a function of twice the center frequency, $2 \times \omega_0$ in Fig. 4.2.⁸ The signal with near-resonant intermediate state is depicted by a solid, red line, and the signal with off-resonant intermediate state by a dashed, blue line. We first discuss the near-resonant situation with the intermediate state $|e\rangle$ at $11,000 \text{ cm}^{-1}$. At first glance, the interpretation of the TPIF signal in this situation is very straightforward: The signal peaks when $2\omega_0 = \omega_f$. The width γ of the resonance is determined by the spectral width of the field envelope (4.29), if the bandwidth σ is larger than the resonance width γ_f , and by the linewidth γ_f , if $\gamma_f > \sigma$. However, as can be seen most clearly for $\sigma = 100 \text{ cm}^{-1}$ by comparison with the off-resonant case, this is not exactly true: When the bandwidth of the pulses are narrow, such that the lifetimes γ_e and γ_f of the states dominate the spectral width of the resonance, the TPIF signal's maximum is shifted to higher frequencies. This is due to the presence of the intermediate state with an energy larger than half the two-exciton energy, $\omega_e > \omega_f/2$. In a simplified picture, it may be rationalized that the two single-photon transitions $|g\rangle \rightarrow |e\rangle$ and $|e\rangle \rightarrow |f\rangle$ are multiplied to create the two-photon absorption resonance. Due to the offset between ω_e and $\omega_f/2$, the resonance is shifted, and only when $\sigma \gg \gamma_e, \gamma_f$ the shift is no longer resolved. In the case of an off-resonant e -state, the single-photon resonance due to the $|g\rangle \rightarrow |e\rangle$ transition is shifted far away from the depicted frequency regime $\omega_0 = 9,250 \cdots 11,500 \text{ cm}^{-1}$. Hence, it only yields an essentially flat contribution, and no longer shifts the two-photon resonance reflected by the TPIF signal. As we will see in the following, this simple rational no longer applies for entangled photons, in which case the two absorption events become strongly entangled.

⁸This unusual representation will become more suggestive when comparing the present results to the entangled-photon signals in section 4.3.1 below.

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Figure 4.2.: The two-photon induced fluorescence (TPIF) signal (4.26) induced by classical laser pulses, with envelopes given in Eq. (4.29), and bandwidths (from top to bottom) $\sigma = 100 \text{ cm}^{-1}$ (corresponding to a pulse duration of 50 fs), 200 cm^{-1} (25 fs), and $1,000 \text{ cm}^{-1}$ (6 fs). The signal obtained for a near-resonant intermediate state ($\omega_e = 11,000 \text{ cm}^{-1}$) is depicted by a red, solid line, and for an off-resonant state ($\omega_e = 17,000 \text{ cm}^{-1}$) by the blue, dashed line. Each signal is normalized with a maximal value set to one.

4.3.1. Entangled two-photon induced fluorescence

After this long introduction, we are finally in a position to discuss the main topic of this chapter: the absorption of entangled photon pairs. For any two-photon state, the four-point field correlation function in Eq. (4.28) factorizes into

$$\langle E^\dagger(\omega'_a)E^\dagger(\omega'_b)E(\omega_b)E(\omega_a) \rangle = \langle \psi | E^\dagger(\omega'_a)E^\dagger(\omega'_b) | 0 \rangle \langle 0 | E(\omega_b)E(\omega_a) | \psi \rangle, \quad (4.34)$$

where $|\psi\rangle$ denotes the initial two-photon state of the field. Since the two absorptions deplete the electric field, we only obtain a contribution from the vacuum state $|0\rangle$, when inserting an identity in the middle of the correlation function. This is why the quantity $\langle 0 | E(\omega_b)E(\omega_a) | \psi \rangle$ is often referred to as the *two-photon wavefunction* [Shih03]: It contains all the information of the two-photon state. Most importantly, for the special case of photon pairs created by parametric downconversion, it may show strong frequency-time correlations. Their detailed derivation is shifted to appendix A. Let it suffice here to state the most important properties: The two-photon wavefunction may be derived by introducing the Schmidt modes of the downconversion process. In this basis, it is

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given by Eq. (A.38a), evaluated for the two-photon state (A.42),

$$\begin{aligned}\langle 0|E(\omega_b)E(\omega_a)|\psi\rangle &= f_{12}(\omega_a, \omega_b) + f_{21}(\omega_a, \omega_b) \\ &= \sum_{k=1}^{\infty} r_k [\phi_k(\omega_a)\psi_k(\omega_b) + \phi_k(\omega_b)\psi_k(\omega_a)],\end{aligned}\quad (4.35)$$

where the summation k runs over the different Schmidt modes. The weights r_k give the strength with which mode k participates in the downconversion process. They form a uniformly decreasing sequence, such that in our parameter regime we may terminate the sum above $k_{\max} = 60$ (see our discussion in appendix A and, e.g., Fig A.3). The mode envelopes ψ_k and ϕ_k are given by the k -th Hermite function (see section A.1.3). Their spectral-temporal correlations are determined by the pump pulse bandwidth σ_p , and two time constants T_1 and T_2 . These time constants are given by the maximal time delay between either one of the photon wave packets in the two modes and the pump pulse, which the three fields can pick up during their propagation through the birefringent crystal, due to their different group velocities. In strong contrast to classical time delays, they also determine the bandwidth of each of the two photon wave-packets (see Fig. A.4). Consequently, they are connected to the entanglement time $T = T_2 - T_1$ (see section 2.2), which represents the maximal time delay between the arrival of the two photons. To choose realistic values, we adapt the parameters obtained in Ref. [Jennewein09] for a BariumBorate (BBO) crystal pumped at 395 nm ($25,300 \text{ cm}^{-1}$). This yields the parametrization of the two time constants $T_1 = 0.00007(T/fs) \text{ cm}$, and $T_2 = 0.00025(T/fs) \text{ cm}$, where T denotes the entanglement time (A.11) in femtoseconds. Strictly speaking, one would have to adjust these values for different pump wavelengths. However, the influence of this correction would be minimal, since the group velocities vary rather slowly far away from absorption resonances of the birefringent crystal.

In this two-photon regime, the *bra* and *ket* sides of Eq. (4.28) decouple, and we may write the excited population as

$$p_f(t; \Gamma) = |T_{fg}(t; \Gamma)|^2, \quad (4.36)$$

with the transition amplitude (not a field operator as in section 3.6, where we had not specified the initial state of the field)

$$T_{fg}(t; \Gamma) = \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \langle f(t)|V^\dagger(\tau_2)V^\dagger(\tau_1)\rangle |g(t_0)\rangle \langle 0|E(\tau_2)E(\tau_1)|\psi\rangle. \quad (4.37)$$

Expanding the matter correlation function, and using the decomposition of the field correlation function (4.37) in terms of Hermite functions, we may evaluate the transition amplitude in the time domain,

$$\begin{aligned}T_{fg}(t; \Gamma) &= \left(-\frac{i}{\hbar}\right)^2 \sum_e \mu_{ge}\mu_{ef} \int_0^\infty ds_2 \int_0^\infty ds_1 e^{-i(\omega_e - i\gamma_e)s_1 - i(\omega_f - i\gamma_f)s_2} \\ &\quad \times (f_{12}(t - s_2 - s_1, t - s_2) + f_{21}(t - s_2 - s_1, t - s_2)),\end{aligned}\quad (4.38)$$

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Figure 4.3.: The two-photon induced fluorescence signal of entangled photons with a pump pulse bandwidth $\sigma_p = 100 \text{ cm}^{-1}$ and, as indicated, entanglement times $T = 10 \text{ fs}$, 100 fs , and 200 fs , respectively. TPIF signals with both resonant ($e = 11,000 \text{ cm}^{-1}$, solid line) and off-resonant ($e = 17,000 \text{ cm}^{-1}$, dashed line) intermediate states are shown, see Fig. 4.1b). Each signal is normalized, such that its maximal value equals one.

or in frequency domain,

$$T_{fg}(t; \Gamma) = \left(-\frac{i}{\hbar}\right)^2 \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \sum_e \frac{i\mu_{ge}}{\omega_a - \omega_e + i\gamma_e} \frac{i\mu_{ef}}{\omega_a + \omega_b - \omega_f + i\gamma_f} \times (f_{12}(\omega_a, \omega_b) + f_{21}(\omega_a, \omega_b)) e^{-i(\omega_a + \omega_b)t}. \quad (4.39)$$

As in Eq. (4.32), we include a summation over possible intermediate states. Integrating over t [see Eq. (4.25)], we obtain the quantum-field analog of Eq. (4.33),

$$S_{\text{TPIF}}(\Gamma) = \sum_{e, e', e''} \frac{|\mu_{ef}|^2}{\hbar^4} \int \frac{d\omega_{\text{sum}}}{2\pi} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega'_a}{2\pi} \frac{\mu_{ge'}\mu_{e'f}}{\omega_a - \omega_{e'} + i\gamma_{e'}} \frac{\mu_{ge''}\mu_{e''f}}{\omega'_a - \omega_{e''} - i\gamma_{e''}} \times \frac{1}{(\omega_{\text{sum}} - \omega_f)^2 + \gamma_f^2} \langle E^\dagger(\omega'_a) E^\dagger(\omega_{\text{sum}} - \omega'_a) E(\omega_{\text{sum}} - \omega_a) E(\omega_a) \rangle, \quad (4.40)$$

where, instead of the product of field amplitudes, we encounter the four-point field correlation function (4.34).

In Fig. 4.3, we depict the normalized TPIF action signal (4.26), *i.e.* with its maximum set to unity, for different entanglement times T , and both resonant ($\omega_e = 11,000 \text{ cm}^{-1}$) and off-resonant intermediate state ($\omega_e = 17,000 \text{ cm}^{-1}$). The entanglement times are chosen such that the bandwidth of each photon is comparable to one of the plots of the

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classical TPIF action signals in Fig. 4.2 (*i.e.* $T = 10$ fs corresponds to a bandwidth on the order of $1,000 \text{ cm}^{-1}$, etc.). The pump bandwidth is fixed at $\sigma_p = 100 \text{ cm}^{-1}$. Apparently, it is the pump bandwidth - and not the photon bandwidth - that determines the width of the TPIF resonance, as the width is identical in all three examples shown in Fig. 4.3. This may be understood as a consequence of the energy conservation in the downconversion process. As described in chapter 2 (see our discussion on page 19), the distribution of the sum frequencies of the absorbed photons has to match the bandwidth of the pump pulse generating them. Thus, since we chose $\sigma_p = 100 \text{ cm}^{-1}$, this determines the frequency resolution of the TPIF resonance - regardless of the bandwidth of the individual photon wavepackets.

However, even in this very simple setup, we can observe signatures of the bandwidth properties of the two photons.⁹ For very short entanglement time (10 fs), there is almost no difference between resonant and off-resonant cases: Due to the almost simultaneous arrival of the two photons (or, put differently, due to the large bandwidth of each photon wavepacket), the position of the intermediate state has no influence on the signal. Conversely, for $T = 200$ fs there are only very weak correlations between the two photons, and the bandwidth of the individual photons roughly matches the distribution of the sum frequencies. In this regime, the intermediate state does matter, and the peak with near-resonant intermediate state is shifted away from the two-exciton resonance at $21,500 \text{ cm}^{-1}$. Hence, the latter case with weak correlations looks very similar to the classical TPIF signal with pulse bandwidth $\sigma = 100 \text{ cm}^{-1}$ in Fig. 4.2. Differences between the two top plots in Figs. 4.2 and 4.3 such as the slightly shifted maximum of the dashed lines arise from residual correlations, which cannot be suppressed in this regime (see appendix A).

So even though the shifts of the resonance peak are rather miniscule in the present example,¹⁰ they already tell us one key difference feature of entangled photons: the ability to independently tune the bandwidth of individual photons on the one hand (and hence the frequency resolution in single-photon transitions), and the frequency resolution of two-photon transitions on the other.

4.3.2. Intensity crossover

With increasing pump intensity (*i.e.* photon flux), different entangled pairs start to overlap temporally, and uncorrelated two-photon absorption events have to be taken into account. As shown in appendix A, this means that the factorization (4.34) of the four-point field correlation function is no longer possible: The initial state of the field then has to be treated as a general N -photon state, and, when inserting the identity in the four-point field correlation function, as described on page 94, not only the vacuum state, but also higher photon numbers yield a nonvanishing contribution. Instead, we

⁹We will discuss later whether this behavior may be understood as a consequence of time-energy entanglement shared between the photons.

¹⁰We could have chosen parameters, in which we observed greater differences. However, we intentionally use the present set of parameters to observe a most pronounced scaling behavior in the next section.

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Figure 4.4.: Left: Normalized two-photon induced fluorescence resonances, Eqs. (4.40) with the correlation function (4.41), of entangled photons for pump pulse bandwidth $\sigma_p = 100 \text{ cm}^{-1}$, entanglement time $T = 10 \text{ fs}$, and different pump intensities α . The mean photon number in each beam, as defined by Eq. (4.43) corresponds to (from bottom to top) $\bar{n} = 0.1$ ($\alpha/\hbar = 0.001$), $\bar{n} = 2.5$ ($\alpha/\hbar = 0.005$), $\bar{n} = 12.5$ ($\alpha/\hbar = 0.01$), and $\bar{n} = 68$ ($\alpha/\hbar = 0.015$).

Right: Relative strength of the coherent two-photon contribution (red, solid), and of the incoherent background (blue, dashed) for $\bar{n} = 2.5$ and 68.

obtain two different kinds of contributions [see Eqs. (A.38a) - (A.38c) for a derivation],

$$\begin{aligned}
 & \langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle \\
 &= (f_{12}^*(\omega'_a, \omega'_b) + f_{21}^*(\omega'_a, \omega'_b)) (f_{12}(\omega_a, \omega_b) + f_{21}(\omega_a, \omega_b)) \\
 &+ (g_1(\omega_a, \omega'_a) + g_2(\omega_a, \omega'_a)) (g_1(\omega_b, \omega'_b) + g_2(\omega_b, \omega'_b)) \\
 &+ (g_1(\omega_a, \omega'_b) + g_2(\omega_a, \omega'_b)) (g_1(\omega_b, \omega'_a) + g_2(\omega_b, \omega'_a)) .
 \end{aligned} \tag{4.41}$$

The first line contains the known two-photon correlation function $f_{12}(\omega_a, \omega_b)$, Eq. (4.35), which stems from the correlated interaction with entangled pairs. With increasing pump intensity, this effect does not simply disappear, but increases in intensity [the linear factor r_k in Eq. (4.35) becomes $\sinh(r_k) \cosh(r_k)$ in the high-intensity regime, Eq. (A.39)], and is amended by the additional contributions given in the second and third line. These are autocorrelation contributions stemming from the uncorrelated interaction with either

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one of the two beams. For instance, the function g_1 reads [see Eqs. (A.36) and (A.37)]

$$\begin{aligned} g_1(\omega, \omega') &= \langle E_1^\dagger(\omega') E_1(\omega) \rangle \\ &= \sum_k \sinh^2(r_k) \psi_k(\omega) \psi_{k'}^*(\omega'), \end{aligned} \quad (4.42)$$

and g_2 is obtained identically from beam 2, $g_2 = \langle E_2^\dagger E_2 \rangle$. Due to the lack of correlations between the two beams, we refer to these additional contributions as *incoherent* contributions, and we refer to the entangled photon-pair contribution as *coherent*. We reiterate that the matter correlation function still factorizes into transition amplitudes, and it is only the emerging correlations between E and $E^\dagger$ in Eq. (4.40) that require additional care.

To define a quantitative criterium for the transition from weak (well-separated two-photon states) to strong pump fields, we relate the pump intensity to the mean photon number $\bar{n}$ in each of the two beams, as defined in Eq. (A.47):

$$\bar{n} = \sum_k \sinh^2(r_k). \quad (4.43)$$

This expression is to be understood as follows: In the limit of weak downconversion, we have $r_k \ll 1 \forall k$, and the (unnormalized) two-photon state reads $\sim \sum_k r_k A_k^\dagger B_k^\dagger |0\rangle$, see Eq. (A.41). Hence, in this limit, the photon number in each Schmidt mode (A.14) is given by, e.g., $\langle A_k^\dagger A_k \rangle = r_k^2$, which is the leading-order of a Taylor expansion of $\sinh^2(r_k)$. The higher-order terms in $\sinh^2(r_k)$ therefore correspond to the additional influence of four-photon states ($\sim r_k^4/3$), six-photon states, etc, and the hyperbolic sine is their mean value. The total photon number is then given by the sum over the number of photons in all the modes k .

Under these premises, we now investigate the behavior of the TPIF signal with increasing pump intensity in two steps. First, we discuss the change of the spectral envelope of the TPIF resonance for a fixed set of control parameters (pump bandwidth and entanglement time). Second, we examine how the crossover from low to high-intensity response depends on the spectral properties of the downconverted light beams.

Spectral impact

In Fig. 4.4, we simulate the full signal according to Eq. (4.40), for $\bar{n} = 0.1 \cdots 68$, with a near-resonant intermediate state (see Fig. 4.1). The right panel separately shows the relative strengths of the coherent, Eq. (A.38a), and of the incoherent contributions, Eqs. (A.38b) and (A.38c), respectively. In all plots, we chose parameters which imply strong frequency correlations, *i.e.* $\sigma_p = 100 \text{ cm}^{-1}$ and $T = 10 \text{ fs}$. Clearly, when $\bar{n} \leq 1$, the incoherent contributions may be safely neglected, and the two-photon state is an excellent approximation for the full quantum state of the incident downconverted light. But as $\bar{n}$ approaches unity, the incoherent contributions gain strength, and need to be taken into account. Due to the lack of frequency correlations in the incoherent contributions, the resonances become markedly broader than the coherent ones, since their

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width is given by the individual photon wavepacket's bandwidth ($\sim 1,000 \text{ cm}^{-1}$), and not by the pump pulse envelope ($\sim 100 \text{ cm}^{-1}$). Hence, with increasing intensity the nonclassical bandwidth properties of entangled photon pairs are overshadowed by the broad, incoherent resonance features of uncorrelated photons. Thus, for $\bar{n} = 68$, the tails of the resonances extend over almost $1,000 \text{ cm}^{-1}$. We further note that the bandwidth of the beams itself also depends on the intensity: The incoherent contribution for $\bar{n} = 12.5$ is considerably broader than for $\bar{n} = 68$ photons, as depicted in the right panels of Fig. 4.4. This may be explained by the Schmidt decomposition we introduced earlier [see also Eq. (A.14)]. Each weight factor r_k depends linearly on the pump amplitude α , and the output fields (A.24) and (A.25) depend nonlinearly ($\sim \cosh / \sinh$) on these weight factors. Hence, with increasing pump intensity, a few strongest modes with the largest weights will be more enhanced with respect to weaker modes, thus effectively reducing the number of contributing modes in the signal. That is why the bandwidth effectively decreases with increasing intensity. Note also that, for the coherent contribution, this scaling behavior has the opposite effect: Fewer participating modes *decrease* the frequency correlations, and hence lead to (small) broadening of the TPIF resonance in the right panel of Fig. 4.4.

Dependence on frequency correlations

To assess how the spectral properties of the entangled photons influence the intensity dependence, we consider the relative weight of coherent and incoherent contributions to the full TPIF signal at resonance [at $\omega_p = 21,500 \text{ cm}^{-1}$, see Fig. 4.1b)], as a function of the mean photon number $\bar{n}$:

$$P_{\text{rel}} = \frac{S_{\text{partial}}}{S_{\text{TPIF}}}, \quad (4.44)$$

where S_{partial} denotes the partial contribution of, either, the coherent or the incoherent part of the field correlation function (4.41) and S_{TPIF} denotes the full signal, Eq. (4.40).

The results of our simulations are shown in Fig. 4.5, for entanglement times $T = 10 \text{ fs}$ (*i.e.* strongly entangled) and 100 fs (weakly entangled), as well as with, both, near-resonant and off-resonant intermediate state $|e\rangle$. Let us first compare the behavior of strongly and weakly entangled states with near-resonant intermediate e -state. At a first glance, both cases exhibit the behavior which we already observed in the previous section: With increasing mean photon number $\bar{n}$, the incoherent contribution becomes stronger, and eventually dominates the signal.

However, this crossover takes place at very distinct photon numbers - in the strongly entangled case [panel a)] at $\bar{n} \approx 220$, and in the weakly entangled case [panel b)] already at $\bar{n} \approx 0.5$! Furthermore, while the weight of the coherent contribution drops to approximately 20 % in the latter case, it remains at around 50 % even for photon numbers ≥ 500 in the former.

This striking difference may be explained most directly by the strongly correlated arrival times of the entangled photons. As pointed out in Ref. [Dayan05], the maximal

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Figure 4.5.: Relative contribution P_{rel} , Eq. (4.44), of the coherent (solid) and incoherent (dashed) part of the field correlation function (4.41) as it enters in Eq. (4.40) at resonance (*i.e.* with $\omega_p = 21,500 \text{ cm}^{-1}$), as a function of the mean photon number $\bar{n}$, Eq. (4.43). a) Near-resonant intermediate state $|e\rangle$ [see Fig. (4.1b)], pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$, and entanglement time $T = 10 \text{ fs}$. b) Near-resonant intermediate state, $\sigma_p = 100 \text{ cm}^{-1}$, $T = 100 \text{ fs}$. c) Strongly off-resonant intermediate state, $\sigma_p = 100 \text{ cm}^{-1}$, $T = 10 \text{ fs}$. d) Strongly off-resonant intermediate state, $\sigma_p = 100 \text{ cm}^{-1}$, $T = 100 \text{ fs}$.

photon flux at which distinct entangled pairs begin to overlap on the time axis is determined by the inverse photon bandwidth. Put differently, for $T = 10 \text{ fs}$, we can fit ten times as many non-overlapping photon pairs into a time interval than for $T = 100 \text{ fs}$. This argument, however, cannot account for the full discrepancy between the two crossover regimes ($\bar{n} = 220$ vs. $\bar{n} = 0.5$, *i.e.* a factor of ~ 400).

In addition, the 10 fs-case simultaneously features narrow correlated two-photon transitions, as well as very broad uncorrelated two-photon transitions (see the right panel of Fig. 4.5), such that at the TPIF resonance at $\omega_p = 21,500 \text{ cm}^{-1}$, the relative contribution of the narrow, coherent peak is even more enhanced at resonance. The top right panel of Fig. 4.5 ($\bar{n} = 69$) shows that, at resonance, the coherent contribution (solid line) is still larger than the incoherent contribution (dashed line), which merely dominates the tails of the signal, due to its broad bandwidth.

It is the combination of these two factors - reduced temporal overlap and a narrow

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lineshape of the correlated two-photon transitions - which is responsible for the remarkably distinct crossover observed for strongly as compared to weakly entangled injected photons. Whereas typically the crossover between the linear and quadratic scaling (that is, when $\bar{n} \approx 1$) of the TPIF signal is regarded as the crossover between the quantum and a “classical” regime [Lee06] (see also our discussion in section 2.2.3), the current result demonstrates that the coherent contribution of entangled photon pairs still dominates the signal at much higher photon numbers (provided they are strongly time-frequency entangled). What was overlooked in this discussion is the fact that, even though incoherent contributions do become stronger, so do the coherent ones.

Finally, let us discuss the TPIF signal with a strongly off-resonant intermediate state $|e\rangle$. The weakly entangled case in panel d) of Fig. 4.5 looks almost identical to the previous case; parity between coherent and incoherent contributions is reached at $\bar{n} \approx 0.5$. In this weakly entangled case, there is very little difference between a correlated and an uncorrelated two-photon transition,¹¹ and since there is little difference between them, their relative strength evolves with $\bar{n}$ largely independently of the structure of the sample system. In stark contrast, the coherent contribution of the strongly correlated case dominates the signal even at very large photon numbers $\geq 40,000$. Strong time correlations are essential for the enhancement of the transition via the strongly off-resonant state. This is the regime in which the results of Ref. [Dayan04] were obtained, and our calculations confirm that the two-photon state still dominates the signal at these very large photon numbers.

4.4. The bacterial reaction center

So far, we studied a simple toy model consisting of only one state ($|g\rangle, |e\rangle, |f\rangle$) in each electronic state manifold. To fully appreciate the influence of different, interfering excitation pathways, we now turn to a model of an actual molecular aggregate. In this situation, the interpretation of optical signals evidently becomes more involved due to the interplay of different states, excitation pathways, and, possibly, relaxation processes. Our subsequent calculations are meant as proof-of-principle demonstrations of the fingerprints of quantum correlations in the incident light in optical signals, and not an in-depth simulation of a particular system. Thus, depending on the phenomena under consideration, we may or may not consider dissipative dynamics which are numerically more expensive to simulate.

Here, we first use Eqs. (4.38) and (4.39) to simulate the excited state distributions induced by the absorption of entangled photons or of classical light - and not actual measurement results. Having understood those, we will discuss the fluorescence signals that they create. This will endow us with an intuition for the interpretation of more involved pump-probe-like signals in the next chapter.

¹¹Weak time-energy correlations imply that the bandwidth of individual photon wavepackets cannot (greatly) exceed the width of the pump pulse, which determines the distribution of the sum frequencies.

Figure 4.6.: a) The pigment-protein complex containing the reaction center (Protein Data Bank code: 1PRC) [Deisenhofer95], and a close-up of the optically active co-factors. Energy and charge transport pathways are sketched. b) The linear absorption spectrum (4.45) based on the model used in this dissertation (see appendix B). The exciton states are indicated by vertical lines. Their height is proportional to the oscillator strength of the transition from the ground state $|g\rangle$, given by the dipole moments squared $|\mu_{ge}|^2$.

4.4.1. The system

We consider a model of the bacterial RC of the purple bacterium *Blastochloris viridis* which has been developed in [Fingerhut12]. Its biological function consists in the initial charge separation after light excitation. The resulting free electron is transported to a quinone where it is eventually stored chemically [Blankenship02].

This RC forms an ideal model system for two main reasons. First, in stark contrast to entire photosynthetic complexes, which have evolved into a vast number of diverse structures, RCs show remarkable structural similarities - regardless of whether they stem from bacteria or from higher plants, RCs have an apparent two-fold symmetry, in which a strongly interacting chlorophyll pair is connected to two branches, see Fig. 4.6a). However, this apparent symmetry is broken, and only one of the two branches is involved in the charge separation process [Holzapfel90, Huppmann03]. More strikingly, the origin of this apparent symmetry still remains an open question [Blankenship02]. Understanding the underlying principles could reveal important insights for bio-inspired organic solar cells [Fingerhut10]. Thus, this model constitutes a novel development in a highly active, and very relevant research area, and its study is very important in its own right. On top, the RC's level structure is ideally suited to be probed by entangled photons: Purple bacteria have evolved to use the near-IR region of the solar radiation, which is not absorbed by higher plants. Incidentally, entangled photons can be created most conveniently in the near-IR to optical regime [Shih03]. Thus, current entangled photon sources lie in

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the ideal frequency window to probe the RC structure.

The detailed modeling of the RC Hamiltonian in Ref. [Fingerhut12] is explained in appendix B. Here, we only discuss the qualitative properties of the complex. The RC consists of four bacteriochlorophylls, two bacteriopheophytins, and two quinones which are not optically active, and therefore not included in the model (see Fig. 4.6). Two closely neighboring chlorophylls, labelled $^P\text{BChl}_L$ and $^P\text{BChl}_M$, form the so-called *special pair*, where the charge separation takes place. Adjacent to this pair, two more chlorophylls, BChl_L and BChl_M , connect to the more electronegative pheophytins BP_L and BP_M , which accept the free electron after the CS. These in turn transfer the electrons to the quinones (not shown in the figure) which may transport them along the photosynthetic membrane. However, this happens on much longer timescales than those discussed in our study, so they are not included in the model. The present model incorporates the optically bright excitonic states on both branches, *i.e.* states where electron and hole reside on the same chlorophyll, as well as the charge separated states on the active branch, where electron and hole reside on different chlorophylls. This amounts altogether to 12 single- and 41 two-exciton states [Fingerhut12]. Since other charges in the complex shield the interaction between electron and hole when residing on different molecular sites, the charge separated states have extremely weak dipole moments. Hence, they couple only weakly to the electromagnetic field, and cannot be detected by direct spectroscopic methods.¹²

The linear absorption spectrum was derived in Eq. (3.149),

$$S_{\text{linear}}(\omega) \propto \Im \langle V G(\omega) V^\dagger \rangle = c \sum_e \frac{|\mu_{ge}|^2}{(\omega - \omega_e)^2 + \gamma_e^2}. \quad (4.45)$$

To account for fluctuations in the energy structure, resonances have been broadened by a phenomenological dephasing time $\gamma_e = 200 \text{ cm}^{-1}$, such that the spectrum agrees reasonably well with experimental results [Holzapfel90, Huppmann03].¹³ The resulting spectrum is plotted in Fig. 4.6b). Of course, this approach cannot incorporate temperature-dependent resonance shifts of the spectrum [Huppmann03], or other subtle features which have been observed experimentally, such as a slightly different broadening of some peaks. The spectrum consists of two bands: a lower exciton resonance, which is given by the lowest molecular exciton delocalized on the special pair (for an in-depth discussion of the Hamiltonian and the exciton states, see appendix B), and the higher-energy band, which is given by the remaining excitons.

As mentioned above, the relevant part of the RC spectrum consists of single excitons, as well as of higher excited states formed by pairs of excitations - the two-exciton states which we summarize within the *f-manifold*. Some of these exciton pairs only interact

¹²This poses, of course, a formidable problem, since it is precisely the coupling between excitonic and charge separated states that lies at the heart of this primary step of photosynthesis. AC Stark shift spectroscopy is however capable of extracting some information about these states (see, e.g., Ref. [Romero12] for an application on the RC of Photosystem II, or [Bublitz97] for a general review).

¹³In writing Eq. (4.45), we assume that the incoming light is given by cw-light with frequency ω . Furthermore, the spectrum is normalized to its global maximum. The explicit dependence on the field intensity and the normalization have been absorbed in the constant c

Figure 4.7.: Dominant excitation pathways of bright two-exciton states of the bacterial RC (see Fig. 4.6) which we refer to in the course of chapters 4 and 5.

very weakly, in which case the f -state energy is given by the sum of the two single-exciton energies. For instance, the state $|f_{22}\rangle$ consists primarily of the excitons $|e_5\rangle$ and $|e_{10}\rangle$, which reside on the special pair and on the pheophytin BP_M , respectively [see also Fig. B.1], and hence are spatially well separated. Thus, in our model we find a tiny shift with respect to the sum $\omega_{e_5} + \omega_{e_{10}}$ of 0.5 cm^{-1} . In chapter 5, we will see that the visibility of such f -states in third-order optical measurements will be drastically reduced, due to destructive interference between two-photon absorption and Raman pathways. On the other hand, there are also incidents of strongly interacting two-exciton states. For instance, state $|f_4\rangle$ is mostly composed of the charge separated state $|e_4\rangle$, and of the exciton state $|e_5\rangle$, both residing on the special pair [see also Fig. B.1]. The presence of a charge separated state on the special pair changes the electronic structure of the pair, and therefore a second excitation of the pair is strongly shifted with respect to an excitation from the ground to the single-exciton state. This is modeled by a detuning of 846 cm^{-1} [Fingerhut12]. Fig. 4.7 shows some possible excitation pathways, which we will discuss later in this chapter. They are chosen due to their relatively large oscillator strengths $|\mu_{ge}\mu_{ef}|^2$, allowing us to observe them spectroscopically.

As shown in Fig. 4.6a), the RC is embedded in a stiff protein skeleton, whose vibrations modulate the local energies of the chromophores. However, they do not (or only very rarely) absorb optical excitations. Due to this coupling, which we will describe by a secular Redfield [Abramavičius09] (time-independent Lindblad [Breuer02]) equation, see Eqs. (B.2)-(B.5), optical excitations are transferred towards lower energy states. As indicated in Fig. 4.6a), the molecular excitons created upon photoexcitation are first transferred to the special pair within hundreds of femtoseconds. The electron is then transferred to the electron-accepting pheophytin BP_L , while the hole resides on ${}^{\text{P}}\text{BChl}_L$. These transport processes will be taken into account in the next section 4.5. For now, we only consider coherent, unitary time evolution, and add the phenomenological dephasing rates $\gamma_e, \gamma_f = 200 \text{ cm}^{-1}$.

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Figure 4.8.: Two-exciton (c.f. Fig. 4.7) population distributions in the bacterial RC created by degenerate, entangled photon pairs, as a function of the center frequency of the pump pulse ω_p with bandwidth a) $\sigma_p = 100 \text{ cm}^{-1}$ and entanglement time $T = 10 \text{ fs}$, b) $\sigma_p = 100 \text{ cm}^{-1}$ and $T = 100 \text{ fs}$. The top panels show the power spectra of the corresponding wavepackets, Eq. (4.42), and of the sum frequency distribution, Eq. (4.35) at $\omega_p = 22,000 \text{ cm}^{-1}$.

4.4.2. Entangled photons

As mentioned before, we use Eq. (4.38) to simulate the two-exciton population distributions induced by the absorption of entangled light. To compare different parameter regimes with one another, we normalize the total population in the f -manifold to one, *i.e.* $\sum_f p_f(t) = 1$, where $p_f(t)$ is given by the modulus square of Eq. (4.38), $|T_{fg}(t, \Gamma)|^2$. We assume that the entangled pulses are centered around the time $t_0 = 0$, and set the final time $t = 56 \text{ fs}$ (which corresponds to 0.01 cm in wavenumber units). The time integrations in Eq. (4.38) are carried out numerically using standard Mathematica routines. The first time variable s_1 was integrated between 0 and $5(T_2 - T_1)$ (since the entangled field correlation function has Gaussian shape, with a width roughly given by $T_2 - T_1$, see appendix A), and the second variable s_2 between 0 and $10/\gamma_f$ (*i.e.* the time scale on which the dephasing rate reduces the signal by a factor 5×10^{-5}). We consider degenerate downconversion where both photons have the same central frequency $\omega_1 = \omega_2 = \omega_p/2$, and we assume a pump amplitude $\alpha/\hbar = 0.001$, corresponding to $\bar{n} = 0.1$ [see Eq. (4.43)]. As we have seen in the previous section 4.3.2, this corresponds to a parameter regime in which higher photon-number contributions to the light field may be safely neglected. We remark, however, that our previous analysis also shows that the effects described here probably persist at much higher pump intensities.

Fig. 4.8 depicts such normalized two-exciton population distributions for two different parameter sets, as a function of the central frequency of the pump pulse ω_p . At a given pump frequency, the space between two adjacent lines accounts for the relative

contribution of one f -state. For instance, at $\omega_p \approx 22,000 \text{ cm}^{-1}$ in panel a), $|f_{11}\rangle$ accounts for about 75 % of the total f -population, and $|f_{15}\rangle$ for about 10 %, as indicated in the figure. Some of the f -states are also labelled to guide the eye. Panels on top of these simulations further show the bandwidth of the individual photon wavepackets, and of the original pump pulse. Panel a) shows the populations created by strongly time-frequency entangled photon pairs (which may be inferred from the much broader bandwidth of the individual photons compared to the pump, see the top panel), whereas panel b) corresponds to a weakly entangled parameter regime (in which the bandwidths of pump and of the generated photons are comparable).

In both cases, the photon pairs are created from a pump pulse with 100 cm^{-1} bandwidth (corresponding to a 56 fs-pulse), and this is why we observe, at first glance, very similar behavior: By varying the pump frequency, one can control the excited two-exciton distributions to a great deal. Whenever an f -state is on resonance with the *sum* of the two photons' frequencies, its excitation is enhanced. For instance, state $|f_{11}\rangle$ with energy $22,160 \text{ cm}^{-1}$ (similarly, states $|f_{22}\rangle$ and $|f_{23}\rangle$ have energies $23,182 \text{ cm}^{-1}$ and $24,109 \text{ cm}^{-1}$, respectively) is most strongly excited around pump frequencies $\omega_p \simeq 22,000 \text{ cm}^{-1}$. The exact maximum is shifted in some cases, due to the interference with transitions to nearby two-exciton states, whose spectral envelopes partially overlap. Since the spectral distribution of the photons' frequencies' sum is very narrow (100 cm^{-1}), the variation of the pump frequency allows for a rather controlled excitation of specific f -states.

However, we also observe strong differences between the population distributions of panels a) and b): For instance, the maximal excitation of state $|f_{11}\rangle$ approaches unity in panel b), whereas it only reaches 0.75 in panel a). Or the excitation of state $|f_{22}\rangle$ is strongly enhanced in panel a), at roughly $\omega_p \approx 23,500 \text{ cm}^{-1}$, while it hardly gets excited at all in panel b). These differences may be explained by the bandwidth properties pertaining to the time-energy entanglement: As indicated in the top panel a), the bandwidth of the strongly entangled photon wavepackets is much larger than their sum. Hence, due to this large bandwidth, the photons can explore all possible excitation paths to the f -states which are on resonance with the pump pulse. For the weakly entangled case, on the other hand [panel b)], each wavepacket has a bandwidth similar to the pump envelope. Hence, some excitation pathways are blocked, since one or both of the intermediate transitions may be far off-resonant. State $|f_{22}\rangle$, mentioned before, is most strongly populated by transitions through the single exciton state $|e_5\rangle$, with energy $10,245 \text{ cm}^{-1}$, and through $|e_{10}\rangle$, with $12,936.8 \text{ cm}^{-1}$. Since the excitation happens via degenerate photons with $\omega_p/2 \approx 11,600 \text{ cm}^{-1}$, both single-photon transitions are strongly off-resonant. However, due to the large bandwidth of the individual photons, when strongly entangled, these transitions may still be accessed. This is no longer possible in the weakly entangled case.

Oscillations with entanglement time

So far, we have discussed two-exciton distributions as a function of the pump frequency ω_p , for a fixed entanglement time T . As we will show in the following, the interference between excitation pathways also manifests itself in an oscillatory behavior with

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Figure 4.9.: a) Relative two-exciton population of $|f_{15}\rangle$ at pump frequency $22,600 \text{ cm}^{-1}$ (blue), and of $|f_{22}\rangle$ at pump frequency $23,200 \text{ cm}^{-1}$ (red), as functions of the entanglement time T (in fs). b) Fourier transform of the functions of panel a). Two solid vertical lines on the horizontal axis indicate the energy differences $\omega_{e_7e_5}$ between states e_7 and e_5 , and $\omega_{e_{10}e_5}$ between e_{10} and e_5 , respectively. Another vertical line denotes the energy difference ω_{pe_5} between half the central photon wavepacket's frequency $\omega_p/2 = 11,600 \text{ cm}^{-1}$ and ω_{e_5} , corresponding to the oscillation of the individual pathway [see the discussion of Eq. (4.46)].

this entanglement time. This effect is reminiscent of the entangled-photon virtual-state spectroscopy proposed in Refs. [Peřina98, Fei97]. However, we will also see that these oscillations depend on the tails of the spectral distributions of the photon wavepackets, and therefore conclude that the effect will be challenging to observe in practice.

To witness the interference most clearly, we start with a simplified model for entangled photons as created by downconversion of a cw-pump [Peřina98]. The transition amplitude to an f -state may be calculated analytically [Roslyak09b], yielding, for degenerate photons,

$$T_{fg}(t; \Gamma) = \frac{1}{\hbar^2} \sum_e \mu_{ge} \frac{e^{i(\omega_p/2 - \omega_e + i\gamma_e)T} - 1}{\omega_p/2 - \omega_e + i\gamma_e} \mu_{ef} \frac{e^{-i\omega_p t}}{\omega_p - \omega_f + i\gamma_f}, \quad (4.46)$$

where T denotes the entanglement time (see appendix A), and ω_p the pump frequency. Eq. (4.46) clearly shows that the entanglement time appears in a sinc-like function, since, for small dephasing rate γ_e , $(e^{i(\omega_p/2 - \omega_e + i\gamma_e)T} - 1)/(\omega_p/2 - \omega_e + i\gamma_e) \sim \text{sinc}((\omega_p/2 - \omega_e)T)$. Hence, each excitation pathway via an intermediate state $|e_i\rangle$ oscillates as a function of T , with a frequency given by the detuning between the central photon energy $\omega_p/2$ (remember we are discussing degenerate downconversion) and ω_{e_i} . Interference terms between two excitation pathways via $|e_i\rangle$ and $|e_j\rangle$ appear in the modulus square $|T_{fg}(t)|^2$ of Eq. (4.46), which then oscillate as $\sim \text{sinc}((\omega_p/2 - \omega_{e_i})T) \times \text{sinc}((\omega_p/2 - \omega_{e_j})T)$, and which contains strong oscillatory frequency components at the energy difference $\omega_{e_i} - \omega_{e_j}$.

Figure 4.10.: Relative two-exciton population of $|f_{11}\rangle$ (blue) and $|f_{15}\rangle$ (red), at pump frequency $22,600 \text{ cm}^{-1}$, as a function of the entanglement time T (in fs). Solid lines: excitation by cw pump [Eq. (4.46)]; dashed lines: excitation by pulsed pump, with bandwidth $\sigma_p = 100 \text{ cm}^{-1}$ and Gaussian phase matching [Eq. (4.38)].

This is demonstrated in Fig. 4.9 where we show two examples, $|f_{15}\rangle$ and $|f_{22}\rangle$, of normalized f -state populations vs. T . In each case, the pump frequency is fixed on resonance with the respective state, in order to observe the oscillations most pronouncedly. The strong oscillations show distinct frequencies, which are direct fingerprints of dominant excitation pathways. Fig. 4.7 shows the dominant excitation pathways of the two states, which both involve the intermediate state $|e_5\rangle$, and additionally $|e_7\rangle$ or $|e_{10}\rangle$, respectively. Hence, we expect to see a beating signal between these two pathways, and, in fact, the Fourier transform of the entanglement time [Fig. 4.9b)] shows distinct peaks at the difference of the exciton frequencies $\omega_{e_7} - \omega_{e_5}$ and $\omega_{e_{10}} - \omega_{e_5}$, indicated by vertical lines at the bottom axis. A third resonance indicated by a dashed, vertical line corresponds to the oscillation of the pathway via $|e_5\rangle$ with the detuning of the individual photonic wavepacket, $\sim \text{sinc}((\omega_p/2 - \omega_{e_5})T)$, as was discussed after Eq. (4.46).

It turns out, however, that the above beating effect is rapidly washed out by, both, a pulsed pump pulse, and the Gaussian phase matching function which screens out the asymptotic tails of the spectral distribution in Eq. (4.46) employed in our model in appendix A, see section A.1.3. Fig. 4.10 compares the relative populations as predicted by the cw-pump model (4.46) with the full model (4.38). We plot the evolution of the population of $|f_{15}\rangle$ vs. the entanglement time, with the same parameters as in Fig. 4.9. Additionally, we show the evolution of the population of $|f_{11}\rangle$, which oscillates at the same frequency as $|f_{15}\rangle$, even though it is predominantly excited via the intermediate state $|e_5\rangle$. Whenever an excitation of $|f_{15}\rangle$ is hindered by destructive interference of excitation pathways, $|f_{11}\rangle$ gets excited instead. Even though the populations of the cw and the full model, respectively, approximately coincide for $T \rightarrow \infty$, the pulsed excitation shows none of the strong oscillations observed before, except, maybe, for a

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Figure 4.11.: Two-exciton population distributions in the bacterial RC created by classical laser pulses (4.47), with bandwidth a) $\sigma = 1, 100 \text{ cm}^{-1}$, and b) $\sigma = 100 \text{ cm}^{-1}$.

transient beating during the first 50 fs.

In any case, it is insufficient to reveal excitation pathways via Fourier transform with respect to the entanglement time. The difference between the two models mostly concerns the tails of the underlying spectral distribution: Whereas the cw-model features a sinc-like distribution, Gaussian phase matching reproduces the main peak of the sinc, but cuts off the smaller side peaks. Since these side peaks are most vulnerable under experimental imperfections such as finite opacity windows of beam splitters or lenses, we conclude that the oscillations revealed by the cw-model will most probably be difficult to discern in a realistic experiment. Similar findings have also been reported by Torres and co-workers [deJ Leon-Montiel13] in their examination of entanglement-induced transparency [Fei97] and of virtual-state spectroscopy [Saleh98].

4.4.3. Classical light

To compare the impact of the different bandwidths, we simulate two-exciton population distributions excited by a classical laser pulse (4.29)

$$E(\omega) = \frac{1}{\pi^{1/4} \sqrt{\sigma}} \exp \left[-(\omega - \omega_0)^2 / 2\sigma^2 \right], \quad (4.47)$$

in Fig. 4.11. Here, we only have one single parameter, the bandwidth σ , to influence the f -state distributions, in contrast to the control parameters σ_p and T of entangled light in Eq. (4.38). Panel a) shows a case where this bandwidth roughly matches that of the strongly entangled wavepackets in Fig. 4.8a), corresponding to a 5.1 fs-pulse (*i.e.* $\sigma = 1, 100 \text{ cm}^{-1}$). Due to this large bandwidth, the exciton distributions may only be influenced to a rather limited degree. When, on the other hand, the classical bandwidth matches the pump bandwidth, as depicted in panel b), we have a similar degree of control. In fact, the distribution in Fig. 4.11b) closely resembles the one of weakly entangled states in Fig. 4.8b). This shows that the distributions induced by (almost)

separable two-photon quantum states may be obtained from classical light as well. The strongly correlated distributions on the other hand cannot be reproduced one-to-one using classical pulses.

4.4.4. Correlated separable state

In a cautious use of language, we have attributed the differences between the various exciton population distributions so far observed to *correlations* rather than to photon *entanglement*, *i.e.* to the nonseparability of the photon wavefunction in the sense of section A.3.1, per se. To scrutinize this difference, we now construct a *correlated separable* state of the incident light field [Zheng13]: It is obtained from the two-photon density matrix of the pure, entangled state, $|\psi\rangle\langle\psi|$ [Eq. (A.41)], by deleting its off-diagonal elements in the energy eigenbasis. Thus, instead of a wavepacket with a given bandwidth, we obtain a classical time-independent distribution of frequencies, which may still contain frequency correlations on the level of a classical probability distribution [Mintert05].¹⁴ In the frequency domain, the state reads

$$\varrho_{\text{sep}} = \mathcal{N} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} |\Phi(\omega_a, \omega_b)|^2 a^\dagger(\omega_a) a^\dagger(\omega_b) |0\rangle\langle 0| a(\omega_a) a(\omega_b), \quad (4.48)$$

where $\mathcal{N}$ denotes the normalization constant, and $\Phi(\omega_a, \omega_b)$ the two-photon wavefunction [see Eq. (4.35)]. The f -state population, Eq. (4.27) with Eq. (4.48) as the incident light state, is then given by

$$p_f(\Gamma) = \left(-\frac{i}{\hbar}\right)^4 \mathcal{N} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} |\Phi(\omega_a, \omega_b)|^2 \times \sum_{e,e'} \frac{\mu_{ge}}{\omega_a - \omega_e + i\gamma_e} \frac{\mu_{ef}\mu_{e'f}}{(\omega_a + \omega_b - \omega_f)^2 + \gamma_f^2} \frac{\mu_{e'g}}{\omega_a - \omega_{e'} - i\gamma_e}. \quad (4.49)$$

Here, for the sake of simplicity, we have only accounted for processes, in which the frequency ω_a drives the $g - e$ transition, and ω_b the $e - f$ transition, since our two-photon wavefunction $\Phi(\omega_a, \omega_b)$ is chosen symmetric with respect to the two variables. Just like Eq. (4.48), the f -state population distribution (4.49) is time-independent. It describes the nonequilibrium steady state population in the f -manifold, when the system is driven by the cw-field (4.48), which was “switched on” at time $t_0 = -\infty$.¹⁵ This is in contrast to the previous examples, where the aggregate was excited by a pulse.

Without further calculations, it is possible to understand the differences between these two cases by looking at the coherence properties of the excited state distributions. Indeed, by virtue of Eq. (4.39), we can immediately write down the off-diagonal elements of the excited state density matrix, $\varrho_{ff'} = T_{fg} T_{f'g}^*$ in case of excitation by a pure two-photon state. Hence, we know that the density matrix in the two-exciton subspace will

¹⁴We will not discuss whether or not this state may be realized experimentally. For our purposes, it merely represents a thought experiment, in which there is no entanglement and no time correlations, but only frequency correlations.

¹⁵If we were to switch on the light field as $t_0 = 0$, we would have to add a Heaviside-function $\Theta(t)$, Eq. (3.14) to Eq. (4.48), which would then induce transient dynamics before relaxing to Eq. (4.49).

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Figure 4.12.: Two-exciton population distributions in the bacterial RC induced by a correlated-separable state and unitary dynamics, Eq. (4.49), with a) bandwidth $\sigma_p = 100 \text{ cm}^{-1}$ and entanglement time $T = 10 \text{ fs}$, b) $\sigma_p = 100 \text{ cm}^{-1}$, $T = 100 \text{ fs}$.

be in a pure state as well. This cannot happen for the correlated separable state (4.48). Due to only two frequency integrations, the *bra* and *ket* sides of the transitions may not be separated as before in Figs. 4.8 to 4.11.

But apart from its coherence properties, we still need to answer our initial question, whether - or to which extent - the excited state population distributions observed in Fig. 4.8 are a proper consequence of photon entanglement, *i.e.* of the nonseparability of the two-photon wavefunction as defined in section A.3.1. To this end, we simulate the steady-state population (4.49), for identical control parameters as in Fig. 4.8, in Fig. 4.12. Indeed, the population distributions are virtually identical to the previously obtained results induced by entangled photons, so entanglement is not essential for this task.

These results are in agreement with related work by Zheng and Fabre [Zheng13], in which the authors examine the efficiency of two-photon absorptions in two non-interacting atoms, and conclude that it is the frequency (anti-)correlations rather than the entanglement that is responsible for the enhancement.¹⁶ As far as unitary dynamics is concerned, it may be rationalized that a frequency distribution may have the same impact as a coherent superposition of frequencies in the case of entangled photons. Once excited, the energy stays there, and so the time correlations that are encrypted in the coherence of the two-photon wavepackets play no essential role. This argument is no longer true, however, when we add dissipation, and energy is no longer conserved, as we will show in the following.

¹⁶Similar results have also been obtained in the investigation of dispersion cancellation in [Torres-Company11].

Figure 4.13.: To describe the open system evolution induced by the coupling of the excitonic degrees of freedom to molecular background dynamics, the unrestricted loop diagram in Fig. 4.1a) describing the leading-order f -population (left) needs to be broken up (right) into three totally time-ordered ladder diagrams (and their Hermitian conjugate).

4.5. Open systems

Having so far discussed excitation pathways, oscillations with the entanglement time, and *frequency correlations* as generated by unitary dynamics, we now turn to dissipative dynamics and the role of *time correlations* between the incident photons. To this end, we first need to break up the transition amplitudes described by the single unrestricted loop diagram in Fig. 4.1a) into fully time-ordered expressions described by ladder diagrams (as described in section 3.5.3).

These expressions will allow us to describe exciton transport within the photosynthetic reaction center of *Blastochloris viridis* introduced in the previous section. We will restrict our discussion to the simplest possible description of open quantum systems - the time-independent Lindblad equation [Breuer02] (or secular Redfield equation in the chemistry nomenclature [Abramavičius09]) where the coherence terms of the density matrix (in the exciton basis) decay with a dephasing rate of 28 fs (corresponding to a line broadening of $\gamma_e = 200 \text{ cm}^{-1}$), and populations undergo (incoherent) transport described by a Pauli rate equation.

4.5.1. Ladder diagrams

To obtain the fully time-ordered expressions, we follow the procedure explained in detail in sections 3.5.2 and 3.5.3. The unrestricted loop diagram is given by two loop diagrams where the final interaction happens either on the *bra* or on the *ket*. These loops may then be broken into a total of six fully time-ordered expressions. They are represented by the three ladder diagrams shown in Fig. 4.13, and three more terms, which are obtained by mirroring these three diagrams with respect to the vertical axis. The mirror images are the complex conjugates of those diagrams displayed in the figure, and therefore it is sufficient to calculate the real part of the latter. The following sum-over-states

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expressions in the time domain may be read off the diagrams:

$$\begin{aligned}
p_{f,(I)}(t; \Gamma) &= \left(-\frac{i}{\hbar}\right)^4 \int_0^\infty dt_4 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \\
&\times \sum_{e,e'} \mathcal{G}_{ff}(t_4) \mu_{e'f} \mathcal{G}_{fe'}(t_3) \mu_{ge'} \mathcal{G}_{fg}(t_2) \mu_{ef} \mathcal{G}_{eg}(t_1) \mu_{ge} \\
&\times \langle E^\dagger(t-t_4-t_3) E^\dagger(t-t_4) E(t-t_4-t_3-t_2) E(t-t_4-t_3-t_2-t_1) \rangle,
\end{aligned} \tag{4.50}$$

$$\begin{aligned}
p_{f,(II)}(t; \Gamma) &= \left(-\frac{i}{\hbar}\right)^4 \int_0^\infty dt_4 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \\
&\times \sum_{e,e',e''} \mathcal{G}_{ff}(t_4) \mu_{e''f} \mathcal{G}_{fe''}(t_3) \mu_{e'e''} \mathcal{G}_{ee';e''e''}(t_2) \mu_{ge'} \mathcal{G}_{eg}(t_1) \mu_{ge} \\
&\times \langle E^\dagger(t-t_4-t_3) E^\dagger(t-t_4) E(t-t_4-t_3-t_2) E(t-t_4-t_3-t_2-t_1) \rangle,
\end{aligned} \tag{4.51}$$

$$\begin{aligned}
p_{f,(III)}(t; \Gamma) &= \left(-\frac{i}{\hbar}\right)^4 \int_0^\infty dt_4 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 \\
&\times \sum_{e,e',e''} \mathcal{G}_{ff}(t_4) \mu_{e''f} \mathcal{G}_{e''f}(t_3) \mu_{e'e''} \mathcal{G}_{ee';e''e''}(t_2) \mu_{ge'} \mathcal{G}_{eg}(t_1) \mu_{ge} \\
&\times \langle E^\dagger(t-t_4-t_3) E^\dagger(t-t_4) E(t-t_4-t_3-t_2) E(t-t_4-t_3-t_2-t_1) \rangle,
\end{aligned} \tag{4.52}$$

The Green's functions $\mathcal{G}$ describing the open system evolution are specified in appendix B.¹⁷ We reiterate that under the Green's functions action, off-diagonal elements in the exciton eigenbasis decay exponentially, while populations are transported towards lower-energy states, on timescales ranging from ~ 30 fs to picoseconds.

We further assumed above that the evolution of the field degrees of freedom remain unitary, such that we may write the field four-point correlation function as Hilbert space correlation functions, and each diagram on the right-hand side of Fig. 4.13 contains the same field correlation function (see section 3.5.3).

4.5.2. Entangled photons

Using Eqs. (4.50)-(4.52), we may repeat our previous simulations of the excited state population distributions, now for open system evolution. Fig. 4.14 again shows the normalized f -state population distributions vs. the central pump pulse frequency ω_p , for two different entanglement times T . Clearly, for $T = 10$ fs, the distributions in Figs. 4.8a) and 4.14a) are virtually identical, while they strongly differ for $T = 100$ fs in panel b). As we know, the entanglement time represents an upper bound for the time delay between the absorption of the two photons. In case a) the system spends

¹⁷Note that the single-exciton Green's function $\mathcal{G}_{ee';e''e''}$ in Eqs. (4.51) and (4.52) contains three indices, since it describes population transport, if $e = e'$.

Figure 4.14.: Two-exciton population distributions in the bacterial RC created by degenerate, entangled photon pairs with a) bandwidth $\sigma_p = 100 \text{ cm}^{-1}$ and entanglement time $T = 10 \text{ fs}$, b) $\sigma_p = 100 \text{ cm}^{-1}$, $T = 100 \text{ fs}$ in the presence of a dissipative environment as described in appendix B.

a maximum of 10 fs in the single-exciton manifold. This is not enough time for the environment-induced transport, which we recall takes places on timescales $\geq 30 \text{ fs}$, to reshuffle the e -states notably, and the resulting f -distribution looks as if there was no intermediate transport. Hence, intermediate population transport may be suppressed using entangled photons with strongly correlated arrival times, *i.e.* with short entanglement times [see Fig. 4.11b)]. This suppression of intermediate transport could also be achieved with ultrashort classical pulses - however, as we saw in the previous section 4.4.3, at the expense of a loss of the control over the f -state distribution, due to the broad bandwidth of ultrashort pulses.

In case b), the system spends up to 100 fs in the e -manifold: Some photon pairs still arrive quasi-simultaneously, others are separated by 100 fs. In the latter case, this is plenty of time for the faster, environmental transport channels to affect the e -distributions, and, therefore, indirectly the f -populations. At first glance, it seems as if the f -state population distributions, especially between $\omega_p = 24,000$ and $26,000 \text{ cm}^{-1}$, does not change very much under the change of T . However, one needs to keep in mind that the entanglement time also affects the bandwidth. The appropriate benchmark to be compared to is therefore given by Fig. 4.8b). Comparison of both plots shows that excitation has in fact been transferred to lower-energy states in Fig. 4.14b): For instance, at $\omega_p \approx 25,600 \text{ cm}^{-1}$, the high-energy state $|f_{32}\rangle$ accounts for more than 70 % of the total f -population. Including transport, in Fig. 4.14b), the $|f_{32}\rangle$ -population is reduced to approximately 40 %. This shows that, in fact, energy has been dissipated between the absorption of two subsequent photons.

With increasing entanglement time, the transport between the two absorption events reshuffles the e -populations, and any redistribution of e -states is reflected in a distinct f -state population distribution after the second photon absorption. Since the entanglement time may be easily adjusted by, e.g., tilting the nonlinear crystal, and in addition, one could also add delay stages in the beam line of one of the two pho-

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Figure 4.15.: a) Contribution of the two-exciton state $|f_{11}\rangle$ to the total f -population, vs. the pump frequency ω_p for entanglement times $T = 10, 30, 40, 60, 80$, and 100 fs. b) Same for $|f_{15}\rangle$, c) $|f_{22}\rangle$, and d) $|f_{24}\rangle$. The resulting populations are shifted along the vertical axis with increasing T , to ease readability.

tons [Richter10, Raymer13], this opens the possibility to probe these transport processes with femtosecond resolution, using entangled photons which are created by much “slower” (picosecond) pump pulses. As a direct consequence, this behavior allows to probe such ultrafast processes under relaxed experimental conditions. Furthermore, as discussed already in the context of the simulation of unitary system dynamics in section 4.4.2, specific f -states may be targeted, exploiting the frequency correlations manifest in the f -manifold, such that only these transport processes which involve the targeted states contribute to the signal. Thus, while conventional photon echo spectroscopy always probes the entirety of transport processes at once, thereby sometimes overshadowing weak transport channels (see section 2.1.2), our present approach may allow for the selected monitoring of certain subsets of transport channels.

In Fig. 4.15, we depict the contribution of various f -states to the total f -population as a function of the pump frequency ω_p for several entanglement times T as indicated in panel a). The different plots are shifted away from the horizontal axis by a constant proportional to their entanglement time, such that the plots from bottom to top show the evolution of the relative f -population for increasing entanglement time. Panel a) shows the evolution of state $|f_{11}\rangle$. For short entanglement times, the only strong contribution is

centered around $\omega_p = 22,000 \text{ cm}^{-1}$, when the pump frequency is on resonance with the f -state. With increasing entanglement time, it develops a pronounced shoulder between $\omega_p = 22,000 - 24,000 \text{ cm}^{-1}$. This stems from the intermediate decay of exciton $|e_6\rangle$ or $|e_7\rangle$ to $|e_5\rangle$.¹⁸ Hence, instead of the state manifold $|f_{15}\rangle - |f_{22}\rangle$, excitation into the f -manifold predominantly reaches $|f_{11}\rangle$. This may also be seen in panels b) and c), which depict the relative population of states $|f_{15}\rangle$ and $|f_{22}\rangle$, respectively. The evolution of the relative populations of the states $|f_{11}\rangle$, and two of the states, $|f_{15}\rangle$, and $|f_{16}\rangle$ is shown in detail separately in Fig. 4.16 as a function of the entanglement time T . The pump frequency has been tuned to resonance with the state $|f_{15}\rangle$. Clearly, most population is transferred from the higher-energy states to $|f_{11}\rangle$ within roughly 70 fs.

The resonance attributed to $|f_{22}\rangle$ in Fig. 4.15c) decays even faster, and has no population left for $T \geq 40$ fs. In contrast to the states $|f_{15}\rangle - |f_{22}\rangle$, the lineshape of state $|f_{24}\rangle$ hardly changes within 100 fs, but the state develops a shoulder towards lower energies, $\omega_p = 23,000 - 24,000 \text{ cm}^{-1}$, with increasing T . In contrast to all lower-energy f -states, $|f_{24}\rangle$ is mainly excited via $|e_6\rangle$ and $|e_7\rangle$, which are both part of the higher-energy band within the single exciton manifold [see Fig. 4.6b)]. Therefore, the lower-energy shoulder cannot stem from intermediate exciton transport (which would correspond to transport to higher-energy excitons of $|e_5\rangle \rightarrow |e_6\rangle$ or $|e_7\rangle$, which does not occur in our transport model). Instead, we may attribute the low-energy excitation to the change of the photon bandwidth, induced by an increase of the entanglement time (see also the discussion of Fig. 4.8). While, for short T , off-resonant intermediate states may still be accessed to excite states such as $|f_{22}\rangle$, these excitation pathways close with shrinking bandwidth, and different f -states are excited instead. Hence, this effect may be observed as well in the case of unitary evolution (compare $|f_{23}\rangle$ in panels a) and b) of Fig. 4.8), and we will encounter the same phenomenon again when discussing fluorescence signals in the next section. Taken together, our discussion shows that the change of the relative population alone cannot always be assigned to either population transport or the change of the photon bandwidth, since both processes take place simultaneously. Instead, the changes need to be assigned by comparison with the corresponding distribution under unitary evolution. Furthermore, as we will show in the next section, the two processes - the exciton transport and the change of photon bandwidths - can be distinguished by the total height of the fluorescence signal.

Interpretation The observed population distributions may also be understood with regards to the diagrams in Fig. 4.13. From our previous discussion and our analysis of the entangled photon correlation functions in appendix A, we know that the two photons arrive within a time delay given by the entanglement time T , which sets an upper bound on the maximal time delay between the two absorption events on either side of the density matrix. This reasoning suggests that diagrams (II) and (III) should contribute very little to the total signal in Fig. 4.15 for small entanglement times, since in these

¹⁸This may be deduced from comparison with Fig. 4.8b), *i.e.* with the result of strictly unitary dynamics, where the shoulder is not created with an entanglement time $T = 100$ fs, and states $|f_{15}\rangle$ and $|f_{16}\rangle$ are still excited.

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Figure 4.16.: Population of the two-exciton states $|f_{11}\rangle$, $|f_{15}\rangle$, and $|f_{16}\rangle$, respectively as a function of the entanglement time T , excited by degenerate entangled photons with $\omega_p = \omega_{f_{15}}$ and $\sigma_p = 100 \text{ cm}^{-1}$.

diagrams all four interactions are required to take place within this short time span. In diagram (I), on the other hand, the absorption events on the *bra* and on the *ket* side are not convoluted. And indeed, this is what we observe numerically: In Fig. 4.17a), we plot the absolute value of the relative contribution of each diagram [Eqs. (4.50) - (4.52)],¹⁹

$$C_{\text{rel},i}(T) = \frac{\sum_f |p_{f,(i)}(t; \Gamma)|}{\sum_f (|p_{f,(I)}(t; \Gamma)| + |p_{f,(II)}(t; \Gamma)| + |p_{f,(III)}(t; \Gamma)|)}, \quad (4.53)$$

for the parameters used in Fig. 4.16 as a function of the entanglement time. While, at a very short entanglement time $T = 10 \text{ fs}$, diagram (I) accounts for roughly 90 % of the total signal, its contribution drops to around 20 % for $T = 70 \text{ fs}$. Similarly, the other two diagrams increase in relative strength. The depletion of states $|f_{15}\rangle$ and $|f_{16}\rangle$, which we observed in Fig. 4.16, therefore coincides with the transition from a signal dominated by diagram (I) to a signal dominated by diagrams (II) and (III).

To understand this transition, let us consider the limit of very short T . Here, the propagation times t_1 and t_3 in diagram (I) are extremely short compared to the system dynamics, so we may approximate the two absorptions to occur simultaneously [this feature is illustrated in Fig. 4.17b)]. The other two diagrams collapse onto instantaneous excitations $g \rightarrow f$ on both sides of the density matrix, and their contribution may be neglected. In this case we may say that *two-photon transitions induced by time-frequency entangled photons behave like direct single-photon transitions from g to f , induced by the original pump pulse photon*. The resulting diagram in Fig. 4.17b) is identical to the linear absorption signal in Fig. 3.8a) - just with two absorptions per interaction.

¹⁹Each individual diagram in the signal may yield negative values, and only their sum needs to be positive. To get an estimate of the relative importance of the diagrams, we therefore take their absolute value.

Figure 4.17.: a) Relative contribution of each diagram, Eq. (4.53), to the population distributions of Fig. 4.16 as a function of the entanglement time T . b) Due to the strong time correlations between the two photons, their arrival time is limited by the entanglement time T . If T is short compared to the timescales of the matter system, the two-photon transition to the two-exciton state $|f\rangle$ looks like a single-photon transition directly from $|g\rangle$ to $|f\rangle$ induced by the pump photon that generated the entangled pair, even though there is no direct dipole moment between $|g\rangle$ and $|f\rangle$.

4.5.3. Correlated separable state

Having investigated the influence of time correlations on the excited state population distributions, we need to verify that similar distributions cannot be obtained with a correlated-separable state, Eq. (4.48), as was the case for unitary dynamics. Hence, we simulate Eqs. (4.50)-(4.52) for this state. Inserting Eq. (4.48) into the four-point correlation functions in Eqs. (4.50) - (4.52),²⁰

$$\langle E^\dagger(\tau'_1)E^\dagger(\tau'_2)E(\tau_2)E(\tau_1) \rangle = \mathcal{N} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} |\Phi(\omega_a, \omega_b)|^2 e^{-i\omega_a(\tau_1 - \tau'_1)} e^{-i\omega_b(\tau_2 - \tau'_2)}, \quad (4.54)$$

²⁰We only account for contributions, in which the first interaction happens with ω_a and the second one with ω_b , see Eq. (4.49).

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Figure 4.18.: Two-exciton population distributions induced by the correlated-separable state (4.48) and dissipative dynamics, Eqs. (4.55)-(4.57), with a) pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$ and entanglement time $T = 10 \text{ fs}$, b) $\sigma_p = 100 \text{ cm}^{-1}$, $T = 100 \text{ fs}$.

we can carry out the time integrations to obtain

$$p_{f,(I)}(t; \Gamma) = \left(-\frac{i}{\hbar}\right)^4 \mathcal{N} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} |\Phi(\omega_a, \omega_b)|^2 \times \sum_{e,e'} \mathcal{G}_{ff}(0) \mu_{e'f} \mathcal{G}_{fe'}(\omega_b) \mu_{ge'} \mathcal{G}_{fg}(\omega_a + \omega_b) \mu_{ef} \mathcal{G}_{eg}(\omega_a) \mu_{ge}, \quad (4.55)$$

$$p_{f,(II)}(t; \Gamma) = \left(-\frac{i}{\hbar}\right)^4 \mathcal{N} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} |\Phi(\omega_a, \omega_b)|^2 \times \sum_{e,e',e''} \mathcal{G}_{ff}(0) \mu_{e''f} \mathcal{G}_{fe''}(\omega_b) \mu_{e'e''} \mathcal{G}_{ee';e''e''}(0) \mu_{ge'} \mathcal{G}_{eg}(\omega_a) \mu_{ge} \quad (4.56)$$

$$p_{f,(III)}(t; \Gamma) = \left(-\frac{i}{\hbar}\right)^4 \mathcal{N} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} |\Phi(\omega_a, \omega_b)|^2 \times \sum_{e,e',e''} \mathcal{G}_{ff}(0) \mu_{e''f} \mathcal{G}_{e''f}(\omega_b) \mu_{e''f} \mathcal{G}_{ee';e''e''}(0) \mu_{ge'} \mathcal{G}_{eg}(\omega_a) \mu_{ge}, \quad (4.57)$$

Carrying out these calculations, we encounter one difficulty: As mentioned above, the correlated separable state represents a time-independent distribution of frequencies, and the equilibrium population distribution of the Pauli rate matrix describing the exciton transport has infinite lifetime [Mukamel99], which renders the Green's function $\mathcal{G}_{ee';e''e''}(0)$ in Eqs. (4.56) and (4.57) divergent, since there is no time correlation between the second and third light-matter interaction (This poses no problem in pulsed excitation considered before, due to the finite pulse duration). To solve this problem, we add a small phenomenological lifetime of 600 fs (corresponding to a broadening of $\eta = 10 \text{ cm}^{-1}$) to each e -state.

Fig. 4.18 shows the resulting f -distributions. Clearly, state $|f_{11}\rangle$ is always most strongly excited for almost any frequency ω_p , and both for $T = 10 \text{ fs}$ and 100 fs . This

may be understood as a consequence of the intermediate relaxation dynamics: Due to the lack of time correlations between individual interaction events, most e -population is transferred to the thermal equilibrium described by the Pauli rate equation, before the second interaction excites it into an f -state. The state $|e_5\rangle$ is the excitonic state with the lowest energy (see Fig. B.1), and low-energy states dominate the thermal distribution at low temperatures considered in the present model [Fingerhut12]. Therefore, excitations from $|e_5\rangle$ always dominate. Nevertheless, we also observe the strong excitation of states such as $|f_4\rangle$, which is excited via the charge separated state $|e_4\rangle$ (see Fig. 4.7). Due to the large timescales of the charge separation process in comparison with the previously discussed transport processes, this further points to the large time delays between the absorption events: To create population in $|e_4\rangle$ (after, for instance, initial excitation of the state $|e_5\rangle$), the system has to evolve in the single exciton manifold for several hundred femtoseconds - orders of magnitude longer than under the illumination by entangled photon pairs. Hence, once time correlations are important, the correlated separable state (4.48) and the entangled photon pairs (4.35) induce completely different population distributions.

4.5.4. Time-energy uncertainty

Our goal in this paragraph is to find a measure to quantify the “nonclassicality” of the created f -state populations. To that end, let us first contemplate how to optimally control the excitation of a specific f -state: From our previous simulations, it has become clear that one seeks to *minimize* the time Δt the system can spend in the single exciton manifold, in order to avoid the relaxation of population between photon absorption events. At the same time, one seeks to *maximize* the frequency resolution $\Delta\omega$ in the f -manifold. For two-photon absorption from a classical pulse, see Fig. 4.11, the single excitation time Δt and the frequency resolution $\Delta\omega$ are Fourier conjugates, and we are therefore limited by²¹

$$\Delta\omega\Delta t \geq 1. \quad (4.58)$$

This inequality cannot be circumvented by the use of multiple pulses either, since the energy resolution $\Delta\omega$ would then be given by the sum of the two beams, $\Delta(\omega_1 + \omega_2)$, and the time resolution Δt by the delay, with which the two absorption events may be separated temporally, $\Delta(t_1 - t_2)$. Hence, their product would still be bounded by the sum of the Fourier uncertainties of the two pulses.

For entangled photons, on the other hand, there is no such limitation: In the limit of strong frequency anti-correlations (see appendix A), Δt may be assessed by the entanglement time T , and $\Delta\omega$ by the pump bandwidth σ_p . Both are independent quantities, and may be minimized at will. This finding is in line with the experiment reported in Ref.

²¹Here, the bound is set to unity. This is the case for the variance of Gaussian wavepackets, as we employ almost exclusively in this dissertation. For general wavepackets, the numerical value may differ, and it further depends on the definition of the uncertainties Δt and $\Delta\omega$, *i.e.* whether one considers the full width at half maximum or the variance of the distribution.

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[Ali Khan06], where the violation of the inequality (4.58) has been measured using Franson interferometry and a spectrometer, obtaining the estimate $\Delta\omega\Delta t \sim 0.00022$, which greatly surpasses the entanglement used in our present simulations: For $\sigma_p = 100 \text{ cm}^{-1}$ and $T = 10 \text{ fs}$, we obtain

$$\Delta\omega\Delta t \sim \sigma_p T = 0.18, \quad (4.59)$$

which, however, still clearly violates Eq. (4.58) for the Gaussian amplitudes used here.

At first glance, this result bears close resemblance to the entanglement of two continuous variable systems, with time and frequency playing the role of position and momentum [Wasak10]: In the one-dimensional beam geometry we considered in the derivation of the entangled photon wavefunction in appendix A, we can associate a momentum p_i with the frequency ω_i of each photon, $p_i = \omega_i/c$, and a position x_i with the time, $x_i = ct_i$. By separating the photon pairs at a polarizing beam splitter, for instance, we can measure - at least in principle - the position and momentum of each photon, and due to our above definition, we obtain for their variance $\Delta p \Delta x = \Delta\omega\Delta t$. Position and momentum are quantum-mechanical observables, for which well-defined entanglement criteria exist [Franson89]: As shown in Refs. [Tan99, Mancini02], given two continuous variable systems with operators q_i and p_i , whose commutator is a c -number, one can find an entanglement criterium for their combined variances. For the operators $u = q_1 - q_2$ and $v = p_1 + p_2$, any separable state ρ satisfies

$$\langle(\Delta u)^2\rangle\langle(\Delta v)^2\rangle \geq |\langle[q_1, p_1]\rangle|^2. \quad (4.60)$$

Hence, any state violating this inequality is entangled. This yields a valid entanglement criterion for the position-momentum entanglement of photon pairs²². Even though this result is sometimes used as an entanglement criterion for time-energy entanglement in the literature [Wasak10], it is not directly applicable to our above discussion, since the above identification of the arrival time with a specific photon position is certainly not a precise equivalence. It does however lend plausibility to the idea that the violation of Eq. (4.58) is in fact an entanglement effect²³: The energy-time entanglement (*i.e.* the nonseparability of the photonic wavefunctions in the frequency and the time domain) and the momentum-position entanglement (the nonseparability in position and momentum space) of entangled photons both originate from the same physical mechanism - parametric downconversion - and are both caused by the interplay between energy and momentum conservation within the downconversion process.

But even though we cannot exclude with certainty the possibility that there exist unentangled states violating Eq. (4.58), we know that - within our model of parametric downconversion - the violation is only possible with entangled two-photon states: The

²²As mentioned in section 2.2, energy and momentum conservation implies that photon pairs created in parametric downconversion are entangled in the position and momentum degrees of freedom as well [Walborn10].

²³In fact, Eq. (4.58) was falsely labelled a Heisenberg uncertainty inequality in Ref. [Ali Khan06].

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separable PDC-state according to Eq. (A.41) reads

$$|\psi_{\text{sep}}\rangle = A_1^\dagger B_1^\dagger |0\rangle \quad (4.61)$$

$$= \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} 4\pi \sqrt{k_1 k_2} e^{-k_1^2(\omega_1 - \omega_1)^2/2 - k_2^2(\omega_b - \omega_2)^2/2} a_a^\dagger(\omega_a) a_b^\dagger(\omega_b) |0\rangle, \quad (4.62)$$

i.e. it is the product of two fields with Gaussian envelopes, for which the Fourier uncertainty evaluates to $\Delta\omega\Delta t = 1$.

Thus, while we have presented strong indication that the violation of the Fourier uncertainty (4.58) lies at the heart of the ability of entangled photon pairs to control f -populations, it is necessary to point out that the opposite argument is not necessarily true: The violation of Eq. (4.58) does not always imply that the excited wavepackets may not be obtained with classical light. Consider, for instance, entangled photon pairs created by a cw pump laser, *i.e.* with $\sigma_p = 0$. They always violate the uncertainty according to our previous discussion, as we have $\Delta\omega_p = 0$ for any entanglement time. However, as we have seen at the beginning of this chapter in section 4.2, the spectral width of a resonance is then determined by the linewidth γ_f of the two-exciton state - and not σ_p . Hence, the more appropriate limit in this situation is given by $\Delta\omega_p = \gamma_f$, and accordingly, if the entanglement time is larger than $1/\gamma_f$, there is no more quantum advantage observable. Similarly, if the transport processes inside the matter system take place on slower time scales than the inverse linewidth of the f -states, the time resolution becomes irrelevant, and exciton distributions may be controlled by classical pulses as well.

This discussion thus shows us that the violation of the Fourier uncertainty may serve as an indicator for nonclassical time-frequency entanglement within our downconversion model (always keeping in mind that we have *not* verified whether it constitutes a proper entanglement witness). However, properties of the light field alone provide insufficient information, whether the created wavepackets can also be obtained with classical light.

4.6. Fluorescence signals of the bacterial reaction center

Despite having discussed the f -state population distributions extensively, we have not yet demonstrated, how they may be observed experimentally. Thus, as the final section of this chapter, we now simulate fluorescence signals created by the decay of the two-exciton distributions which we derived in the preceding section, using Eq. (4.25). The fluorescence signal will allow us to discuss signatures of the excited state distributions, and furthermore introduce a new dimension to our discussion: So far, we only simulated normalized two-exciton population distributions, where the overall probability for the excitation of an f -state has been discarded. The intensity of the fluorescence measurements provides this additional information.

We note that, in practice, the detection of the two-photon induced fluorescence (TPIF, see Fig. 4.1) signal has to compete with fluorescence from the e -manifold stemming from the absorption of individual photons. However, we are mostly interested in the regime of strong frequency anti-correlations where the bandwidth of the individual photons is

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much larger than that of the pump pulse. Collecting the fluorescence as a function of the pump frequency ω_p , the fluorescence from the e -manifold should then constitute an almost flat background.²⁴

Since the time integration in Eq. (4.25) leads to a delta-function in the frequency domain, see Eqs. (4.31) and (4.40), it is actually beneficial to evaluate the TPIF signal in the frequency domain. Using the frequency decomposition of the field operators,

$$E(t) = \int \frac{d\omega}{2\pi} e^{-i\omega t} E(\omega), \quad (4.63)$$

as well as Eqs. (4.50)-(4.52), the time integrated f -population reads:

$$\begin{aligned} \int dt p_{f,(I)}(t; \Gamma) &= \left(-\frac{i}{\hbar}\right)^4 \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} 2\pi\delta(\omega_a + \omega_b - \omega'_a - \omega'_b) \\ &\times \sum_{e,e'} \mathcal{G}_{ff}(\omega_a + \omega_b - \omega'_a - \omega'_b) \mu_{e'f} \mathcal{G}_{fe'}(\omega_a + \omega_b - \omega'_a) \\ &\times \mu_{ge'} \mathcal{G}_{fg}(\omega_a + \omega_b) \mu_{ef} \mathcal{G}_{eg}(\omega_a) \mu_{ge} \langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle, \quad (4.64) \\ \int dt p_{f,(II)}(t; \Gamma) &= \left(-\frac{i}{\hbar}\right)^4 \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} 2\pi\delta(\omega_a + \omega_b - \omega'_a - \omega'_b) \\ &\times \sum_{e,e',e''} \mathcal{G}_{ff}(\omega_a + \omega_b - \omega'_a - \omega'_b) \mu_{e''f} \mathcal{G}_{fe''}(\omega_a + \omega_b - \omega'_a) \\ &\times \mu_{e''f} \mathcal{G}_{ee';e''e''}(\omega_a - \omega'_a) \mu_{ge'} \mathcal{G}_{eg}(\omega_a) \mu_{ge} \langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle, \quad (4.65) \\ \int dt p_{f,(III)}(t; \Gamma) &= \left(-\frac{i}{\hbar}\right)^4 \int \frac{d\omega'_a}{2\pi} \int \frac{d\omega'_b}{2\pi} \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} 2\pi\delta(\omega_a + \omega_b - \omega'_a - \omega'_b) \\ &\times \sum_{e,e',e''} \mathcal{G}_{ff}(\omega_a + \omega_b - \omega'_a - \omega'_b) \mu_{e''f} \mathcal{G}_{e''f}(\omega_a - \omega'_a - \omega'_b) \\ &\times \mu_{e''f} \mathcal{G}_{ee';e''e''}(\omega_a - \omega'_a) \mu_{ge'} \mathcal{G}_{eg}(\omega_a) \mu_{ge} \langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle. \quad (4.66) \end{aligned}$$

To make use of the frequency correlations encoded in the four-point field correlation function, it is further helpful to change to the variable $\omega_{\text{sum}} = \omega_a + \omega_b$, which is very sharply centered around the pump frequency. The integrated f -populations are then calculated numerically by sampling ω_{sum} within ten standard deviations $\pm 10\sigma_p$ of the pump pulse envelope around ω_p , and ω_a/ω'_a between $\pm 10/T$ (corresponding to roughly ten times the photon bandwidth) around the beam center frequency $\omega_p/2$.

Fig. 4.19 shows the TPIF signal (4.25) as a function of the pump frequency of the entangled photons ω_p (*i.e.* of the excitation frequency), and of the dispersed fluorescence frequency ω (*i.e.* of the frequency, at which the energy is reemitted). The signal maximum in each plot is normalized to one, and the delta-function for the $f \rightarrow e$ transition in

²⁴We do not compare the signals directly, since the linear signal depends on the two-point field correlation function, and the TPIF signal on the four-point correlation function. The difference between the two signals therefore also depends on the field normalization constant, *i.e.* on experimental details.

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Figure 4.19.: Normalized two-photon induced fluorescence (4.25) plotted vs the pump frequency ω_p and the dispersed fluorescence frequency ω . The two-photon induced fluorescence signal is created by degenerate entangled photons with pump bandwidth $\sigma_p = 50 \text{ cm}^{-1}$, and entanglement time a) $T = 10 \text{ fs}$, b) $T = 100 \text{ fs}$.

Eq. (4.25) has been replaced by a Lorentzian with width 200 cm^{-1} , in order to present the results graphically. Panels a) and b) show the signals for degenerate entangled photons with pump bandwidths $\sigma_p = 50 \text{ cm}^{-1}$, and entanglement times $T = 10$ and 100 fs , respectively, which clearly differ tremendously (note that the two plots nearly correspond to the fluorescence signal of the population distributions shown in Fig. 4.14).

Let us first discuss the signal in panel a): For $T = 10 \text{ fs}$, we observe two strong resonances at $\omega_p \simeq 22,100 \text{ cm}^{-1}$: one at $\omega \simeq 10,000 \text{ cm}^{-1}$, featuring a strong shoulder towards higher pump frequencies, and one at $\omega \simeq 12,000 \text{ cm}^{-1}$. Another strong fluorescence band stretches between $\omega_p \simeq 24,000$ and $26,000 \text{ cm}^{-1}$, and fluoresces predominantly at $\omega \simeq 12,000 \text{ cm}^{-1}$ and with a small peak also at $\omega \simeq 10,000 \text{ cm}^{-1}$.

To analyze this spectrum, we turn to its marginal spectra, obtained from integrating out one of the frequencies, in Figs. 4.20a) and 4.21a). When integrating over the dispersed frequency ω , we obtain the fluorescence action spectrum (4.26). To guide the eye, we add the positions of each two-exciton state, and the height of the vertical lines indicates their maximally possible dipole strength $|\sum_e \mu_{ge} \mu_{ef}|^2$.²⁵ As we can see, this already provides us with a reasonable measure to interpret the action spectrum: The signal peaks, whenever the pump frequency is on resonance with a bright two-exciton state. Of course, this oversimplification cannot describe the real resonance strengths accurately - especially, when several resonances overlap into a band, as is the case between $\omega_p \simeq 24,000 - 25,500 \text{ cm}^{-1}$. Nevertheless, the resonance structure can be clearly explained by the presence of f -states with strong maximal dipole strength. This reaffirms our previous result that due to the large bandwidth of the individual photons in this

²⁵This dipole strength for the transition is reached when the f -state is excited by pulses with infinite bandwidth, such that each transition is driven with by a field with identical spectral density. For finite bandwidth, the dipole strength is instead determined by the overlap of the pulse bandwidth with each transition.

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Figure 4.20.: Two-photon induced fluorescence action spectrum (4.26), obtained from integrating out the dispersed frequency ω in Fig. 4.19 for entanglement times a) $T = 10$ fs, and b) $T = 100$ fs. The vertical lines indicate the positions of two-exciton states, and their height is taken proportional to $|\sum_e \mu_{ge}\mu_{ef}|^2$, as a measure of their maximally possible dipole strength.

regime all the possible excitation pathways may be accessed, thus rendering $|\sum_e \mu_{ge}\mu_{ef}|^2$ a good measure for the actual brightness of an f -state. One has to keep in mind, however, that the dipole strength is not the actual brightness in the fluorescence signal, since the dipole moments μ_{ef} connecting f - and e -manifold have to be counted twice (once for the excitation, once for the decay into the electromagnetic vacuum).

This analysis allows us to clearly interpret the structure of the two-dimensional plot in Fig. 4.19a): The two strong resonances at $22,000 \text{ cm}^{-1}$ correspond to decay channels of state $|f_{11}\rangle$, and the shoulder may be attributed to the decay of states $|f_{15}\rangle$ and $|f_{16}\rangle$ (compare tables B.2 and B.3 for the energies and dipole couplings). The higher-energy fluorescence band stems from states $|f_{23}\rangle - |f_{32}\rangle$, which are made up of two excitons from the higher-energy band in the absorption spectrum. Hence, they mostly fluoresce at $12,000 \text{ cm}^{-1}$.

Integrating out the pump frequency in Fig 4.21a), we can examine in greater detail at which frequencies the brightest $f \rightarrow e$ transitions fluoresce. For comparison, here we show the single-exciton frequencies as vertical lines, with their heights proportional to their dipole coupling $|\mu_{ge}|^2$ to the ground state [just like in the linear absorption spectrum in Fig. 4.6b)]. Comparing the fluorescence from the f -manifold with the transitions from the e -manifold gives us an idea on the anharmonicity of the involved transitions (*i.e.* their detuning of the $f \rightarrow e$ with respect to the $e \rightarrow g$ transition). Clearly, the strong $f \rightarrow e$ transitions in this regime are only weakly detuned from possible $e \rightarrow g$ transitions, since each resonance can be assigned to a single-exciton energy. This again reflects the weak coupling between the different chromophores underlying our present model (see section 4.4.1). In a potential sample with stronger interactions between the sites, resulting in the creation of delocalized excitonic states, the presence of a second excitation in the system should shift emitted fluorescence light spectrally, and thereby provide indirect information of excitonic delocalization [Pullerits96]. On the other hand,

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Figure 4.21.: Two-photon induced fluorescence marginal obtained from integrating out the pump frequency ω_p in Fig. 4.19, for the entanglement time a) $T = 10$ fs, and b) $T = 100$ fs. Vertical lines indicate the positions of single-exciton states, and their height is taken proportional to $|\mu_{ge}|^2$.

in a sample system, in which the eigenstates show weak spatial overlap (and hence, weak interactions), there will be weak spectral shifts - as is the case here.²⁶

So fluorescence from $f \rightarrow e$ and from $e \rightarrow f$ cannot be distinguished spectrally in this system. Nevertheless, as we have argued earlier in this section, the strong dependence of the TPIF signal on the pump frequency should, however, represent a possibility to experimentally distinguish the two signals.

The corresponding signal for $T = 100$ fs is shown in panels b) of Figs. 4.19 - 4.21, and may be interpreted analogously. Clearly, the fluorescence spectrum changes dramatically [see Fig. 4.19b): The resonances stemming from $|f_{11}\rangle$ disappear almost entirely, leaving only a very weak resonance at $\omega \simeq 10,000$ cm⁻¹, and the fluorescence band between $\omega_p \simeq 24,000$ and $26,000$ cm⁻¹ merges into one strong resonance at $\omega \simeq 12,200$ cm⁻¹, with a smaller side peak at $\omega_p \sim 23,500$ cm⁻¹ and $\omega = 12,000$ cm⁻¹. This can be seen in Fig. 4.21b), where - in comparison to panel a) - the signal at $10,200$ cm⁻¹ (*i.e.* at the energy of state $|f_{11}\rangle$) has almost disappeared. The corresponding resonance in the fluorescence action spectrum in Fig. 4.20b) at $\omega_p \simeq 22,000$ cm⁻¹ has similarly lost intensity. Clearly, in contrast to the previous case $T = 10$ fs, the indicated f -states on the horizontal axis of Fig. 4.20b) cannot explain the resonance structure at all: The previously strong resonances at $\omega_p \simeq 22,000$ cm⁻¹ (corresponding to the states $|f_{11}\rangle$ - $|f_{16}\rangle$) lose their intensity, and the resonance band between $\omega_p \simeq 24,000$ and $26,000$ cm⁻¹ evolved into a single pronounced peak at $\omega_p \simeq 24,500$ cm⁻¹. Furthermore, we observe one pronounced sidepeak at $\omega_p \sim 23,500$ cm⁻¹ [see Fig. 4.20b)]. The action spectrum in Fig. 4.20b) confirms that the peak cannot be directly attributed to a two-exciton state, since the peak lies in the center of the spectral gap between $\omega_p = 23,000$ and $24,000$ cm⁻¹ in which there are no f -states. In the following, we will argue how the change of the TPIF signal may be understood as a consequence of the two competing

²⁶Note, however, that there are also methods in conventional multidimensional spectroscopy, such as the DQC signal discussed in chapter 2 that are designed to detect these spectral shifts.

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mechanisms we already encountered in our discussion of the wavepackets: the change of photon bandwidth and the intermediate population transport.

The shrinking of the photon bandwidth with increasing entanglement time (see our discussion in section 4.3.1) closes excitation channels, in which the intermediate e -state is far detuned from the central photon frequency $\omega_p/2$. This can explain the loss of intensity of the resonances pertaining to states $|f_{11}\rangle - |f_{16}\rangle$ at $\omega_p \simeq 22,000 \text{ cm}^{-1}$. These states are two-exciton states with a strong contribution of the single exciton $|e_5\rangle$. As can be seen in the linear absorption spectrum in Fig. 4.6b), $|e_5\rangle$ has a substantially smaller energy ($\geq 1,000 \text{ cm}^{-1}$) compared to the excitons $|e_6\rangle - |e_{10}\rangle$, and f -states composed of $|e_5\rangle$ and one of the higher-energy states can only be excited via far-detuned single-photon transitions (in the case of *degenerate* entangled photons considered here). If we employed nondegenerate entangled photons, we could observe the opposite effect, in which the absorption band between $\omega_p \simeq 24,000$ and $26,000 \text{ cm}^{-1}$ is excited via off-resonant transitions, and therefore eliminated by a shrinking photon bandwidth.

The emergence of the new resonance at $\omega_p \sim 23,500 \text{ cm}^{-1}$ in Fig. 4.20b) cannot be explained by the change of the photon bandwidth. Due to energy conservation, the sum of the two photon frequencies is still centered around the pump frequency ω_p with the pump bandwidth $\sigma_p = 50 \text{ cm}^{-1}$. But the resonance is separated from any f -state resonance by $\sim 500 \text{ cm}^{-1}$. Hence, it must correspond to the excitation of lower-energy f -states, where energy ϵ_{lost} has been dissipated between the $g \rightarrow e$ and the $e \rightarrow f$ transition, such that we find the resonance at $\omega_f + \epsilon_{\text{lost}}$.

4.7. Summary

We have investigated the absorption of entangled photon pairs - first in a simple toy model, then in a more complex model describing the bacterial RC of *Blastochloris viridis* - and investigated the influence of the experimentally controllable parameters in the photons' wavefunctions. To investigate this influence in complex quantum systems, we simulated the excited state population distributions created by these entangled pairs. We derived expressions for both unitary evolution and open system dynamics.

In the first part, we showed that, in two-photon induced fluorescence measurements of a simple toy model, the entangled photon bandwidth as well as the mean photon number in the two beams can be traced back to distinct features in the signal: Both the central resonance of the signal and its linewidth vary with the control parameters. It was shown that even in the high intensity regime, when different entangled photon pairs overlap temporally, the coherent interaction of entangled pairs may dominate the signal. This finding could be of great importance for the practical implementation of quantum spectroscopy with entangled pairs, since it establishes that the strong time-frequency correlations of these pairs can be exploited even at much higher photon fluxes than previously believed [Lee06].

The second part of this chapter investigated the excited state population distributions in the bacterial RC created upon absorption of entangled pairs. It was shown that, even in the unitary case, the nonclassical bandwidth properties of entangled photons lead to

very different two-exciton state distributions than classical laser pulses. However, it could be shown that the same distributions may also be obtained using correlated separable states (*i.e.* mixed two-photon states in which the time-frequency entanglement has been replaced by a classical frequency distribution with entirely classical correlations). In other words, the selectivity is due to the frequency (anti-)correlations - and not to the entanglement. These excited state population distributions are however created by exploiting the quantum nature of the light in the sense that they cannot be reproduced one-to-one with classical light. It was shown at the beginning of this chapter (see section 4.1) that this can be interpreted as a consequence of the back-action of the matter system onto the electromagnetic field: In a classical description of the field, the state of the electromagnetic field itself is unaffected by the interaction with the sample system. In the case of a two-mode two-photon Fock states however, the absorption of one photon depletes the mode, such that the second interaction must stem from the correlated field. This is in stark contrast to the absorption of two classical, correlated light fields which are frequency-correlated, *e.g.* by anti-correlated chirping [Resch07]. After the first absorption, the second photon may stem from the same field, in which case it shows no correlations with the first absorption event [Schlawin13a]. Without additional post-processing such as phase cycling to suppress these uncorrelated two-photon absorption events [Resch07], these limit the degree of control over the excited f -state distribution.

The situation becomes even more involved when the system is coupled to an environment: The dynamics turn irreversible, and time correlations gain importance. It was shown that by tuning the entanglement time, the effect of intermediate population transfer (*i.e.* between the two absorption events) can be suppressed. The correlated separable state (4.48) does not show time correlations, and therefore dissipation destroys the impact of the frequency correlations. In this situation, time-energy entanglement (*i.e.* the nonseparability of the photonic wavefunction as described in section 2.2) *does* offer a clear advantage.

This advantage was traced back to the violation of the classical time-energy uncertainty: To gain control over the excited two-exciton distribution, one has to minimize the time between successive absorption events, and at the same time maximize the frequency resolution in the two-exciton manifold. For classical light, their product is fundamentally limited by the Fourier uncertainty. In the case of entangled photons, however, the two quantities can be varied independently, such that there is no lower bound for their combined time and energy resolution.

Finally, spectrally dispersed fluorescence signals created by the excited wavepackets have been simulated. This represents one possible measurement tool to probe the different population distributions that are created by the absorption of entangled photon pairs. It was shown that the resulting signals show clear signatures of the different contributions as well as of the photon bandwidth. The change of resonance line shapes with the entanglement time provides information on energy dissipation pathways.

5. Pump-probe measurements with entangled photons

Having understood the non-equilibrium dynamics induced by the absorption of entangled photon pairs in complex quantum systems, we now turn to the simulation of the corresponding absorption signals in measurements of the entangled fields. Just like in the preceding chapter, we will build up intuition step by step: Starting with simple toy models where we may distinguish resonant and off-resonant cases, we discuss the cancellation of harmonic signals (in which two-exciton states are simply given by the sum of single-exciton states) by destructive interference, and the enhancement of anharmonic peaks (in which two-excitons are shifted away from the sum of single excitons) by constructive interference which occurs both for quantum and classical fields. This will lead us to discuss the difference between signals induced by classical sources and by entangled photons, still at hand of a simple toy model. Finally, the chapter closes again with simulations of the bacterial RC, where we apply the results to be derived within this chapter to a realistic system.

5.1. Absorption signals

As mentioned several times in the previous sections, nonlinear absorption signals are subject to interference effects between different pathways that contribute to the signal. Just like in the previous chapter, we first illustrate this effect in a three-level system, which is depicted as a reminder in Fig. 5.1, where we again distinguish near-resonant and strongly off-resonant intermediate states. The system consists of a single ground state, an intermediate state at $11,000 \text{ cm}^{-1}$, and a doubly excited state at $21,500 \text{ cm}^{-1}$. For a near-harmonic system, we choose the dipole strength $\mu_{ef} = \sqrt{2}\mu_{ge}$.¹ Our signal is given by the time-integrated absorption signal, Eq. (3.37),

$$S_{\text{abs}}(\Gamma) = \frac{2}{\hbar} \int_{-\infty}^{\infty} dt \Im \langle E_+^\dagger(t) V_+(t) \rangle_{\text{final}}, \quad (5.1)$$

where, as usual, Γ denotes the set of control parameters of the fields, and we recall from chapter 3 that $\langle \dots \rangle_{\text{final}}$ refers to the expectation value with respect to the final density matrix (*i.e.* after the interaction with the excitation pulses). We further recall from our derivation of Eq. (3.37) that the obtained expression describes the change in the intensity

¹This may be understood as follows: Consider a harmonic oscillator as a simplification of the matter system, with eigenstates $|1\rangle, |2\rangle, \dots$. In this case, the negative-frequency component of the dipole operator V , see Eq. (3.7), acts like $V|n\rangle = \sqrt{n}|n-1\rangle$.

5. Pump-probe measurements with entangled photons

Figure 5.1.: The toy model consists of a three-level system, where the intermediate state is either close to resonance ($11,000 \text{ cm}^{-1}$), or far off-resonant ($17,000 \text{ cm}^{-1}$) with respect to single-photon transitions.

of the transmitted field. We may calculate this change by either evaluating processes, in which finally a photon is emitted ($\sim E^\dagger$) or absorbed ($\sim E$) from the sample (see the discussion on page 40), and here chose the former option.

The leading order in the matter-field interaction, *i.e.* the linear absorption signal, shall not be our concern here, as it can be separated experimentally [Fidder93] from the desired third-order signal. Expanding the signal (5.1) to third order in the interaction Hamiltonian (3.6), we recover the diagrams in the first line of Fig. 3.9. Using Eqs. (3.159), (3.165), (3.166), as well as (3.170) and (3.171), they are given by the frequency domain expressions,

$$S_{\text{abs, (I)}}(\omega; \Gamma) = \frac{2}{\hbar^4} \Im \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_{\text{sum}}}{2\pi} \int \frac{d\omega'_a}{2\pi} A(\omega_a) A(\omega_{\text{sum}} - \omega_a) A^*(\omega'_a) A^*(\omega_{\text{sum}} - \omega'_a) \frac{\mu_{ge}}{\omega_a - \omega_e + i\gamma_e} \frac{\mu_{ef}}{\omega_{\text{sum}} - \omega_f + i\gamma_f} \frac{\mu_{fe}}{\omega'_a - \omega_e - i\gamma_e} \mu_{eg}, \quad (5.2)$$

$$S_{\text{abs, (II)}}(\omega; \Gamma) = \frac{2}{\hbar^4} \Im \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_{\text{sum}}}{2\pi} \int \frac{d\omega'_a}{2\pi} A(\omega_a) A(\omega_{\text{sum}} - \omega_a) A^*(\omega'_a) A^*(\omega_{\text{sum}} - \omega'_a) \times \frac{\mu_{ge}}{\omega_a - \omega_e + i\gamma_e} \frac{\mu_{ef}}{\omega_{\text{sum}} - \omega_f + i\gamma_f} \frac{\mu_{fe}}{\omega_{\text{sum}} - \omega'_a - \omega_e + i\gamma_e} \mu_{eg}. \quad (5.3)$$

$$S_{\text{abs, (III)}}(\omega; \Gamma) = \frac{2}{\hbar^4} \Im \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_-}{2\pi} \int \frac{d\omega'_a}{2\pi} A(\omega_a) A(\omega'_a - \omega_-) A^*(\omega'_a) A^*(\omega_a - \omega_-) \times \frac{\mu_{ge}}{\omega_a - \omega_e + i\gamma_e} \frac{\mu_{eg}}{\omega_- - \omega_g - i\gamma_g} \frac{\mu_{ge}}{\omega'_a - \omega_e - i\gamma_e} \mu_{eg}, \quad (5.4)$$

$$S_{\text{abs, (IV)}}(\omega; \Gamma) = \frac{2}{\hbar^4} \Im \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_-}{2\pi} \int \frac{d\omega'_a}{2\pi} A(\omega_a) A(\omega'_a - \omega_-) A^*(\omega'_a) A^*(\omega_a - \omega_-) \times \frac{\mu_{ge}}{\omega_a - \omega_e + i\gamma_e} \frac{\mu_{eg}}{\omega_- - \omega_g + i\gamma_g} \frac{\mu_{ge}}{\omega'_a - \omega_e + i\gamma_e} \mu_{eg}, \quad (5.5)$$

where - instead of the infinitesimal complex factor $i\eta$ in section 3.6 - we added the finite

Figure 5.2.: a) Contributions of diagrams (Ia), Eq. (5.2), and (IIa), Eq. (5.3), to the third-order absorption signal. b) Contributions of diagrams (IIIa), Eq. (5.4) and (IVa), Eq. (5.5). c) Full third-order absorption signal, Eqs. (3.169) and (3.172). The simulations are carried out for the model system shown in Fig. 5.1. The diagrams representing the individual contributions are shown as insets in panels a) and b). The zero-signal line is indicated by the dashed, black line.

inverse lifetimes γ_g, γ_e , and γ_f , which account the broadening of the resonances,² and replace the quantum field correlation functions by classical field amplitudes $A(\omega)$.

As shown in section 3.6, Eqs. (5.2) - (5.5) may be written in terms of transition amplitudes to the ground state $|g\rangle$, Eq. (3.172), the single excited state $|e\rangle$, Eqs. (3.169) and (3.172), and the doubly excited state $|f\rangle$, Eq. (3.172). In the previous chapter 4, we investigated the two-photon induced fluorescence, which - as can be seen in Eq. (4.25) - is proportional to the time-integrated population in the doubly-excited state $|f\rangle$, which is simply the last of the named transition amplitudes. Hence, we may already conclude that this part of the third-order absorption signal contains the same information as our previously discussed TPIF signal, and that differences stem from transition amplitudes to $|g\rangle$ and $|e\rangle$. The discussion of the novel information content of the additional pathways will be the main goal of this chapter.

In Fig. 5.2, the third-order absorption signal induced by a classical excitation pulse (4.29) in the three-level toy model as introduced in Fig. 5.1 is depicted as a function of its center frequency ω_0 (at fixed bandwidth at $\sigma = 50 \text{ cm}^{-1}$), for a near-resonant intermediate state. Each state is broadened by a phenomenological inverse lifetime $\gamma_g = \gamma_e = \gamma_f = 200 \text{ cm}^{-1}$. The plots in each panel are normalized to their maximum value. The final signal in panel c) shows a double-peak structure, which is characteristic for the third-order spectrum of weakly anharmonic systems, see e.g. Refs. [Fidder93, Renger01]. A positive resonance at $\omega_0 = 11,000 \text{ cm}^{-1}$ results from the emission of a photon from the single exciton state, $|e\rangle \rightarrow |g\rangle$. As can be seen from panel b), these resonances stem from the Raman pathways, which in the language of pump-probe spectroscopy correspond to the ground state bleach and the excited state emission pathways [Mukamel00].³ The

²The ground state is subject to a lifetime, even though it cannot decay. This is justified, since a more careful analysis of the time evolution of the ground state in the presence of population decay reveals that its Green's function also obtains an effective width (see chapter 8 in Ref. [Mukamel99]).

³The identity is not perfect since the theory of pump-probe spectra is typically formulated in terms of

5. Pump-probe measurements with entangled photons

Figure 5.3.: Same as Fig. 5.2, for a strongly off-resonant intermediate state in Fig. 5.1, with $\omega_e = 17,000 \text{ cm}^{-1}$. a) Diagrams (Ia), Eq. (3.161), and (IIa), Eq. (3.163). b) Diagrams (IIIa) and (IVa), Eq. (3.172). c) full third-order absorption signal, Eqs. (3.169) and (3.172).

negative feature in panel c) at $\omega_0 = 10,750 \text{ cm}^{-1}$ (*i.e.* at $\omega_f/2$) stems from the two-photon absorption (TPA) pathways which are plotted separately in panel a). In pump-probe spectroscopy they are referred to as the excited state absorption contribution. Note that our signal has the opposite sign compared to the pump-probe spectra of Ref. [Fidder93], for instance. Experiments typically depict the so-called differential absorption, *i.e.* the change of absorption due to the excitation of the sample by the pump pulse, whereas we defined our signal as the change in detected intensity [Eq. (3.37)]. Hence, the excited state absorption reduces the number of photons in the light field, and therefore shows up as a *negative* peak, but of course, it increases the absorption, and therefore appears as a *positive* peak in a differential absorption experiment [see also our discussion of Eqs. (3.169) and (3.172)].

Clearly, the signal is created by partially destructive interference between the two TPA and Raman pathways, respectively, which are depicted in panels a) and b). The TPA pathways already cancel one another partially, whereas the two Raman pathways interfere constructively, thus creating the double-peak structure. If the f -state was found at exactly twice the single-exciton energy, $\omega_f = 2\omega_e$, the positive and the negative peaks would coincide, and cancel one another. Any residual signal would be due to the finite excited state lifetimes $\gamma_g^{-1}, \gamma_e^{-1}$ and γ_f^{-1} considered in the figures. We remark that this cancellation is exact for harmonic oscillators where it is a consequence of Wick's theorem [Wick50], and where nonlinear classical response functions of the form $\langle \mathcal{V}_+ \mathcal{V}_- \cdots \mathcal{V}_- \rangle$ identically vanish [Mukamel11]. Hence, the more anharmonic a system appears (*i.e.* the stronger f -states are detuned from sums of e -states), the less destructive this interference becomes, and the remainder is what constitutes the resulting signal in panel c).

The strongly anharmonic regime is simulated in Fig. 5.3, where the intermediate state was shifted to $17,000 \text{ cm}^{-1}$, off resonance from the single-photon transitions. Both TPA pathways now interfere constructively [panel a)], such that the f -state resonance at $21,500 \text{ cm}^{-1}$ may be observed in the final signal. The Raman pathways, shown

ladder diagrams, which can not be equated one-to-one to loop diagrams. We will however discuss fluorescence-based analogs of these signals in chapter 8.

in panel b), are far off-resonant from the intermediate state, and enter with opposite sign, thus canceling each other. Apart from the overall sign, the resulting signal in panel c) is identical to the TPIF signals discussed in the previous chapter, see e.g. Fig. 4.2. Therefore, in a regime where the intermediate single-photon transitions are off-resonant, it does not really matter whether one is collecting the fluorescence from the f -state, or measuring the transient absorption of a probe beam, from the point of view of the information content of the signal. This justifies *ex post* our somewhat loose, interchangeable use of the expressions two-photon absorption and two-photon induced fluorescence (see, e.g. chapter 2).

5.2. Pump-probe-like signals of model systems

Having understood the time-integrated signal, we now introduce a slightly more elaborate measurement setup, in which the signal is collected, and spectrally dispersed. The dispersed frequency gives us an additional dimension for the signal, which contains useful information on excitation pathways in a complex quantum system, as we will see in the following. We had derived the spectrally dispersed intensity signal in chapter 3, Eq. (3.43),

$$S_{PP}(\omega; \Gamma) = \frac{2}{\hbar} \Im \langle E_2^\dagger(\omega) V(\omega) \rangle_{\text{final}} \quad (5.6)$$

$$= \frac{2}{\hbar} \Im \int dt e^{i\omega t} \langle E_2^\dagger(\omega) V(t) \rangle_{\text{final}} \quad (5.7)$$

Here, we introduced the subscript 2 for the measured beam, to distinguish this field from other excitation pulses, which are not recorded. As mentioned in chapter 3 following Eq. (3.43), the spectrally dispersed signal contains different information as compared to the time-resolved signal (3.37). However, by integrating over the dispersed frequency, we recover Eq. (5.1), since

$$\int \frac{d\omega}{2\pi} \langle E^\dagger(\omega) V(\omega) \rangle = \int dt_1 \int dt_2 \int \frac{d\omega}{2\pi} e^{i\omega(t_1-t_2)} \langle E^\dagger(t_1) V(t_2) \rangle \quad (5.8)$$

$$= \int dt \langle E^\dagger(t) V(t) \rangle, \quad (5.9)$$

where we used the Fourier representation of the delta distribution $\int d\omega \exp(i\omega(t_1 - t_2))/2\pi = \delta(t_1 - t_2)$.

To start, we first discuss the single-photon absorption signal mediated by a photon from the entangled pair, and point out how this signal may be distinguished from the pump-probe-like nonlinear response. Said pump-probe signal will then be discussed in the remainder of this chapter.

5.2.1. Linear response

Our goal in this chapter remains, of course, the simulation of nonlinear absorption signals in weakly anharmonic systems, where two-exciton states are found near the sum of single-

5. Pump-probe measurements with entangled photons

exciton energies. Since - so far - nonlinear absorption signals of entangled photon beams have only been obtained in two-photon absorbing systems with strongly off-resonant intermediate states [Dayan05, Guzman10], where anharmonic oscillators are clearly no longer an adequate description of the system, we first need to discuss how such signals may be separated from the linear background in weakly anharmonic systems.

Expanding Eq. (5.7) to leading order in the interaction Hamiltonian (3.6), we obtain

$$S_{\text{PP}}(\omega; \Gamma) = \frac{2}{\hbar} \Im \left(-\frac{i}{\hbar} \right) \int dt \int_{t_0}^t d\tau e^{i\omega t} \langle E_2^\dagger(\omega) V(t) H_{\text{int},-}(\tau) \rangle \quad (5.10)$$

$$= \frac{2}{\hbar} \Im \left(-\frac{i}{\hbar} \right) \int dt \int_0^\infty ds e^{i\omega t} \langle V G(s) V^\dagger \rangle \langle E_2^\dagger(\omega) E_2(t-s) \rangle \quad (5.11)$$

$$= \frac{2}{\hbar^2} \langle E_2^\dagger(\omega) E_2(\omega) \rangle \sum_e \frac{|\mu_{ge}|^2}{(\omega - \omega_e)^2 + \gamma_e^2}. \quad (5.12)$$

In the second line, we have repeated the derivation of the linear absorption signal in section 3.6.1 leading to Eq. (3.146). Finally, in the second step, we have employed the sum-over-states expression (3.147), and used the frequency decomposition of the field operator $E_2(t-s) = \int d\omega' \exp(-i\omega'(t-s)) E_2(\omega') / (2\pi)$ to obtain Eq. (5.12).

Hence, the linear absorption signal consists of the product between the frequency domain linear response function (4.45) of the sample system and the frequency domain power spectrum of beam 2. Since this power spectrum is typically very broadband (compare, for instance, panel a) in Fig. 4.8), it can be assumed to be roughly constant over the extent of a molecular resonance. In other words, the structure of the frequency-dispersed linear absorption signal induced by entangled photons is determined by the matter correlation function $\langle V G(\omega) V^\dagger \rangle = \sum_e |\mu_{ge}|^2 / [(\omega - \omega_e)^2 + \gamma_e^2]$, and the signal is not influenced by the quantum correlations with the other beam.⁴ Due to the broad bandwidth of the two-point field correlation function, the linear signal remains almost constant when varying the pump frequency ω_p (compare, in contrast, the f -state distributions in Fig. 4.11b), which are created by classical light with similar bandwidth). By removing this constant background, it is possible to filter out the third-order contributions to the absorption signal, which were derived in section 3.6, and which are related to the four-point correlation function of the electric fields. As shown in the previous chapter 4, these four-point correlation functions show a distinct structure due to quantum correlations as a function of the pump frequency ω_p , and whose investigation is the main goal of this chapter. Another, more involved experimental setup to remove the linear background was proposed in Ref. [Raymer13]: By detecting beam 1 as well, one can discard events where this beam has not been absorbed, and thereby separate the desired third-order contribution. In the following, we will be concerned with the resulting signal.

⁴This was, of course, to be expected. The frequency resolution of the dispersed signal is determined by the linewidth of the resonances [Mukamel99], and the two-point correlation function of entangled photons can always be reproduced by classical light [Schlawin12].

Figure 5.4.: The pump-probe-like setup considered in this chapter: Entangled photon pairs are separated by a beam splitter, and both beams are directed onto the sample. The probe beam E_2 is spectrally dispersed, and its change in intensity is recorded.

5.2.2. The signal

Having investigated the linear response of a quantum system to entangled photons, we now turn to a nonlinear, pump-probe-like measurement setup, in which beam 1 acts as a pump, and the transmission of beam 2 probes the system. This means, of course, that we only consider events in which the photon from beam 1 interacts first with the sample. This will be reflected in the field correlation functions which we derive later in this section. In the present dissertation, we only consider degenerate downconversion, in which case the signal does not depend on whether we detect field 1 or field 2. We provide, however, general expressions for the signal which could also be applied to nondegenerate photon pairs.

In contrast to conventional pump-probe spectroscopy, where the time delay and the center frequency of the pump pulse are varied [Renger01], we will not sweep time delays, but rather vary the control parameters specific to entangled photons, *i.e.* the pump frequency ω_p and the entanglement time T . This approach will allow us to observe signatures of the excited state distributions that were discussed in chapter 4.

The expectation value in Eq. (5.7) is given by the diagrams (Ia)-(IVa) of Fig. 3.9, with the exception that the field operator pertaining to the final de-excitation of the matter system is evaluated at the detection frequency ω . Due to the time integration in the definition (5.7) of the signal, it is most convenient to evaluate the signal in the frequency domain. Hence, we can use the recipe given in section 3.5.4 to obtain the frequency domain expressions of the correlation function $\langle E_2^\dagger(\omega)V(t) \rangle_{\text{final}}$ in Eq. (5.7), and then carry out the time integrations, which yields an additional delta-function in

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Figure 5.5.: Level scheme of the model system employed in this section. The intermediate states in the e -manifold are chosen either close to resonance with respect to a single-photon transition (solid horizontal lines), or strongly off-resonant (dashed lines). Each state within the e -manifold is coupled to any other state in the neighboring electronic g - and f -manifolds with equal strength, where again (see also Fig. 5.1) we use $\mu_{ef} = \sqrt{2}\mu_{ge}$.

the involved frequencies. We finally obtain the TPA pathways

$$S_{\text{PP, (I)}}(\omega; \Gamma) = \frac{2}{\hbar^4} \Im \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_{\text{sum}}}{2\pi} \langle E^\dagger(\omega_{\text{sum}} - \omega) E_2^\dagger(\omega) E(\omega_{\text{sum}} - \omega_a) E(\omega_a) \rangle \\ \times \sum_{e, e', f} \frac{\mu_{ge}}{\omega_a - \omega_e + i\gamma_e} \frac{\mu_{ef}}{\omega_{\text{sum}} - \omega_f + i\gamma_f} \frac{\mu_{fe'}}{\omega_{\text{sum}} - \omega - \omega_{e'} - i\gamma_{e'}} \mu_{e'g}, \quad (5.13)$$

$$S_{\text{PP, (II)}}(\omega; \Gamma) = \frac{2}{\hbar^4} \Im \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_{\text{sum}}}{2\pi} \langle E_2^\dagger(\omega) E^\dagger(\omega_{\text{sum}} - \omega) E(\omega_{\text{sum}} - \omega_a) E(\omega_a) \rangle \\ \times \sum_{e, e', f} \frac{\mu_{ge}}{\omega_a - \omega_e + i\gamma_e} \frac{\mu_{ef}}{\omega_{\text{sum}} - \omega_f + i\gamma_f} \frac{\mu_{fe'}}{\omega - \omega_{e'} + i\gamma_{e'}} \mu_{e'g}. \quad (5.14)$$

The field correlation functions are evaluated (for the evaluation of field correlation functions, see section A.2), keeping in mind that the final interaction takes place with field 2,

$$\langle E^\dagger(\omega_{\text{sum}} - \omega) E_2^\dagger(\omega) E(\omega_{\text{sum}} - \omega_a) E(\omega_a) \rangle \\ = f_{12}(\omega_{\text{sum}} - \omega, \omega) [f_{12}^*(\omega_{\text{sum}} - \omega_a, \omega_a) + f_{21}^*(\omega_{\text{sum}} - \omega_a, \omega_a)], \quad (5.15)$$

and

$$\langle E_2^\dagger(\omega) E^\dagger(\omega_{\text{sum}} - \omega) E(\omega_{\text{sum}} - \omega_a) E(\omega_a) \rangle \quad (5.16)$$

$$= f_{12}(\omega, \omega_{\text{sum}} - \omega) [f_{12}^*(\omega_{\text{sum}} - \omega_a, \omega_a) + f_{21}^*(\omega_{\text{sum}} - \omega_a, \omega_a)], \quad (5.17)$$

where the field correlation functions are defined in Eqs. (A.38a) and (A.39). Note the asymmetry in the four-point correlation functions (5.15) and (5.17) between f_{12} and

5.2. Pump-probe-like signals of model systems

$f_{12}^* + f_{21}^*$, which reflects the fact that we only record the change in transmission in beam 2.

Similarly, the Raman pathways [diagrams (III) and (IV)] read

$$S_{\text{PP, (III)}}(\omega; \Gamma) = \frac{2}{\hbar^4} \Im \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \langle E^\dagger(\omega_a + \omega_b - \omega) E(\omega_b) E_2^\dagger(\omega) E(\omega_a) \rangle \\ \times \sum_{e, e', g'} \frac{\mu_{ge}}{\omega_a - \omega_e + i\gamma_e} \frac{\mu_{eg'}}{\omega_a - \omega - \omega_{g'} - i\gamma_g} \frac{\mu_{g'e'}}{\omega_a + \omega_b - \omega - \omega_{e'} - i\gamma_e} \mu_{e'g'}, \quad (5.18)$$

$$S_{\text{PP, (IV)}}(\omega; \Gamma) = \frac{2}{\hbar^4} \Im \int \frac{d\omega_a}{2\pi} \int \frac{d\omega_b}{2\pi} \langle E_2^\dagger(\omega) E(\omega_b) E^\dagger(\omega_a + \omega_b - \omega) E(\omega_a) \rangle \\ \times \sum_{e, e', g'} \frac{\mu_{ge}}{\omega_a - \omega_e + i\gamma_e} \frac{\mu_{eg'}}{\omega - \omega_b - \omega_{g'} + i\gamma_g} \frac{\mu_{g'e'}}{\omega - \omega_{e'} + i\gamma_e} \mu_{e'g'}. \quad (5.19)$$

In Eqs. (5.18) and (5.19), we have included a summation index g' running over several possible ground states. In the following, we will only consider unique ground states, but for general applications, this summation has to be taken into account.

Note also that, whereas the TPA pathways correspond to excitation pathways with normally ordered field correlation functions (and anti-normally-ordered matter correlation functions), which are given in Eq. (A.38a), the Raman pathways need to be treated separately. Using the formalism of appendix A, and restricting ourselves to weak intensities (*i.e.* $r_k \ll 1$) in which case we can neglect diagrams with four interactions with beam 2,⁵ we obtain for the field correlation function of Eq. (5.18) two contributions

$$\langle E^\dagger(\omega_a + \omega_b - \omega) E(\omega_b) E_2^\dagger(\omega) E(\omega_a) \rangle \\ = \langle E_1^\dagger(\omega_a + \omega_b - \omega) E_2(\omega_b) E_2^\dagger(\omega) E_1(\omega_a) \rangle \\ + \langle E_1^\dagger(\omega_a + \omega_b - \omega) E_1(\omega_b) E_2^\dagger(\omega) E_2(\omega_a) \rangle. \quad (5.20)$$

Using the input-output relations (A.19) and (A.20), as well as the decomposition of the field operators in terms of Schmidt modes (A.24) and (A.25), the first term in Eq. (5.20) evaluates to

$$\langle E_1^\dagger(\omega_a + \omega_b - \omega) E_2(\omega_b) E_2^\dagger(\omega) E_1(\omega_a) \rangle \\ = \sum_{k, k', k'', k'''} \psi_k(\omega_a + \omega_b - \omega) \phi_{k'}^*(\omega_b) \phi_{k''}(\omega) \psi_{k'''}^*(\omega_a) \\ \times \langle 0 | \left(\cosh(r_k) A_k^\dagger + \sinh(r_k) B_k \right) \left(\cosh(r_{k'}) B_{k'} + \sinh(r_{k'}) A_{k'}^\dagger \right) \\ \times \left(\cosh(r_{k''}) B_{k''}^\dagger + \sinh(r_{k''}) A_{k''} \right) \left(\cosh(r_{k'''}) A_{k'''} + \sinh(r_{k'''}) B_{k'''}^\dagger \right) | 0 \rangle \quad (5.21)$$

$$= f_{12}(\omega_a + \omega_b - \omega, \omega) f_{12}^*(\omega_a, \omega_b) + g_1(\omega_a + \omega_b - \omega, \omega_a) \sum_k \cosh^2(r_k) \phi_k^*(\omega_b) \phi_k(\omega), \quad (5.22)$$

⁵Four interactions with beam 2 can only stem from events in which two photons are present in each field (see section 4.3.2), and not from a two-photon state.

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and, after an identical calculation for the second term, we obtain

$$\begin{aligned} & \langle E^\dagger(\omega_a + \omega_b - \omega) E(\omega_b) E_2^\dagger(\omega) E(\omega_a) \rangle \\ &= f_{12}(\omega_a + \omega_b - \omega, \omega) (f_{12}^*(\omega_a, \omega_b) + f_{21}^*(\omega_a, \omega_b)) \\ &+ g_1(\omega_a + \omega_b - \omega, \omega_a) \sum_k \cosh^2(r_k) \phi_k^*(\omega_b) \phi_k(\omega). \end{aligned} \quad (5.23)$$

The second line in the above equation corresponds to the normally ordered contribution, but the last line contains terms which correlate the two fields separately. To leading order in r_k , we have $\cosh^2(r_k) = 1 - 2r_k^2 + \dots$. Hence, we obtain

$$\sum_k \cosh^2(r_k) \phi_k^*(\omega_b) \phi_k(\omega) \approx \delta(\omega - \omega_b) + \mathcal{O}(r_k^2), \quad (5.24)$$

where we used the orthonormality of the Schmidt modes $\{\phi_k\}$. This means that this leading-order contribution corresponds to the field commutator $[E_2(\omega_b), E_2^\dagger(\omega)] = \delta(\omega - \omega_b)$.

With the experience from our derivation of the signal in chapter 2, we can also find a clear interpretation of this term: Whereas the normally-ordered correlation functions correspond to *stimulated* interactions between the fields, the second line of Eq. (5.23) describes the fluorescence signal as derived in Eq. (3.57). Beam 1 excites an electronic state, which then decays into field 2. The corresponding four-point correlation function has the same leading-order dependence on the pump intensity as the normally-ordered correlation functions. Hence this contribution needs to be taken into account as well.⁶ Similarly, we obtain for Eq. (5.19)

$$\begin{aligned} & \langle E_2^\dagger(\omega) E(\omega_b) E^\dagger(\omega_a + \omega_b - \omega) E(\omega_a) \rangle \\ &= f_{12}(\omega, \omega_a + \omega_b - \omega) [f_{12}(\omega_a, \omega_b) + f_{21}(\omega_a, \omega_b)] \\ &+ g_2(\omega, \omega_a) \delta(\omega - \omega_a). \end{aligned} \quad (5.25)$$

In contrast to Eq. (5.23), here the third line features a commutator of field 1, *i.e.* $[E_1(\omega_b), E_1^\dagger(\omega_a + \omega_b - \omega)]$, and does not correspond to a fluorescence signal. Instead, it may be interpreted as the leading-order QED correction to the linear absorption signal (5.12), where a virtual photon is emitted into field 1 and reabsorbed between the two interactions with beam 2 [Buhmann07]. The slowly varying envelope approximation may become problematic in this regime, since, in principle, one has to take quantum fluctuations at *any* frequency into account - and not only near a center frequency. For the simulations of our signals, we use our present model as a first indicator for the strength of the effect here, assuming that these commutator contributions are only appreciable near the (narrow) sample resonances, such that the slowly varying envelope approximation can still yield a valid result.

⁶Note that this necessity is brought about by the low light intensities we work with. In the third-order signals induced by laser pulses containing a macroscopic number of photons, in Figs. 5.2 and 5.3, stimulated interactions are dominant, and the spontaneous decay may be safely neglected.

5.2. Pump-probe-like signals of model systems

Figure 5.6.: a) Contribution of diagram (I), Eq. (5.13), for the model system depicted in Fig. 5.5, with off-resonant intermediate states. b) Same for diagram (II), Eq. (5.14). c) Pump-probe signal with off-resonant intermediate states: sum of all four contributions, Eqs. (5.13)-(5.19). The simulations are obtained for entangled photon pairs with pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$, and entanglement time $T = 10 \text{ fs}$. All figures are normalized with respect to their maximum value, and the minimum has been set to zero. The signal strength is quantified by the color code on the right.

In the following, we first simulate the four diagrams (5.13) - (5.19) using the level scheme of Fig. 5.5, with two states in the intermediate e -manifold, and two more states in the f -manifold. Each state is connected to all the states in adjacent manifolds with identical dipole strengths. To account for the bosonic character of excitons in molecular aggregates, as described, e.g., by the Frenkel exciton model [Frenkel31], we further take $\mu_{ef} = \sqrt{2}\mu_{ge}$ (see footnote 1 at the beginning of this chapter). Hence, this model allows us to explore harmonic ($0 \rightarrow 10,000 \rightarrow 20,000 \text{ cm}^{-1}$), near-harmonic ($0 \rightarrow 11,000 \rightarrow 21,500 \text{ cm}^{-1}$), and strongly anharmonic transition ladders (e.g. $0 \rightarrow 11,000 \rightarrow 20,000 \text{ cm}^{-1}$). Again, each state is broadened by a lifetime $\gamma_g = \gamma_e = \gamma_f = 200 \text{ cm}^{-1}$.⁷

5.2.3. Off-resonant intermediate states

We start our discussion with the simpler case: As we have seen from the comparison of Figs. 5.2 and 5.3, the system with off-resonant intermediate states is simpler to analyze. Since the $g - e$ transitions are far off-resonant, the Raman pathways should not yield a significant contribution in comparison to the TPA pathways. This is demonstrated numerically in Fig. 5.6, where we simulate the frequency-dispersed signal of the model system in Fig. 5.5, with off-resonant e -manifold. The central pump frequency ω_p is varied to sweep through the positions of the two f -states, and the detected frequency ω is varied to cover the bandwidth of beam 2. Panel a) only shows the contribution of diagram (I), panel b) that of diagram (II), and panel c) the sum of all four diagrams (I) - (IV) in Fig. 3.9. Clearly, diagrams (I) and (II) are sufficient to determine the structure

⁷See footnote 2 for the broadening of the ground state.

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Figure 5.7.: a) Contribution of diagram (I), Eq. (5.13), for the model system depicted in Fig. 5.5, with near-resonant intermediate states. b) Same for diagram (II), Eq. (5.14). c) Sum of both contributions. The simulations are obtained for entangled photon pairs with pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$, and entanglement time $T = 10 \text{ fs}$. All figures are normalized with respect to their maximum value, and the minimum has been set to zero. The signal strength is quantified by the color code as defined by the legend on the right. The vertical black lines indicate the positions of the single exciton resonances ω_e , and the horizontal line those of the two-exciton states ω_f .

of the final signal, thus validating our initial guess on the negligibility of Raman signals with off-resonant intermediate states.

Along the dispersed frequency, we observe elongated resonances pertaining to the broad bandwidth of the photon wavepackets. Small shifts of the maxima of the two resonances along the horizontal axis reveal that the f -states are excited by degenerate entangled photons: Hence, the maxima of the two broad resonances are found at roughly $\omega = \omega_f/2$ (*i.e.*, at $\omega = 10,000 \text{ cm}^{-1}$ for $|f_1\rangle$, and at $\omega = 10,750 \text{ cm}^{-1}$ for $|f_2\rangle$). Due to time-frequency entanglement, the resonances appear much sharper along the ω_p -axis. Here, the width of the resonance is given by the natural linewidth γ_e of the state, together with the (small) broadening due to the finite pump bandwidth σ_p .

5.2.4. Resonant intermediate states

We now simulate pump-probe signals with near-resonant intermediate states. In this situation, the transitions in the Raman pathways need to be taken into account as well. To simplify our discussion, and since this chapter is meant to provide proof-of-principle simulations, we first discuss TPA and Raman pathways separately. At the end of this section, we will then present their sum.

TPA pathways

Fig. 5.7 shows the TPA contributions, Eqs. (5.13) and (5.14), vs. central pump frequency ω_p and detected frequency ω . To guide the eye, we have indicated the position

5.2. Pump-probe-like signals of model systems

of the e -states along the ω -axis, and those of the f -states along the ω_p -axis. The signal is created by entangled photon pairs with entanglement time $T = 10$ fs, and pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$ [same as in Fig. 4.8a)]. Panel a) shows the contribution of diagram (I), it features three negative resonances (with respect to the off-resonant constant value) in the depicted frequency range: one at $\omega_p = 20,000 \text{ cm}^{-1}$, and two at $21,500 \text{ cm}^{-1}$. Similarly, the contribution of diagram (II) in panel b) shows four positive resonances (again with respect to the off-resonant constant value), two each at $20,000 \text{ cm}^{-1}$ and $21,500 \text{ cm}^{-1}$. Note that each of the resonances appears along the detected-frequency (horizontal) axis at the position of its intermediate state (hence the $g \rightarrow e$ transition) in panel b), whereas it appears at the position of the $e \rightarrow f$ transition in panel a). For instance, state $|f_1\rangle$ at $20,000 \text{ cm}^{-1}$ can be excited either through a harmonic transition via $|e_1\rangle$ at $10,000 \text{ cm}^{-1}$, or anharmonically via $|e_2\rangle$ at $11,000 \text{ cm}^{-1}$. Consequently, we observe the two resonances at $10,000$ and $11,000 \text{ cm}^{-1}$ in panel b). Panel a) can only show the corresponding $|e_1\rangle \rightarrow |f_1\rangle$ transition at $11,000 \text{ cm}^{-1}$, and shoulders of the anharmonic $|e_2\rangle \rightarrow |f_1\rangle$ transition at $9,000 \text{ cm}^{-1}$ can be observed at the left edge of the plot. Analogously, the resonances at $10,500 \text{ cm}^{-1}$ and at $11,500 \text{ cm}^{-1}$ indicate the two transitions $|e_2\rangle \rightarrow |f_2\rangle$ and $|e_1\rangle \rightarrow |f_2\rangle$.

As can be seen in the sum of the two diagrams [panel c)], the harmonic transitions interfere destructively, such that in the sum the peak at $(10,000; 20,000)$ is completely suppressed. The remaining signal in the vicinity stems from our use of phenomenological lifetimes γ_e^{-1} in the simulations, which relaxes the conservation of probability, and thereby amends the completely destructive interference of the diagrams. The anharmonic transitions do not experience such a destructive interference since the $e \rightarrow f$ transitions are shifted with respect to the $g \rightarrow e$ transitions: The resonance at $\omega = 11,000 \text{ cm}^{-1}$ and $\omega_p = 21,500 \text{ cm}^{-1}$ has no counterpart in diagram a), and may be clearly resolved in the final signal. Similarly, four resonances along $21,500 \text{ cm}^{-1}$ can all be resolved in the sum. The $g \rightarrow e$ transitions appear as positive, and the $e \rightarrow f$ as negative resonances. This can be understood in terms of the decomposition in transition amplitudes as derived in section 3.6: Diagram (I) (time-integrated) corresponds to the transition amplitudes $\langle |T_{fg}|^2 \rangle$, where both photons need to be absorbed to create the signal. Hence, it reduces the number of photons in beam 2, *i.e.* yields a negative change of the photon count rate. Similarly, diagram (II) was shown to represent $\Re \langle T_{eg}^{(1)\dagger} T_{eg}^{(3)} \rangle$, where $T^{(3)}$ contains a photon emission at the end, which can increase the photon number in beam 2, and thus add positive resonances to the signal.

When decreasing the bandwidth of the photon wavepackets, the anharmonic transitions become inaccessible. In Fig. 5.8, we depict the TPA pathways of entangled photons with an entanglement time $T = 100$ fs [same as in Fig. 4.8b)], where the photon bandwidth is comparable to the pump bandwidth. Due to this smaller bandwidth, transitions such as $|e_2\rangle \rightarrow |f_1\rangle$ can no longer be accessed. For instance, along $\omega_p = 20,000 \text{ cm}^{-1}$, only the harmonic transition remains. The width of the resonance along the ω -axis is greatly reduced [see panels a) and b)] compared to the previous, strongly entangled case of Fig. 5.7. This is reasonable since, in both plots, the resonances are created by their natural linewidth convoluted with the bandwidth of the exciting photon wavepacket.

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Figure 5.8.: a) Contribution of diagram (I), Eq. (5.13), for the model system depicted in Fig. 5.5 with near-resonant intermediate states. b) The same for diagram (II), Eq. (5.14). c) Sum of the two contributions. The simulations are obtained for entangled photon pairs with pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$, and entanglement time $T = 100 \text{ fs}$ (In contrast, Fig. 5.7 was obtained for $T = 10 \text{ fs}$, but otherwise identical parameters). All figures are normalized with respect to their maximum value, and the minimum has been set to zero. The signal strength is quantified by the color code as defined by the legend on the right. The vertical black lines indicate the positions of the single exciton resonances ω_e , and the horizontal line those of the two-exciton states ω_f (see Fig. 5.5).

Still, the final resonance at $\omega_p = 20,000 \text{ cm}^{-1}$ in panel c) looks very similar to the one shown previously in Fig. 5.8c), except that it has gained strength relative to the other (anharmonic) resonances.

In the following, we will restrict our attention to the short entanglement time $T = 10 \text{ fs}$, where the signal shows a richer structure.

Raman pathways

The Raman pathways [diagrams (III) and (IV), Eqs. (5.18) and (5.19)], which also contribute to the full third-order intensity signal, are depicted in Fig. 5.9. Panels a) - c) show the contributions of diagrams (III), (IV), and of the associated commutator contributions, respectively, and panel d) depicts their sum. Diagram (IV) as well as the commutator contributions (5.23) and (5.25) create elongated peaks along ω_p which are found at both single-exciton resonances along the dispersed frequency, *i.e.* at $\omega = 10,000$ and $11,000 \text{ cm}^{-1}$. This may be easily rationalized since the single-exciton resonances are covered by the broad bandwidth of the entangled photons for almost any pump frequency. The width of the resonance along the dispersed frequency axis is given by the phenomenological lifetime γ_e^{-1} . The more surprising feature are the well-defined resonances in panel a). With regard to Eq. (5.18), they are caused by the resonance $1/(\omega_a + \omega_b - \omega - \omega_{e'} - i\gamma_e)$, which creates resonances along the narrow line defined by $\omega_p - \omega = \omega_{e'}$, with a width given by the narrow pump bandwidth σ_p (since $\sigma_p < \gamma_e$).

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Figure 5.9.: a) Contribution of diagram (III), Eq. (5.18), for the model system depicted in Fig. 5.5 with near-resonant intermediate states. b) Same for diagram (IV), Eq. (5.19). c) Commutator contributions (5.23) and (5.25) to Eqs. (5.18) and (5.19). d) Total signal given by the sum of panels a) - c). The simulations are obtained for entangled photon pairs with pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$, and entanglement time $T = 10 \text{ fs}$. All figures are normalized with respect to their maximum value, and the minimum has been set to zero. The signal strength is quantified by the color code as defined by the legend on the right.

Along these lines, the resonant signal is further enhanced when the other single-exciton resonance, defined by $1/(\omega_a - \omega_e + i\gamma_e)$ is on resonance as well. This is the case at $\omega_p = 20,000, 21,000$, and $22,000 \text{ cm}^{-1}$. But just like in the case of the other diagrams, these latter resonances are washed out due to the broad bandwidth of the entangled photons, yielding elongated peaks along $\omega_p - \omega = \omega_{e'}$.

Not very surprisingly, the well-defined resonances dominate the sum of the Raman signals in panel d).

Full signal

Fig. 5.10 finally shows the full frequency-dispersed absorption signal induced by entangled photons with an entanglement time $T = 10 \text{ fs}$ and a pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$. With our previous results, it is straightforward to assign the peaks to the dif-

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Figure 5.10.: Sum of TPA (Fig. (5.7)) and Raman pathways (Fig. 5.9) depicted vs. the pump frequency ω_p and the dispersed frequency ω . The simulations are obtained for entangled photon pairs with pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$, and entanglement time $T = 10 \text{ fs}$. All figures are normalized with respect to their maximum value, and the minimum has been set to zero. The signal strength is quantified by the color code as defined by the legend on the right

ferent diagrams. The resonance band at the anharmonic f_2 -state at $\omega_p = 21,500 \text{ cm}^{-1}$ [compare Fig. 5.7c)] has merged with the Raman resonances at 21,000 and 22,000 cm^{-1} . The negative resonance at $\omega = 10,500 \text{ cm}^{-1}$ in Fig. 5.7c) is overshadowed by Raman contributions, but its more anharmonic counterpart at 11,500 cm^{-1} is still clearly visible. Another strongly anharmonic transition at $\omega_p = 21,000 \text{ cm}^{-1}$ and $\omega = 11,000 \text{ cm}^{-1}$ can be clearly identified.

5.2.5. Comparison: Classical laser pulses

It is hard to say how the quantum correlations shared by entangled photons exactly influence the pump-probe signal by simply looking at the simulated signal in Fig. 5.10. Therefore, we now simulate the corresponding signals induced by classical pulses with Gaussian envelope,

$$E(\omega) = \frac{1}{\pi^{1/4}\sqrt{\sigma}} e^{-(\omega-\omega_0)^2/2\sigma^2}. \quad (5.26)$$

The results are shown in Fig. 5.11. To ease the comparison with the previous simulations, we depict the signals vs. twice the central frequency $2 \times \omega_0$ (*i.e.* similar to the pump frequency ω_p) and the dispersed frequency ω .

Panels a)-c) show the TPA (a), the Raman contributions (b) as well as the final signal (c), respectively, created by classical pulses with a bandwidth $\sigma = 1,000 \text{ cm}^{-1}$, *i.e.* a very similar bandwidth as the entangled photon wavepackets in Fig. 5.10. Not very surprisingly, due to the lack of frequency correlations within the classical light, the resonances are broadened a lot along the $2 \times \omega_0$ -axis, as compared to the entangled photon

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Figure 5.11.: Top row: Frequency-dispersed pump-probe spectra of a classical pulse (5.26) with bandwidth $\sigma = 1,000 \text{ cm}^{-1}$. a) TPA contributions. b) Raman contributions. c) Sum. Bottom row: Same, with a bandwidth $\sigma = 100 \text{ cm}^{-1}$.

signal, where the frequency resolution is determined by the narrow pump bandwidth σ_p . That is why we further simulate the signals of narrowband classical pulses with $\sigma = 100 \text{ cm}^{-1}$ in panels d)-f). And, indeed, the TPA contribution in panel d) looks fairly similar to the weakly entangled photon signal in Fig. 5.8, in agreement with our discussion of the wavepacket excitation mechanism in chapter 4: Since the bandwidth of entangled photons with $T = 100 \text{ fs}$ is comparable to the width σ_p of the pump pulse, the induced two-exciton population distribution was found to be similar to a “classical” distribution.

Furthermore, however, the final signals in panels c) and f) are clearly dominated by the Raman contributions, and the TPA pathways only affect the tails of the resonances. In panel c), they lead to slightly stronger negative contributions at $\omega \approx 11,500 \text{ cm}^{-1}$ compared to panel b), and in panel f), they create a negative feature at $2 \times \omega_0 \leq 19,500 \text{ cm}^{-1}$. In stark contrast to this, the TPA pathways have a much stronger influence on the entangled photon signal in Fig. 5.10. This can be understood with regards to the loop diagrams: Due to the structure of the four-point field correlation function of two-photon states [see Eq. (4.34)],

$$\langle E^\dagger E^\dagger E E \rangle = \langle \psi | E^\dagger E^\dagger | 0 \rangle \langle 0 | E E | \psi \rangle, \quad (5.27)$$

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Figure 5.12.: Pump-probe signals of downconverted beams including their incoherent contributions for a) mean photon number $\bar{n} = 2.5$ (corresponding to a pump amplitude, Eq. (A.6), $\alpha/\hbar = 0.005$), b) $\bar{n} = 12.5$ ($\alpha/\hbar = 0.01$), and c) $\bar{n} = 2.1 \times 10^{19}$ ($\alpha/\hbar = 0.05$). The mean photon number is evaluated according to Eq. (4.43).

the two absorption events in Eqs. (5.13)-(5.19) are strongly correlated, while they exhibit no correlations with the emission events (and vice versa). In the TPA diagrams, this structure of the field correlation function leads to a factorization of the entire signal into strongly correlated two-photon transition amplitudes. However, the correlations in the Raman pathways are convoluted between all four interactions. The consequence can be best understood in the time domain: For instance, in diagram (IV), the first and the third, as well as the second and fourth interactions are correlated, meaning they have to take place within the entanglement time T . Therefore, the four-interaction process has to take place within less than twice the entanglement time. For the TPA diagrams, there is no such restriction, and the signals can be created by interaction during the entire time span allowed by the pump pulse duration $\sim 1/\sigma_p$. Similar findings have been reported in Ref. [Roslyak09a] for the investigation of the pump-probe signal induced by a single-mode squeezed state.

5.2.6. Intensity crossover

To obtain nonlinear signals with the best possible signal-to-noise ratio, it is of course desirable to maximize the photon count rate. However, as we have seen in section 4.3.2, this may have the undesirable effect of uncorrelated two-photon events. Therefore, we finally investigate the dependence of the pump-probe signal of the downconverted beams on the photon number to assess the influence of these uncorrelated events. We have already examined this dependence in the TPIF signal in Figs. 4.4 and 4.5, where we recall that, with increasing intensity, incoherent autocorrelation contributions from each of the two beams need to be taken into account, which are given by Eqs. (A.38b) and (A.38c).

Fig. 5.12 shows the third-order absorption signal for different mean photon numbers in each of the two beams. When the photon number is very small [panel a)], the signal

looks identical to the one created by the two-photon state in Fig. 5.10, and the incoherent contributions may be safely neglected. When the photon number increases in panel b), the TPA resonances at $\omega_p = 21,500 \text{ cm}^{-1}$ as well as at $20,000 \text{ cm}^{-1}$ (at $\omega = 11,000 \text{ cm}^{-1}$) loose intensity. Furthermore, the Raman resonances increase in their width along the ω_p -axis, indicating their origin from uncorrelated photon pairs, which do not show frequency correlations, and are therefore broadened according to the photon bandwidth. At very large photon numbers in panel c), the Raman resonances clearly dominate the signal, such that it looks similar to the classical signal in Fig. 5.11c).⁸ Hence, the nonclassical features of the entangled photons are diminished once different photon pairs overlap temporally, just as one might expect intuitively: Uncorrelated interaction events become more likely, and since they share no correlations, the created signals look very similar to those created by broadband, classical pulses. We recall from our discussion of the intensity crossover of the TPIF signal in section 4.3.2 that the crossover between the regime dominated by correlated events, and the “classical” regime only takes place at fairly high photon numbers. Hence, we have to use very high intensities to obtain the signal in panel d), where the correlated events can no longer be observed.

5.3. Pump-probe signals of the bacterial reaction center

Equipped with our results from the simple model system, we now turn towards simulations of our model for the bacterial RC (appendix B). We only discuss the entanglement time $T = 10 \text{ fs}$ at a pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$. As we have seen in the preceding section, this is the more interesting regime for the considered pump-probe signal, since the broad bandwidth that goes in hand with the strong time-energy entanglement in this parameter regime allows to explore all possible excitation pathways, while the narrow pump bandwidth allows for the selective excitation of specific two-exciton states. Furthermore, we have seen in chapter 4 that a short entanglement time suppresses population transport in the intermediate single-exciton manifold (see Fig. 4.14). Thus, the current treatment based on loop diagrams may be used to simulate realistic spectra - even in the presence of complicated environmental couplings.

Fig. 5.13 shows the TPA pathways of the RC in a similar fashion as for the model system studied before: Panel a) depicts the contribution of diagram (I), panel b) that of diagram (II), and panel c) depicts their sum [recall Eqs. (5.13) - (5.19)]. The contribution of diagram (I) has a very similar resonance structure as encountered in the two-photon induced fluorescence spectra in chapter 4 [see Fig. 4.19a)]: Two strong resonances at $\omega_p \approx 22,100 \text{ cm}^{-1}$, one at $\omega = 10,000 \text{ cm}^{-1}$, and one broad resonance around $12,000 \text{ cm}^{-1}$, as well as another resonance band between $\omega_p = 24,000$ and $26,000 \text{ cm}^{-1}$. This should come as no surprise to us, since we have seen in our previous discussion that diagram (I) reveals the $e \leftrightarrow f$ transition along its dispersed frequency axis ω . Hence, we should

⁸The smaller width of the resonances along the ω_p -axis compared to the classical signal in Fig. 5.11c) may be attributed to the intensity-dependent bandwidth of the beams (see our discussion in section 4.3.2).

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Figure 5.13.: a) Contribution of diagram (I), Eq. (5.13), for the model of the bacterial RC (appendic B). b) The same for diagram (II), Eq. (5.14). c) Sum of the two contributions. The simulations are obtained for entangled photon pairs with pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$, and entanglement time $T = 10 \text{ fs}$. All figures are normalized with respect to their maximum value, and the minimum has been set to zero. The signal strength is quantified by the color code on the right.

expect it to look similar to the TPIF signal of chapter 4.⁹ The contribution of diagram (II) in panel b), on the other hand, reveals $g \leftrightarrow e$ transitions along its ω -axis. At first glance, we observe the same three strong resonances of panel a), and - just like in our previous discussion of the toy model - they appear with opposite sign. However, some of them are slightly shifted in frequency due to the weak anharmonicity of the $e \leftrightarrow f$ transitions. This is most obvious in the relative shift of the resonances in the vicinity of $\omega \approx 12,000 \text{ cm}^{-1}$: The strong negative resonance at $\omega_p = 22,000 \text{ cm}^{-1}$ in panel a) faces a moderately strong positive resonance in panel b), which is shifted to higher values of ω . Their sum therefore yields a negative resonance in panel c). Due to the partially destructive interference between the two TPA pathways, its maximum is shifted away from the original maximum position. Similarly, the resonance band between $\omega_p = 24,000$ and $25,000 \text{ cm}^{-1}$ stretches almost to $\omega = 13,000 \text{ cm}^{-1}$, whereas it is confined to a rather narrow resonance line in panel b). Their sum therefore yields negative resonances between $\omega = 12,000$ and $13,000 \text{ cm}^{-1}$ in panel c), as well as a weak, positive shoulder at $\omega_p \geq 25,000 \text{ cm}^{-1}$.

The Raman transitions are more straightforward to interpret due to their constructive interference, as we have seen in the previous section. Therefore, we only show the sum of the Raman pathways in Fig. 5.14a). Just like the individual TPA pathways, the Raman contribution features three strong resonances: two at $\omega_p \approx 22,100 \text{ cm}^{-1}$, and one band between $24,000$ and $25,000 \text{ cm}^{-1}$. This is consistent with our finding in the

⁹We reiterate that Fig. 5.13 was calculated using loop diagrams (see Fig. 3.9), whereas the TPIF signal was calculated with ladder diagrams (see Fig. 4.13), taking into account environment-induced population transport. The similarity between the two signals reaffirms our initial claim that transport may be neglected in the current parameter regime.

Figure 5.14.: a) Contribution of the Raman pathways, Eqs. (5.18) and (5.19), for the model of the bacterial RC (appendix B). b) The total signal. The simulations are obtained for entangled photon pairs with pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$, and entanglement time $T = 10 \text{ fs}$. All figures are normalized with respect to panel b), and the minimum has been shifted to zero. The color code is indicated by the legend on the right.

simulation of the TPIF signal in chapter 4 that the brightest $e \leftrightarrow f$ transitions in the bacterial RC only show very weak anharmonicities. Since the TPA pathways cancel each other on resonance, the broad Raman resonances clearly dominate the final signal in panel b). However, since they are summed up with the TPA pathways, their flanks are considerably reduced. Some negative features stemming from the more anharmonic transitions at $\omega_p = 22,000 \text{ cm}^{-1}$ can still be identified.

5.4. Summary

We have investigated the frequency-dispersed absorption signal induced by entangled photons, and compared it to similar classical signals.

The frequency correlations that were discussed elusively in chapter 4 are clearly observed in the third-order absorption signals as well: A narrow pump pulse envelope can be employed to selectively probe specific two-exciton states, while the broad bandwidth of individual photons can access even far off-resonant intermediate transitions. By spectrally dispersing the transmitted intensity, it is possible to reveal frequency differences between the $g \leftrightarrow e$ and the $e \leftrightarrow f$ transitions.

In contrast to the fluorescence signals discussed in the previous chapters, the interpretation of third-order absorption signals is complicated by the interference between two-photon absorption (TPA) and Raman pathways. It was shown that, due to the peculiar structure of the entangled-photon four-point correlation function governing the signals, the impact of TPA pathways onto the total signal is much stronger than in comparable signals with classical light. While in the latter case the Raman pathways strongly dominate the signals, and overshadow weakly anharmonic two-exciton resonances, TPA pathways can be clearly identified in the entangled-photon signal. This

5. *Pump-probe measurements with entangled photons*

finding may represent a clear advantage of entangled photon spectroscopy, even in the absence of population transport, as was discussed in chapter 4.

When the intensity of the pump pulse creating the entangled photons increases (that is to say: when the number of photons in each field increases), the features of quantum correlations are washed out, and a signal very similar to a classical counterpart is obtained. Uncorrelated photon pairs create signals in which each photon pair interacts with its own bandwidth (as opposed to the two-photon amplitude in correlated interactions), such that the signal looks very similar to a classical signal with broadband pulses.

Finally, simulations of the absorption signal in the bacterial RC were presented. The brightest transitions in this system are only weakly anharmonic, such that it is hard to identify clear signatures of TPA pathways. However, it could be shown that these are in fact responsible for some distinct negative features in the vicinity of the dominant resonances.

6. Interferometric setups

In the previous chapters, we simulated nonlinear spectroscopic signals induced by entangled photon pairs, where both photons interacted with the sample. We showed that the quantum correlations between the two photons are clearly reflected in the induced excited state population distributions, as well as in fluorescence and in pump-probe-like signals. We now consider a different scenario, where one of the two photons interacts with the sample, while the other one is used as a reference to filter the signal. Our setup closely relates to interferometric setups widely used in quantum optics, be it photon interferometry [Hong87, Ou88, Franson92] discussed in chapter 2 or matter wave interferometry [Hornberger12], where, in conventional approaches, an off-resonant interaction shifts the phase of one of the two beam lines, which are then recombined and detected, turning the phase shift into an amplitude change in the measurement. Here, we consider resonant interactions, in which the photon number in one beam is affected, and their change creates the signal. As we will show in this chapter, the quantum correlations shared between the two photons are nevertheless clearly reflected in the resulting signal.

Similar setups have already been employed to suppress background noise and extract signals from very noisy samples [Kalashnikov14, Phan14] (see section 2.2). We will build upon these results, and point out how the simultaneous time and frequency resolution beyond the Fourier limit of time-frequency entangled photons (compare section 4.5.4) may be exploited.

First, we introduce and derive expressions for the frequency-resolved photon counting signal obtained from the simultaneous detection of photon pairs. We need to consider irreversible, dissipative dynamics since we have seen in chapter 4 that only in this case we may see an impact of *simultaneous* time and frequency resolution. As before, we first exemplify basic features at the hand of a simple model system - the two-state jump model, which we introduce in section 6.2. The model was developed to describe the low-temperature limit of chemical exchange in molecules¹ [Tanimura06, Šandra06, Dorfman13, Dorfman14b], and constitutes a simple example of a four-level system undergoing relaxation. We simulate its optical response in a pump-probe scheme employing classical pulses as well as entangled photon pairs. In contrast to the previous chapters, we *first* discuss the classical signal, since the frequency correlations add an additional dimension to the signal, and complicate its interpretation without the classical reference at hand. Finally, we present simulations of our - by now - well-known bacterial reaction center as an example of a realistic model.

¹Chemical exchange denotes a situation in which the environment, such as a chemical ligand, changes from one stable conformation to another - thereby affecting the electronic structure, and incidentally shifting optical resonances.

6. Interferometric setups

In contrast to previous chapters, we focus on the parameter regime of entangled photons with *positive* frequency correlations (see Fig. A.4 and the discussion in section A.3.2). Here, the physical origin of the time and frequency resolution of the entangled pairs is reversed. Whereas in the anti-correlated regime a narrowband pump pulse is responsible for the frequency resolution, and the phase matching function generates the time resolution between absorption events, here an ultrafast (broadband) pump pulse is responsible for the time resolution, while the phase matching function allows for the frequency resolution.

6.1. Frequency-resolved measurements

We consider an experimental setup as depicted in Fig. 6.1a): Two entangled beams are separated by a beam splitter. One of them, E_1 , is used as the probe beam in a pump-probe measurement in combination with the classical pump E_a (in the context of Raman spectroscopy, the latter is often termed an *actinic pulse*²). The other beam E_2 is detected in coincidence with E_1 in order to utilize the quantum correlations between the beams. We consider frequency-dispersed detection, as in the previous chapter 5.

The frequency-resolved two-photon counting signal was derived in Eq. (3.49),

$$S_{\text{TPC}}(\omega, \omega_r; \Gamma) = \frac{2}{\hbar} \Im \langle E_2^\dagger(\omega_r) E_1^\dagger(\omega) V(\omega) E_2(\omega_r) \rangle_{\text{final}}, \quad (6.1)$$

where we absorbed the field normalization in the dipole moments of the matter system, and describes the change of the two-photon count rate, when beam 1 is sent through a sample system. We define the detection frequency ω , at which beam 1 is recorded, and the reference frequency ω_r , at which beam 2 is measured. As usual, Γ denotes the set of control parameters of the excitation pulses. We reiterate that beam 2 never interacts with the sample itself, but, due to its joint detection with beam 1, the time-frequency correlations between the beams are exploited. It may be thought of as a sort of post-selection of the acquired spectroscopic data, which is encrypted in beam 1. Here, we are interested in the effects when the sample is first excited by the ultrafast actinic pulse E_a , and the subsequent nonequilibrium dynamics is probed by the photon in beam 1.

To describe such a situation, we expand the interaction Hamiltonian to third order, and obtain

$$S_{\text{TPC}}(\omega, \omega_r; \Gamma) = \frac{2}{\hbar} \Im \left(-\frac{i}{\hbar} \right)^3 \int_{-\infty}^{\infty} dt e^{i\omega(t-t_0)} \int_{t_0}^t d\tau_3 \int_{-\infty}^{\tau_3} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 \\ \times \langle E_{2+}^\dagger(\omega_r) E_{2+}(\omega_r) E_{1+}^\dagger(\omega) V_+(t) H_{\text{int},-}(\tau_3) H_{\text{int},-}(\tau_2) H_{\text{int},-}(\tau_1) \rangle. \quad (6.2)$$

The first two interactions correspond to excitations by the ultrafast actinic pulse, which - to simplify our discussion - we approximate to be impulsive, *i.e.* $E_a(t) = E_a \delta(t)$. The

²This nomenclature is motivated by the fact that the “actinic” (*i.e.*, caused by radiation or light) pulse initiates the nonequilibrium wavepacket, which is then probed by stimulated Raman spectroscopy [Kukura07].

Figure 6.1.: a) Proposed setup: Entangled beams E_1 and E_2 are split on a beam splitter. Together with a classical, ultrafast pulse E_a , E_1 is employed in a pump-probe measurement on the sample, while E_2 is detected in coincidence. b) The two contributions to Eq. (6.2); for their interpretation, see section 3.7.

third interaction involves the entangled beam E_1 , centered at the time t_0 , such that we obtain the two contributions shown in Fig. 6.1b). The two diagrams are closely related to the diagrams (Ia) and (IIIa) of Fig. 3.9 with respect to the temporal succession of (de-)excitations. As we shall see later in this chapter, the comparison with the decomposition of the diagrams in Fig. 3.9 allows us to explain the relative sign of the two contributions to the full signal. Nevertheless, here we deal with totally time-ordered ladder diagrams (see section 3.7), since we aim at the investigation of dissipative dynamics.

Carrying out the integrations of the delta-functions associated with E_a , the expression for diagram (I) in Fig. 6.1b) reads

$$S_{\text{TPC}, (I)}(\omega, \omega_r; \Gamma) = -\frac{2}{\hbar} \Im \left(-\frac{i}{\hbar} \right)^3 |E_a|^2 \int_0^\infty dt e^{i\omega(t-t_0)} \int_0^t d\tau F_I(t-\tau, \tau) \times \langle E_2^\dagger(\omega_r) E_1^\dagger(\omega) E_1(\tau) E_2(\omega_r) \rangle, \quad (6.3)$$

where we have further introduced the matter correlation function

$$F_I(t_2, t_1) \equiv \sum_{e, e', e'', f} \langle \mu_{ge} \mu_{ge'}^* | \mu_{e''f} |^2 G_{fe''}(t_2) G_{ee'}(t_1) \rangle_{\text{env}}. \quad (6.4)$$

The summation indices refer to our regular manifold structure in Fig. 3.1, and the expectation value $\langle \dots \rangle_{\text{env}}$ denotes the average with respect to the environmental degrees of freedom. In the case of the two-state jump model to be described later in the chapter, it corresponds to the average over the spin degrees of freedom. For the bacterial RC, it constitutes the vibrational environment of the RC, which will restrict the possible combinations of states e, e' and e'' .

Similarly, diagram (II) in Fig. 6.1b) yields

$$S_{\text{TPC}, (II)}(\omega, \omega_r; \Gamma) = \frac{2}{\hbar} \Im \left(-\frac{i}{\hbar} \right)^3 |E_a|^2 \int_0^\infty dt e^{i\omega(t-t_0)} \int_0^t d\tau F_{II}(t-\tau, \tau) \times \langle E_2^\dagger(\omega_r) E_1(\tau) E_1^\dagger(\omega) E_2(\omega_r) \rangle. \quad (6.5)$$

6. Interferometric setups

with the matter correlation function

$$F_{II}(t_2, t_1) \equiv \sum_{e, e', e''} \langle \mu_{ge} \mu_{ge'}^* | \mu_{ge''} |^2 G_{e''g}(t_2) G_{ee'}(t_1) \rangle_{\text{env}}. \quad (6.6)$$

Note that the field correlation function in Eq. (6.5) is not normally-ordered [this is indicative of a Raman pathway, compare Eqs. (5.18) and (5.19)], since the interaction with $E_1(\tau)$ takes place with the *bra* side of the density matrix. Just like in our discussion of Eq. (5.18), we may identify the commutator contribution $[E_1(\tau), E_1^\dagger(\omega)]$ with the spontaneous fluorescence of excitation in the sample system into field 1. We neglect this contribution, since here we consider the coincidence measurements of ultrafast entangled beams, for which fluorescence (which takes place on nanosecond time scales in molecular aggregates [Blankenship02]) can be neglected.

6.1.1. Classical measurements

To compare the photon-counting signal with classical signals, we now derive the classical pump-probe signal. Instead of the change of the two-photon counting signal (6.1), we monitor the change of transmission of a classical probe pulse E_{pr} . The corresponding signal is obtained by expanding the intensity signal (3.43) to third order. We obtain the same matter correlation function as before, but convoluted with classical field envelopes E_{pr} ,

$$S_{\text{PP, cl.}}(t_0, \omega) = \frac{2}{\hbar} \Im \left(-\frac{i}{\hbar} \right)^3 |E_a|^2 \int_0^\infty dt e^{i\omega t} \int_0^t d\tau \\ \times E_{pr}^*(\omega) E_{pr}(\tau) [F_I(t - \tau, \tau) + F_{II}(t - \tau, \tau)]. \quad (6.7)$$

Note that Eq. (6.7) contains the same matter correlation functions as the two-photon counting signal in Eqs. (6.3) and (6.5). Hence, both, the classical pump-probe signal and the two-photon counting signal may - in principle - access the same information on the material target. However, the presence of the quantum correlations between E_1 and E_2 above acts as an additional time and frequency filter, as we will show in the following.

6.2. Two-State Jump Model

The two-state jump (TSJ) model in its simplest form is described by an electronic excited state $|e\rangle$, which is coupled to two spin states *up* $|\uparrow\rangle$ and *down* $|\downarrow\rangle$ [Šandra06]. Additionally, we invoke a two-exciton state $|f\rangle$, which is dipole-coupled to both $|e, \uparrow\rangle$ and $|e, \downarrow\rangle$ (see Fig. 6.2). We assume that the excited electronic states are broadened by a phenomenological dephasing rate γ , and the two spin states be coupled by a stochastic Liouville equation [Tanimura06], described by an effective Markovian master equation. In this sense, our model is very similar to the secular Redfield equation used in the description of the bacterial RC (see appendix B). We focus on the low-temperature limit of this model, in which only the decay process $|\uparrow\rangle \rightarrow |\downarrow\rangle$ is relevant [Dorfman13]. In

Figure 6.2.: Level scheme as described by the two state jump (TSJ) model: The intermediate state $|e\rangle$ of three electronic states $|g\rangle$, $|e\rangle$ and $|f\rangle$ is coupled to a spin system, which undergoes relaxation. In the low temperature limit considered here, we only account for relaxation from the higher-energy state $|\uparrow\rangle$ to the lower-energy state $|\downarrow\rangle$, which occurs incoherently, with rate k . The dipole couplings between the electronic states are indicated by the pulsed arrows.

this model, the spin-coupling is strictly incoherent, such that we only need to take the two spin populations into account, and the coupling between the two populations can be described by a classical rate equation: The population in $|e, \uparrow\rangle$ is represented by the vector $(1, 0)^T$, and the one in $|e, \downarrow\rangle$ by $(0, 1)^T$ (the identity is then given by $Id \triangleq (1, 1)^T$). In this case, the propagator within the e -manifold may be represented by a 2×2 matrix [Dorfman13]

$$\mathcal{G}_{ee}(t) = \Theta(t) \begin{pmatrix} e^{-kt} & 0 \\ 1 - e^{-kt} & 1 \end{pmatrix}, \quad (6.8)$$

where k denotes the decay constant. If the system is initially in the state $|e, \uparrow\rangle$, the dynamics is given by $\mathcal{G}_{ee}(t)(1, 0)^T$; hence, with probability $\exp(-kt)$, the system remains in the upper state, and with probability $1 - \exp(-kt)$, it decays into the lower state. On the other hand, if the system is initially in $|e, \downarrow\rangle$, it remains there with unit probability, since we do not consider the process $|\downarrow\rangle \rightarrow |\uparrow\rangle$ in the present low-temperature limit.

The coherence element of the Green's function between $|f\rangle$ and $|e\rangle$ is similarly given by

$$\mathcal{G}_{fe}(t) = \Theta(t) \begin{pmatrix} e^{-(k+i\omega_-)t} & 0 \\ \frac{k}{k+2i\delta} [e^{-i\omega_+t} - e^{-(k+i\omega_-)t}] & e^{-i\omega_+t} \end{pmatrix}, \quad (6.9)$$

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where δ denotes the energy difference between the two spin states, and $\omega_{\pm} = \omega_{fe} \pm \delta$.³

Using these propagators, we can carry out the average with respect to the spin degrees of freedom, and obtain for the matter correlation function in Eq. (6.3)

$$\begin{aligned} F_I(t_2, t_1) &= \langle |\mu_{ge}|^2 |\mu_{ef}|^2 G_{fe}(t_2) G_{ee}(t_1) \rangle_{\text{env}} = \langle Id | |\mu_{ge}|^2 |\mu_{ef}|^2 G_{fe}(t_2) G_{ee}(t_1) | \uparrow \rangle \\ &= |\mu_{ge}|^2 |\mu_{ef}|^2 e^{-\gamma(t_1+2t_2)} \left(e^{-i\omega_+ t_2} + \frac{2i\delta}{k+2i\delta} e^{-kt_1} \left[e^{-(k+i\omega_-)t_2} - e^{-i\omega_+ t_2} \right] \right). \end{aligned} \quad (6.10)$$

The exponential factor $\exp(-\gamma(t_1+2t_2))$ accounts for the additional electronic dephasing in our model [Dorfman13], and was added phenomenologically here. Since the TSJ model in the present study merely represents a simple toy model, which we use to elaborate properties of the light field, we now choose the parameters (*i.e.* $\omega_{\pm}$, γ , and k) such that our analysis becomes most transparent. To this end, we assume that the entangled photons are far detuned from the $|e\rangle - |g\rangle$ transition, while on resonance with the $|e\rangle - |f\rangle$ transition. In this regime, digram (II), Eq. (6.5), may be neglected, and the signal is exclusively given by Eq. (6.3). When discussing a similar signal from the bacterial RC later in this chapter, Eq. (6.5) however needs to be taken into account as well.

6.2.1. Frequency domain expressions

We evaluate the two-photon counting signal (6.3) in the frequency domain, since this reduces the number of integrals to be evaluated to one, due to the frequency-resolved detection scheme (6.1). Rewriting the field operator in its frequency decomposition,

$$E_1(\tau) = \int \frac{d\omega_b}{2\pi} e^{-i\omega_b(\tau-t_0)} E_1(\omega_b), \quad (6.11)$$

which already takes the time delay with respect to the pump pulse E_a into account, we can carry out the time integrations in Eq. (6.3), and obtain

$$\begin{aligned} S_{\text{TPC}, (I)}(t_0, \Gamma) &= \frac{2}{\hbar^4} |E_a|^2 \Re \int \frac{d\omega_b}{2\pi} \langle E_2^\dagger(\omega_r) E_1^\dagger(\omega) E_1(\omega_b) E_2(\omega_r) \rangle \\ &\quad \times \tilde{F}_I(\omega_b, \omega; t_0), \end{aligned} \quad (6.12)$$

with the frequency domain matter correlation function

$$\begin{aligned} \tilde{F}_I(\omega_b, \omega; t_0) &= |\mu_{ge}|^2 |\mu_{ef}|^2 \left(\frac{e^{-i(\omega-\omega_b)t_0}}{\omega_b - \omega_+ - i\gamma} \left[\frac{1}{\omega - \omega_b + 2i\gamma} - \frac{1}{\omega - \omega_+ + i\gamma} \right] \right. \\ &\quad + \frac{2i\delta}{k+2i\delta} \frac{e^{-i(\omega-\omega_b)t_0}}{\omega_b - \omega_- - i\gamma} \left[\frac{1}{\omega - \omega_b + i(k+2\gamma)} - \frac{1}{\omega - \omega_- + i(k+\gamma)} \right] \\ &\quad \left. - \frac{2i\delta}{k+2i\delta} \frac{e^{-i(\omega-\omega_b)t_0}}{\omega_b - \omega_+ - i(k+\gamma)} \left[\frac{1}{\omega - \omega_b + i(k+2\gamma)} - \frac{1}{\omega - \omega_+ + i\gamma} \right] \right). \end{aligned} \quad (6.13)$$

³ Note that $\omega_{\pm}$ denotes the frequency difference between single and two-exciton state. When the intermediate state loses energy to the environment, the frequency difference to the f -state *increases*. Hence, the frequency changes from ω_- to ω_+ with time.

Note that, due to the integration boundaries of the time integrals in Eq. (6.3), $\tilde{F}_I(\omega_b, \omega; t_0)$ is *not* simply the Fourier transform of $F_I(t_2, t_1)$. To distinguish the two, $\tilde{F}_I(\omega_b, \omega, t_0)$ is denoted with a tilde.

Classical measurements

Carrying out the same calculation for the classical pump-probe signal (6.7), we obtain

$$S_{\text{PP, cl.}}(t_0, \omega) = \frac{2}{\hbar} \Im \left(-\frac{i}{\hbar} \right)^3 |E_a|^2 \int_0^\infty dt e^{i\omega t} \int_0^t d\tau F_I(t - \tau, \tau) \times |\mu_{ge}|^2 |\mu_{ef}|^2 E_{pr}^*(\omega) E_{pr}(\tau) \quad (6.14)$$

$$= \frac{2}{\hbar^4} |E_a|^2 \Re \int \frac{d\omega_b}{2\pi} E_{pr}^*(\omega) E_{pr}(\omega_b) \tilde{F}_I(\omega_b, \omega). \quad (6.15)$$

Excursion: The impulsive limit As a nice comparison, and to gain additional intuition from an analytical solution, let us briefly discuss the limit of an infinitely, *i.e.* impulsively, short classical probe pulse E_{pr} . This signal gives a best-case scenario in the sense that we use impulsive excitation and readout pulses yielding perfect time resolution, but, due to the frequency-dispersed detection, we also resolve the dynamics spectrally.

The impulsive limit is obtained by sending the bandwidth of the probe pulse to infinity, *i.e.*

$$E_{pr}(\omega_b) \longrightarrow 1. \quad (6.16)$$

In this case, the frequency integration in Eq. (6.15) may be performed by closing the integration contour at $+i\infty$, and applying residue calculus. We obtain

$$S_{\text{PP, cl.}}(t_0, \omega) = \frac{2}{\hbar^4} |E_a|^2 |\mu_{ge}|^2 |\mu_{ef}|^2 e^{-2\gamma t_0} \times \Re \left[\frac{2i\delta e^{-kt_0}}{(\omega - \omega_+ + i\gamma)(\omega - \omega_- + i(k + \gamma))} - \frac{1}{\omega - \omega_+ + i\gamma} \right]. \quad (6.17)$$

The dephasing rate γ affects both terms in the brackets identically. But in addition, the first term decays with the decay constant k , such that after delay times $t_0 \sim 1/k$ the signal is dominated by the single resonance at ω_+ . We recall the footnote of page 158 - the resonance shifts with time from ω_- to ω_+ .

6.2.2. Results

We now discuss various simulations of the classical pump-probe signal for the TSJ model. First, we show simulations with a finite bandwidth probe pulse, to demonstrate the trade-off between frequency and time resolution, and in a second stage discuss the difference with respect to the impulsive limit.

6. Interferometric setups

The classical pump-probe signal for our model system is given by Eq. (6.15). Just like in previous chapters [see Eq. (4.29)], we employ classical pulses in our simulations, with a Gaussian envelope⁴

$$E(\omega) = \frac{1}{\pi^{1/4}\sqrt{\sigma}} \exp [-(\omega - \omega_0)^2/2\sigma^2]. \quad (6.18)$$

We chose the following parameters: $\omega_{fe} = 11,000 \text{ cm}^{-1}$, $\delta = 200 \text{ cm}^{-1}$, $k = 120 \text{ cm}^{-1}$, and $\gamma = 100 \text{ cm}^{-1}$. We recall that we assume ω_{eg} to be far detuned from ω_{fe} , which allows us to neglect the contribution of diagram (II) in Fig. 6.1b).

Fig. 6.3 shows the spectrally dispersed pump-probe signal as a function of the dispersed frequency ω and of the time delay t_0 . The signal (*i.e.* the change in the photocount rate) is negative,⁵ and has been normalized such that the minimum is set to -1 .

The central frequency ω_0 of the probe pulse is set on resonance with the unperturbed transition ω_{fe} , and we vary its bandwidth (and thus its time resolution). Panel a) shows the signal induced by a 6-fs probe pulse. Two resonances at $\sim \omega_{fe} \pm \delta$ can be clearly identified, and due to the spectrally dispersed detection, their individual widths are determined by the linewidth γ , rather than by the bandwidth of the probe pulse. The maxima of the two resonances have been slightly shifted away from their “actual” values. The resonance at $\omega_{fe} + \delta$ is shifted to lower values, and the one at $\omega_{fe} - \delta$ towards higher values. This effect can be explained by the comparable values of the line splitting δ and of the line broadening γ : The flanks of one resonance stretches over to the other resonance, such that the resonance is sitting on a “tilted background”, thus shifting its minimum.

For very small time delays t_0 , the signal of both resonance increases in amplitude. As t_0 increases further, the lower resonance at $10,800 \text{ cm}^{-1}$ quickly reaches its maximum, and then decays rapidly, while the higher-energy resonance at $11,200 \text{ cm}^{-1}$ peaks at longer delay times. The initial rise of the signal may be attributed to our definition of the signal (6.7) as the change in the photon count rate after transmission through the sample: Only after the entire pulse has passed the sample, the signal reaches its maximum, and then starts to decay. The different time delays t_0 , at which the two resonances reach their maxima, however, is due to the intermediate population decay $|\uparrow\rangle \rightarrow |\downarrow\rangle$.

With decreasing probe bandwidth σ [panels b) - f)], we lose time resolution, such that the primary resonance at $\omega_{fe} - \delta$ becomes weaker, and can no longer be identified for $\sigma \leq 400 \text{ cm}^{-1}$. As a second consequence, the two resonances merge into one resonance at the transition frequency ω_{fe} . Due to the long duration of the probe pulse, the two resonances are averaged out, and cannot be detected any more, not even with spectral

⁴Since all the simulations are normalized with respect to the maxima signal, the overall intensity of the laser pulse is irrelevant in the present simulation, as it merely appears as a constant prefactor in Eq. (6.15).

⁵Since the $|e\rangle - |g\rangle$ transitions are off-resonant, the excitation by the pump pulse enables beam 1 to interact with the $|e\rangle - |f\rangle$ transition. Consequently, the absorption of beam 1 is enhanced, and the photon count rate decreases (*i.e.* the change in the count rate is negative).

6.2. Two-State Jump Model

Figure 6.3.: Classical pump-probe signal, Eq. (6.15), as a function of the time delay t_0 of the probe with respect to the pump pulse (in fs), and of the dispersed detected frequency ω (in cm^{-1}), with a probe bandwidth of a) $\sigma = 1,000 \text{ cm}^{-1}$ (corresponding to a 5.6 fs pulse in time domain), b) 800 cm^{-1} , c) 600 cm^{-1} , d) 400 cm^{-1} , e) 200 cm^{-1} , and f) 50 cm^{-1} (111 fs).

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Figure 6.4.: a) Classical pump-probe signal S_{PP} with impulsive probe pulse, Eq. (6.17), as a function of the time delay t_0 to the pump pulse (in fs), and the dispersed frequency ω (in cm^{-1}). b) Comparison between impulsive probe pulse (red) and finite bandwidth pulse with $\sigma = 1,000 \text{ cm}^{-1}$ (blue), at frequencies $\omega = 11,200 \text{ cm}^{-1}$ (solid lines), and at $\omega = 10,800 \text{ cm}^{-1}$ (dashed lines).

dispersion (This is an example of *motional line narrowing*) [Ernst90].⁶

For comparison, we further depict the impulsive probe pulse limit of $S_{PP}(\omega, t_0)$ in Fig. 6.4. Panel a) shows a two-dimensional plot of the frequency-dispersed signal with impulsive probe, which looks rather similar to the signal with broadband probe in Fig. 6.3a) - except for the initial rise of the signal. This difference can be most clearly seen in the direct comparison of the two signals in panel b): For $t_0 \leq 15$ fs, both resonances in the finite-bandwidth signal increase. Since their bandwidth corresponds to a 5.6 fs pulse, this may be attributed to the fact that the probe pulse has not interacted entirely with the sample. The impulsive signal at the low-energy resonance ($10,800 \text{ cm}^{-1}$), on the other hand, immediately decays with the decay constant $k + 2\gamma$ [see Eq. (6.17)]. The higher-energy resonance at $\omega = 11,200 \text{ cm}^{-1}$ first peaks at $t_0 \approx 10$ fs, and then decays as well, with decay constant 2γ . This behavior again shows that the initial rise of both resonances in the previous discussion was due to the ongoing pulse propagation across the sample.

In contrast to the classical signal, the two-photon counting signal (6.12) generated with entangled photons offers additional control parameters: On the one hand, we have the dispersed frequency ω , the pump frequency ω_p and its bandwidth σ_p , which loosely play the role of classical center frequency ω_0 and bandwidth σ of the probe pulse, as we will show in the following. Besides, we may further vary the entanglement time T and the detected frequency of the reference beam ω_r . These will allow us to dissect the

⁶It needs to be pointed out that these results are by no means new or surprising. They simply present conventional pump probe simulations for our current model system.

6.2. Two-State Jump Model

Figure 6.5.: Two-photon counting, frequency-dispersed signal $S_{\text{TPC}}(\omega, \omega_r; t_0)$, Eq. (6.12), of entangled photons plotted vs. the dispersed frequency ω of beam 1, and the time delay t_0 . The reference frequency ω_r of beam 2 is fixed as indicated on top of each panel. The parameters are a) $\omega_r = 10,400$ cm $^{-1}$, entanglement time $T = 90$ fs, and pump bandwidth $\sigma_p = 1,000$ cm $^{-1}$, b) $\omega_r = 11,400$ cm $^{-1}$, $T = 90$ fs, and $\sigma_p = 1,000$ cm $^{-1}$, c) $\omega_r = 10,400$ cm $^{-1}$, $T = 358$ fs, and $\sigma_p = 2,000$ cm $^{-1}$, and d) $\omega_r = 11,400$ cm $^{-1}$, $T = 358$ fs, and $\sigma_p = 2,000$ cm $^{-1}$.

classical signal into smaller components, and thereby disentangle congested spectra. In our previous discussion of the classical pump-probe signal, we already saw that - even in the simple model system considered here - it may become very hard to discern the two states of the e -manifold due to the broadening of the resonances. We will improve

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on this situation using time-frequency entangled photons.

Fig. 6.5 shows simulations of the two-photon counting signal $S_{\text{TPC}}(\omega, \omega_r; t_0)$, Eq. (6.12), of degenerate entangled photons vs. dispersed frequency ω and time delay t_0 . The pump bandwidth generating the photon pair [see Eq. (A.27)] is set to $\sigma_p = 1,000 \text{ cm}^{-1}$ or $2,000 \text{ cm}^{-1}$, respectively, and the center frequency of the entangled photon beams E_1 and E_2 is set on resonance with the electronic transition in Fig. 6.2, $\omega_p/2 = \omega_{fe}$. We vary the remaining control parameters, *i.e.* the reference frequency ω_r , at which the photons in E_2 are detected, and the entanglement time T .

The left column [panels a) and c)] show signals where the reference frequency ω_r is detuned to $10,400 \text{ cm}^{-1}$. Due to the frequency correlations between the entangled photons, this enhances the resonance at $\omega_{fe} - \delta$, and suppresses its counterpart. Conversely, the right column [panels b) and d)] shows signals where the reference frequency is set to $11,400 \text{ cm}^{-1}$, thereby enhancing $\omega_{fe} + \delta$, and suppressing its low-energy counterpart.

The top row in Fig. 6.5 [panels a) and b)] shows the signal created by entangled photons with entanglement time $T = 90 \text{ fs}$, while the bottom row [panels c) and d)] is obtained for the entanglement time 358 fs . Clearly, the larger entanglement time in panels c) and d) allows to select a more narrow frequency window from the total signal, and to investigate the relaxation dynamics of this part of the signal separately. In panel c), we observe the build-up of the maximal signal, as well as its subsequent decay. Panel d) only shows a decay of the signal, in agreement with the actual molecular dynamics. However, the decay takes place on much larger time scales $\sim 120 \text{ fs}$ as opposed to $\sim 30 \text{ fs}$ in Fig. 6.4a). Thus, we also observe that - even though we increased the pump bandwidth compared to panels a) and b) to $\sigma_p = 2,000 \text{ cm}^{-1}$ - the longer entanglement time results in the loss of time resolution: Even though the maximum in panel c) can be attributed to the intermediate decay $|\uparrow\rangle \rightarrow |\downarrow\rangle$, the signal is broadly stretched along the t_0 -axis, and the actual time constants cannot be read off this plot. As we discussed elusively in chapter 4, the entanglement time yields an upper bound for the maximal time delay between the arrival time of entangled pairs. Hence, even though we stated earlier that in the case of an ultrafast pump pulse the time resolution stems from this pump pulse, it is destroyed by a too large temporal walk-off between the entangled photon pair during their propagation through the nonlinear crystal. Thus, in the case of $T = 358 \text{ fs}$, which is much larger than the pump duration $\sim 2.8 \text{ fs}$, it is the entanglement time that restricts the time resolution.

This is why we investigate the relation between time resolution and entanglement time and pump bandwidth in more detail in Figs. 6.6 and 6.7. In both figures, we fix the dispersed frequency at the positions of the two resonances $\omega_{fe} \pm \delta$. Fig. 6.6 shows the time delay dependence of the TPC signal, at fixed pump bandwidth and for different entanglement times. Each plot is normalized with respect to its maximum value, and the impulsive classical signal is plotted for comparison.⁷ Crudely speaking, the smaller the

⁷At first glance, it may appear as if the impulsive signal in panel b) decays much slower than in Fig. 6.4a), where the signal reaches the value ~ 0.4 at $t_0 = 30 \text{ fs}$, whereas in Fig. 6.6b) it remains at ~ 0.8 ! This apparent discrepancy is due to the different normalization in the latter case: The maximal value in Fig. 6.4a) is reached at $\omega = 10,800 \text{ cm}^{-1}$, while the signal at $11,200 \text{ cm}^{-1}$, corresponding

Figure 6.6.: a) Two-photon counting signal $S_{\text{TPC}}(t_0)$ for $\omega = 10,800 \text{ cm}^{-1}$, $\omega_r = 10,400 \text{ cm}^{-1}$, and $\sigma_p = 1,000 \text{ cm}^{-1}$. The different plots correspond to (from top to bottom) $T = 18, 45, 90, 179$, and 358 fs . b) Same for $\omega = 11,200 \text{ cm}^{-1}$, and $\omega_r = 11,400 \text{ cm}^{-1}$. In both panels, the classical pump-probe, impulsive signal at $\omega = 10,800$ ($11,200$) cm^{-1} is plotted as a blue, solid line for comparison.

entanglement time, the closer the maximum of the signals moves towards the impulsive limit: For $T = 18 \text{ fs}$, the signal in panel b) almost coincides with the impulsive signal for $t_0 \geq 30 \text{ fs}$, even though it is not able to resolve the faster decay in panel a). For larger entanglement times, the time resolution decreases, and the signal is spread further along t_0 - except for $T = 358 \text{ fs}$ in panel b), where the time resolution appears to increase compared to the signal with $T = 179 \text{ fs}$ (the signal decay faster). The reason behind this apparent “increase” of the time resolution may be found in a close inspection of the corresponding 2d-contour plot in Fig. 6.5d), where we observe that the signal with $T = 358 \text{ fs}$ is so narrow along the ω -axis, that it almost vanishes at $\omega = 11,200 \text{ cm}^{-1}$. What we observe in Fig. 6.6b) is not a proper signal, but rather a numerical artifact stemming from our normalization to the maximal value. This case should serve as a warning that, in fixing control parameters such as the reference frequency ω_r - the frequency correlations between the two photons can “destroy” the desired signal, and instead we only observe residual tails of the dominant signal.⁸

Fig. 6.7 investigates the dependence of the signal on the pump bandwidth σ_p at $\omega = 10,800 \text{ cm}^{-1}$ and $11,200 \text{ cm}^{-1}$ for a fixed entanglement time $T = 18 \text{ fs}$. To better distinguish the signals created at different bandwidths, which show rather similar lineshapes, we only plot the first 30 fs of the time delay t_0 . Clearly, the maximum value of the signal is reached faster, the larger the pump bandwidth is chosen; keeping in mind that doubling the pump pulse bandwidth σ_p cuts the pulse duration in half - the

to Fig. 6.6b), evolves from ~ 0.5 to 0.4 , in agreement with Fig. 6.6.

⁸Experimentally, one may not be able to observe these weak tails anyway, so the problem with the signal normalization is a purely theoretical problem, which tempted us to see things that are not really there.

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Figure 6.7.: a) Two-photon counting signal $S_{\text{TPC}}(t_0)$ for $\omega = 10,800 \text{ cm}^{-1}$, $\omega_r = 10,400 \text{ cm}^{-1}$, and $T = 18 \text{ fs}$. The different, dashed plots correspond to $\sigma_p = 1,000, 2,000, 3,000$, and $4,000 \text{ cm}^{-1}$ (with increasing spacing between the dashes, see Fig. 6.6). b) Same for $\omega = 11,200 \text{ cm}^{-1}$, and $\omega_r = 11,400 \text{ cm}^{-1}$. The classical, impulsive pump-probe signal at $\omega = 11,200 \text{ cm}^{-1}$ is plotted as a blue, solid line for comparison.

improvement in resolution between $\sigma_p = 1,000 \text{ cm}^{-1}$ and $2,000 \text{ cm}^{-1}$ is (very roughly) twice as large as the one between $2,000$ and $4,000 \text{ cm}^{-1}$. Hence, the time resolution can be enhanced for a given entanglement time by increasing the pump bandwidth. However, as we described in the previous paragraph, the temporal walk-off between the photons fundamentally restricts the time resolution. As already implemented in early experiments on type-II downconverted photons (see, e.g., the review [Shih03]), this could be adjusted by adding a second birefringent crystal into the beam line, which is rotated with respect to the first one, where the photons are created, such that the temporal walk-off is compensated.

To conclude, we have shown how we can use the time-frequency correlations of entangled photons to manipulate the two-photon counting signal (6.1). Whereas the classical pump-probe signal cannot control the excitation of specific states, we can achieve this with entangled photons by controlling the entanglement time and the pump bandwidth. Hence, the simultaneous time and frequency resolution can be enhanced compared to the classical signal. However, it was shown that the situation is more involved than in the case of the two-photon absorption events discussed in chapter 4: The enhanced frequency resolution of a larger entanglement time comes at the price of a diminished time resolution due to the temporal walk-off of the photons during their propagation in the birefringent crystal. It should, however, be possible to compensate for this delay by adding additional birefringent crystals in the beam line.

6.3. Interferometric signals of the bacterial reaction center

Following our strategy of the previous chapters, we will now apply what we have learned from the simple two-state jump model (Fig. 6.2) to our model of the bacterial reaction center. We start with the derivation of the impulsive pump-probe signal. This constitutes the best-case scenario for what can be done with classical light. Finally, we use the two-photon counting setup to filter the signal.

6.3.1. Frequency domain signals

In contrast to the TSJ model, the $e - g$ and the $e - f$ transitions are in the same parameter regime. Therefore, we need to take diagram (II), Eq. (6.5), into account as well. Its evaluation proceeds completely analogous to our evaluation of diagram (I) in the TSJ model. Following the same derivation as before [compare Eq. (6.13)], we obtain the following correlation functions in the frequency domain:

$$\begin{aligned} \tilde{F}_I(\omega_b, \omega; t_0) = & \sum_{e, e', e'', f} \mu_{ge} \mu_{ge'} e^{-i(\omega - \omega_b)t_0} \\ & \times \left[(1 - \delta_{e, e'}) \delta_{e', e''} \frac{\mu_{ef}^2}{\omega_b - \omega_{fe''} + i(\gamma_{fe} - \gamma_{ee'})} \left(\frac{i}{\omega - \omega_b - \omega_{ee'} + i\gamma_{ee'}} - \frac{i}{\omega - \omega_{fe'} + i\gamma_{fe}} \right) \right. \\ & \left. + \delta_{e, e'} \sum_p \frac{\chi_{pe''}^L \chi_{pe}^R}{D_p} \frac{\mu_{e''f}^2}{\omega_b - \omega_{fe''} + i(\gamma_{fe} - \lambda_p)} \left(\frac{i}{\omega - \omega_b + i(\lambda_p + \eta)} - \frac{i}{\omega - \omega_{fe''} + i\gamma_{fe}} \right) \right], \end{aligned} \quad (6.19)$$

$$\begin{aligned} \tilde{F}_{II}(\omega_b, \omega; t_0) = & \sum_{e, e', e''} \mu_{eg} \mu_{e'g} \mu_{ge''} e^{-i(\omega - \omega_b)t_0} \\ & \times \left[(1 - \delta_{ee'}) \delta_{e, e''} \frac{\mu_{e'g}}{\omega_b - \omega_{e''} + i(\gamma_e - \gamma_{ee'})} \left(\frac{-i}{\omega - \omega_b - \omega_{ee'} + i\gamma_{ee'}} - \frac{-i}{\omega - \omega_{eg} + i\gamma_e} \right) \right. \\ & \left. + \delta_{ee'} \sum_p \frac{\chi_{pe''}^L \chi_{pe}^R}{D_p} \frac{\mu_{ge''}}{\omega_b - \omega_{e''g} + i(\gamma_e - \lambda_p)} \left(\frac{-i}{\omega - \omega_b + i(\lambda_p + \eta)} - \frac{-i}{\omega - \omega_{e''g} + i\gamma_e} \right) \right]. \end{aligned} \quad (6.20)$$

Here, we have added the small lifetime $\eta = 10 \text{ cm}^{-1}$ to the population transport diagrams (compare section 4.6), so that we can obtain a non-divergent expression in the frequency domain.⁹

6.3.2. Classical pump-probe signal

As in the previous section, we first discuss the classical pump-probe signal of the reaction center. For the sake of simplicity, here we only consider the impulsive limit (6.16) to

⁹We recall the lowest transport eigenmode has infinite lifetime, *i.e.* $\lambda_1 = 0$. Hence, its Fourier representation diverges (see, for instance, our discussion after Eq. (4.57).

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Figure 6.8.: a) Contribution of Eq. (6.21), *i.e.* of the matter response function $\tilde{F}_I$ [diagram (I)] to Signal $S_{PP}(\omega, t_0)$ with impulsive pump and impulsive probe. b) Contribution of Eq. (6.22), *i.e.* of $\tilde{F}_{II}$ [diagram (II)]. c) The total signal $S_{PP}(\omega, t_0) = S_{PP(I)}(\omega, t_0) + S_{PP(II)}(\omega, t_0)$, Eqs. (6.21) and (6.22). The signals are normalized such that the minimum is set to zero, and the maximum value to one.

simplify our discussion. Closing the integration contour at $+i\infty$, we obtain, by inserting Eqs. (6.19) and (6.20) in Eq. (6.7),

$$S_{PP, (I)}(\omega, t_0) = \frac{2}{\hbar} \Im \left(-\frac{i}{\hbar} \right)^3 |E_a|^2 \sum_{e, e', e'', f} \mu_{ge} \mu_{ge'} \times \left[(1 - \delta_{e, e'}) \delta_{e', e''} \frac{\mu_{ef}^2 e^{-i(\omega_{ee'} - i\gamma_{ee'})t_0}}{\omega - \omega_{fe} + i\gamma_{fe}} + \delta_{e, e'} \sum_p \frac{\chi_{pe''}^L \chi_{pe}^R}{D_p} \frac{\mu_{e''f}^2 e^{-\lambda_p t_0}}{\omega - \omega_{fe''} + i\gamma_{fe}} \right], \quad (6.21)$$

$$S_{PP, (II)}(\omega, t_0) = -\frac{2}{\hbar} \Im \left(-\frac{i}{\hbar} \right)^3 |E_a|^2 \sum_{e, e', e''} \mu_{eg} \mu_{e'g} \mu_{ge''} \times \left[(1 - \delta_{ee'}) \delta_{e, e''} \frac{\mu_{e'g} e^{-i(\omega_{ee'} - i\gamma_{ee'})t_0}}{\omega - \omega_e + i\gamma_e} + \delta_{ee'} \sum_p \frac{\chi_{pe''}^L \chi_{pe}^R}{D_p} \frac{\mu_{ge''} e^{-\lambda_p t_0}}{\omega - \omega_{e''g} + i\gamma_e} \right]. \quad (6.22)$$

We first simulate the classical pump-probe signal, Eqs. (6.21) and (6.22), as a reference for the signals that can be obtained by coincidence measurements with entangled photon pairs. The results are shown in Fig. 6.8, where we depict the contribution $S_{PP, (I)}$ in panel a), that of $S_{PP, (II)}$ in panel b), and the final signal $S_{PP, (I)} + S_{PP, (II)}$ in panel c). To develop an intuition for the signal, we will draw from our experience in chapter 5. Note that diagram (I) represents a “two-photon absorption pathway”: The sample absorbs one photon from each of the two beams, and evolves in the two-exciton f -manifold between the two interactions with E_1 . Formally, this may be seen, if one breaks up the loop diagram (Ia) in Fig. 3.9 by enforcing full time-ordering between *bra* and *ket* side of the density matrix (see section 3.5.3), diagram (I) is one of the resulting ladder diagrams. Hence, its contribution to the total signal has a negative sign [panel a)], just

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like the TPA contributions to the pump-probe-like signal in section 5.1. With a similar reasoning, we can identify diagram (II) as a “Raman pathway”, which has positive sign, since it increases the photon number in the probe pulse. This is akin to the situation in Fig. 5.10, where the Raman pathways contribute with a positive sign, and the TPA pathways with a negative one.

We start with the simpler interpretation of the latter diagram (II) in panel b): The pump pulse at time $t_0 = 0$ creates a wavepacket in the single-exciton manifold, which covers all the excitons due to the effectively infinite bandwidth of the impulsive pump. Therefore, we observe one resonance at $10,100 \text{ cm}^{-1}$ (due to the exciton $|e_5\rangle$), and one at $\sim 12,000 - 13,000 \text{ cm}^{-1}$ (excitons $|e_6\rangle - |e_{10}\rangle$). This resonance structure is very similar to the linear absorption signal in Fig. 4.6b). At finite time delays, the relaxation changes this picture: At small time delays $t_0 \leq 2/\gamma \sim 100 \text{ fs}$, the resonances oscillate with the time delay, due to the excitation of coherences in the density matrix (in the exciton eigenbasis) by the pump pulse, such that the system oscillates with the exciton energy difference as a function of the time delay [see the first terms in Eqs. (6.21) and (6.22)]. With increasing time delay t_0 , the coherences die off, the remaining signal is created by the populations, and shows signs of their dynamics: The initially excited wavepacket relaxes to the lowest-energy exciton $|e_5\rangle$ residing on the special pair with the energy $\sim 10,100 \text{ cm}^{-1}$ (see Fig. B.1). Hence, we observe how the resonance at this frequency emerges with increasing delay t_0 . Since $|e_5\rangle$ also happens to be the exciton with the largest dipole coupling to the ground state (see table B.2), the signal strength increases with t_0 . If we were to plot the signal for even longer times, the charge separation taking place in the special pair would reduce the population of $|e_5\rangle$. Charge-separated states only have a very small dipole moment [Blankenship02], and cannot be detected by direct spectroscopic means (therefore, we do not show these long time delays).

The interpretation of diagram (I) in panel a) is more involved: The pump pulse also creates a wavepacket, which first shows oscillations, and then relaxes to $|e_5\rangle$. In contrast to diagram (II), the probe pulse then promotes the system briefly into a coherence between an f -state, and the final e -manifold wavepacket. Since $|e_5\rangle$ is already occupied, it can mostly excite the other excitons remaining in the system. Hence, this contribution to the signal mainly shows resonances along the upper exciton band of the RC, after the oscillations have died off.

The total signal [panel c)] can be clearly interpreted on the basis of our previous discussion: At small time delays, $t_0 \leq 100 \text{ fs}$, the signal shows strong oscillations stemming from coherences. As these coherences die off, so do the oscillations, and the transport pathways take over. After the initial oscillations, the two features are spectrally well-separated, and do not interfere. Diagram (I) creates a negative resonance around $\omega \sim 12,000 \text{ cm}^{-1}$, and diagram (II) a positive resonance at $\omega \sim 10,100 \text{ cm}^{-1}$.

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Figure 6.9.: a) Two-photon counting signal $S_{\text{TPC}}(\omega, t_0)$, Eq. (6.23), for $\omega_r = 9,000$ cm $^{-1}$ created by degenerate entangled photon pairs with entanglement time $T = 90$ fs, pump frequency $\omega_p = 22,000$ cm $^{-1}$, and pump bandwidth $\sigma_p = 2,000$ cm $^{-1}$. b) the same with reference frequency $\omega_r = 13,000$ cm $^{-1}$. c) Absolute value of the field correlation $f_{12}(\omega_r, \omega_b)$ with the light parameters of panels a) and b).

6.3.3. Two-photon counting setup

We now discuss the TPC signal of the RC,

$$S_{\text{TPC}}(t_0, \Gamma) = \frac{2}{\hbar^4} |E_a|^2 \Re \int \frac{d\omega_b}{2\pi} \langle E_2^\dagger(\omega_r) E_1^\dagger(\omega) E_1(\omega_b) E_2(\omega_r) \rangle \times \left(\tilde{F}_I(\omega_b, \omega; t_0) + \tilde{F}_{II}(\omega_b, \omega; t_0) \right), \quad (6.23)$$

which is given by the sum of the two correlation functions $\tilde{F}_I$, Eq. (6.19), and $\tilde{F}_{II}$, Eq. (6.20).

In the discussion of the TSJ model, we have seen that the coincidence detection of entangled photons can act as a “frequency filter”, which can enhance or suppress features of the signal. Having discussed the impulsive classical pump-probe signal of the bacterial RC, we can now investigate in detail how this filter affects the spectrum. Fig. 6.9 shows simulations of the two-photon counting signal of entangled photons with pump bandwidth $\sigma_p = 2,000$ cm $^{-1}$ and entanglement time $T = 90$ fs. Thus, the two photons have positive frequency correlations, as can be seen in panel c), where we depict the absolute value of the field correlation function $|f_{12}(\omega_r, \omega_b)|$ as a function of the reference frequency ω_r and of the frequency ω_b interacting with the sample [compare Eq. (6.23)]. By varying the reference frequency ω_r , we may select a specific range of frequencies along ω_b , from which the signal is selected. This is illustrated in panels a) and b), where we set the reference frequency to $\omega_r = 9,000$ cm $^{-1}$ (*i.e.* well below any excitonic resonance) or to $\omega_r = 13,000$ cm $^{-1}$ (above the resonances), respectively. The former choice selects the signal pertaining to the exciton $|e_5\rangle$, while the latter one selects the upper resonance band. In contrast to the impulsive signal before, we do not observe oscillatory signals in our simulations, as the finite time resolution (in contrast to the

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Figure 6.10.: a) Contribution of Eq. (6.19) to the two-photon counting signal $S_{\text{TPC}}(\omega, t_0)$, Eq. (6.23), for $\omega_r = 9,000 \text{ cm}^{-1}$, created by degenerate entangled photon pairs with entanglement time $T = 90 \text{ fs}$, pump frequency $\omega_p = 22,000 \text{ cm}^{-1}$, and pump bandwidth $\sigma_p = 2,000 \text{ cm}^{-1}$. b) Contribution of Eq. (6.20). c) Total signal $S_{\text{TPC}}(\omega, t_0)$, see Eq. (6.23).

impulsive limit discussed previously) washes out these oscillations. Instead, we observe in panel a) a negative feature for $t_0 \leq 50 \text{ fs}$, which then turns into an rising, positive signal, similar to its classical counterpart. Depicting the contributions of the individual diagrams separately in Figs. 6.10a) and b), we note that the negative feature stems from diagram (I). Its classical counterpart in Fig. 6.8a) also shows a negative resonance at this point, it is however cloaked by the oscillations at these small delay times. If we remove these oscillations in Fig. 6.11, we also observe the negative feature at small delays $t_0 \leq 50 \text{ fs}$. The positive feature resonance in Fig. 6.10c) at larger delay times is in agreement with the classical signal, and the timescale of its rise is also consistent. Hence, we can conclude that the two-photon counting does in fact resolve this resonance exclusively. The initially negative resonance is caused by the two-photon absorption diagram (I), as depicted in panel a) of Fig. 6.10. and the positive resonance is created by the Raman diagram (II) in panel b). Oscillatory contributions are destroyed by the finite time resolution of the twin photons.

However, we note that - whereas the negative and positive features in the classical pump-probe signal in Fig. 6.11 show up at the same frequency ω - the two are shifted, both on absolute frequency, and with respect to one another in the corresponding TPC signal in Fig. 6.9a). The resonance peaks between $\omega = 10,100 - 10,200 \text{ cm}^{-1}$, while the we would expect to see it at the transition frequency of the exciton state, $\omega_{e_5} = 10,245 \text{ cm}^{-1}$. Furthermore, the negative (TPA) resonance shows up at a slightly higher frequency ω , such that in the total signal in panel c) the negative features extend up to $t_0 \simeq 100 \text{ fs}$ on the high-frequency flank of the rising, positive (Raman) signal. A similar shift can also be observed in Fig. 6.9b):

The signal in Fig. 6.9b) only shows the resonance of the higher-energetic resonance band consisting mainly of the resonance at $|e_6\rangle$ (see Fig. B.1). We can see, however, that the resonances are shifted away from their real values: Panel b) shows the main

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Figure 6.11.: Close-up view of the lower energy part of the classical pump-probe signal in Fig. 6.8c), after subtracting the oscillatory features.

Figure 6.12.: Two-photon counting signal $S_{\text{TPC}}(\omega, t_0)$ for $\omega_r = 9,000 \text{ cm}^{-1}$ (a) or $\omega_r = 13,000 \text{ cm}^{-1}$ created by degenerate entangled photon pairs with entanglement time $T = 18 \text{ fs}$, pump frequency $\omega_p = 22,000 \text{ cm}^{-1}$, and pump bandwidth $\sigma_p = 2,000 \text{ cm}^{-1}$. c) Absolute value of the field correlation $f_{12}(\omega_r, \omega_b)$ with the field parameters of panels a) and b).

resonance at $\omega \sim 11,800 \text{ cm}^{-1}$, while we would expect to see it at $\omega_{e_6} = 11,908 \text{ cm}^{-1}$. Both shifts in panels a) and b) of Fig. 6.9 may be explained by the frequency correlations, as shown in the field correlation function Fig. 6.9c): While one of the two correlation functions f_{12} in the four-point correlation function in Eq. (6.12) couples ω_r and ω_b as depicted, the other function couples ω and ω_r . Hence, the selection of a specific (in the present case off-resonant) ω_r also “skews” the ω -axis, and thereby shifts the resulting resonance structure.

Fig. 6.12 again shows simulations of $S_{\text{TPC}}(\omega, t_0)$, Eq. (6.23), in panels a) and b), and the corresponding frequency correlation function $f_{12}(\omega_r, \omega_b)$. It is thus similar to Fig. 6.9, but here we consider frequency *anti-correlations* - with pump bandwidth $\sigma_p = 2,000 \text{ cm}^{-1}$ and entanglement time of 18 fs [as shown by the correlation function in Fig. 6.12c)]. Panels a) and b) again show signals with $\omega_r = 9,000$ and $13,000$

cm^{-1} , respectively. In stark contrast to the positive frequency correlations before, the anti-correlations ensure that only processes are possible in which the sum of the two frequencies, $\omega_r + \omega_b$, adds up to ω_p . Thus, panel a) shows the dynamics of the higher-energy manifold $|e_6\rangle - |e_{10}\rangle$ (see Fig. B.1), for which $\omega_r + \omega_{e_i} \sim \omega_p = 22,000 \text{ cm}^{-1}$, and panel b) the dynamics at $|e_5\rangle$, for which $\omega_r + \omega_{e_5} \sim 22,000 \text{ cm}^{-1}$ holds. The roles of the two panels is thus reversed compared to Fig. 6.9. Additionally, we observe a strong flank of the strongest resonance at $\omega \sim 11,900 \text{ cm}^{-1}$ towards higher energies in panel a), which was not resolved in the corresponding simulation with positive frequency correlations in Fig. 6.9b). Due to the shorter entanglement time $T = 18 \text{ fs}$ associated with the frequency anti-correlated regime, the time resolution has been enhanced. Hence, the evolution of the higher-energy band is resolved, even some (however weak) oscillations can be identified around $\omega \sim 12,100 \text{ cm}^{-1}$.

6.4. Summary

In this chapter, we investigated nonlinear pump-probe spectroscopy using a two-photon counting setup: One photon of an entangled pair interacts with a sample, while the other photon merely serves as a reference to exploit the quantum correlations shared between the two. The sample is first excited by classical laser pulses, and the time delay to the final photon detection is varied. In contrast to previous chapters, we employed photons with positive frequency correlations, where the high time resolution is obtained by an ultrafast pump pulse, and the frequency resolution is due to the phase-matching function inside the birefringent crystal, where the photons are created.

We saw that the frequency correlations of entangled photons may be used to enhance or suppress resonances by tuning the novel control parameters - the entanglement time, and the detection frequency of the reference photon - in our detection scheme. This may help resolve and better distinguish overlapping features in complex pump-probe spectra. Due to the interference between the reference frequency and the dispersed frequency in the signal, the obtained spectra are however not straightforward to interpret. The effect of the frequency correlations can be rationalized by viewing the two-photon counting setup as an additional frequency filter. By varying the reference frequency, different slices of the “full” classical signal are revealed. Hence, the role of quantum correlations in the present setting is very different from their roles in chapters 4 and 5: While in the former cases the time-frequency correlations of the entangled photonic wavefunction were exploited to enhance or suppress the excitation of specific states, here they are used to post-select parts of the broadband signal from one of the photons. In contrast to the simulation of the excited state population distributions in chapter 4, we did not investigate, whether entanglement is necessary for this setup. Already at the beginning of the chapter, we had speculated that the coincidence detection may be thought of as a “post-selection” of the signal, *i.e.* a classical concept. Hence, it may well be the case that entanglement does not offer an advantage in this setup.

7. Frequency conversion

So far, our treatment of quantum light has focussed on using entangled photon pairs for spectroscopic measurements. As we discussed, entangled photons may be created in optical nonlinear processes by the annihilation of a single pump photon in a medium showing a $\chi^{(2)}$ -nonlinearity, or by two pump photons in a $\chi^{(3)}$ -nonlinearity. However, downconversion constitutes but one of many nonlinear wave-mixing processes which are commonly employed in quantum optics (see, e.g., [Boyd03]). The goal of this chapter is to point out that other nonlinear processes may also induce quantum correlations between different light fields, and that these correlations may, in principle, be observed in appropriate experimental setups. In this sense, the chapter puts our previous results in a broader perspective: The entangled photon pairs discussed before constitute one example of a broader class of quantum-correlated light fields, which could be used for spectroscopic purposes.

At the current stage, this chapter cannot present a comprehensive investigation of the stated goal. It is merely a first step in the investigation of the possible use of quantum correlations induced by parametric processes (other than downconversion) in spectroscopy, and summarizes the state of the work to date. Sometimes we simply refer to results in the literature, and some of the results may not be presented in the most accessible way. This chapter therefore will have to be complemented by subsequent publications, which could not be finished in the course of this dissertation.

Specifically, we here consider *frequency conversion* (FC) [Huang92] - a process, in which a photon from an incoming seed pulse is shifted in frequency, due to the interaction with a second pump pulse. We will see that the FC Hamiltonian has a very similar structure to the downconversion Hamiltonian (A.1), only the roles of the different fields are interchanged. The basic setup is depicted in Fig. 7.1. Due to the interaction of the two beams via the $\chi^{(2)}$ -nonlinearity of the crystal, a photon of the seed pulse with frequency ω_a can be destroyed, and a new photon in the field E_2 with frequency $\omega_a \pm \omega_p$ created (hence, shifted in frequency). This process is of great importance in photonic quantum computation where it constitutes an important building block in the development of photonics-based quantum networks [Cirac97], e.g., to effectively couple entangled photons with matter degrees of freedom or to couple them to optical fibers [McGuinness10, Ates12, Ikuta13, Christ13b]. In these applications, it is typically desirable to conserve specific properties of the annihilated photon, such as its polarization state, as faithfully as possible, and therefore one aims to carry out FC in the single-mode regime [McKinstry12, Reddy13]. Here, we will investigate the opposite regime, where many modes contribute to the FC process.

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Figure 7.1.: Setup of the FC experiment we discuss in this chapter: By virtue of the interaction with a strong narrowband pump field E_p in a birefringent crystal, part of a seed pulse E_1 is shifted in frequency, and emitted as a second pulse E_2 . Due to energy and momentum conservation in the crystal, the two fields may be correlated.

7.1. Frequency Conversion Hamiltonian

Our main goal will be to demonstrate how the multimode nature of the FC process is reflected in the output fields, and what correlations are created between the fields via the FC. We start with the basic interaction Hamiltonian for the FC process in a collinear setup [Christ13b],

$$H_{\text{FC}}(t) = \int_{L/2}^{L/2} dz \chi^{(2)}(z) E_p(z, t) E_1(z, t) E_2^\dagger(z, t) + h.c., \quad (7.1)$$

which describes a nonlinear optical process in which two photons in the strong, classical pump field $E_p(\omega'_p)$ and in the (quantum) field $E_1(\omega_a)$ are destroyed, and a photon in the field $E_2(\omega_c)$ is created (as well as the inverse process). This process is commonly referred to as *sum frequency generation* [Boyd03]:¹ Energy conservation tells us that we have for any such process [compare Eq. (2.4) for PDC]

$$\omega_c = \omega_a + \omega'_p, \quad (7.2)$$

where the distribution of ω_a is determined by the seed pulse amplitude (or, more generally, its quantum state), and ω'_p by the pump pulse amplitude. The ω_c -distribution is therefore determined by these two input distributions, and the phase matching inside the crystal, as we will specify in the following.

In Eq. (7.1), the spatial integration covers the length L of the crystal in propagation direction (see our discussion of the downconversion Hamiltonian (A.1) in appendix A),

¹By injecting the seed pulse in field E_2 , one could also lower the frequency of an incident photon (*difference frequency generation*).

7.1. Frequency Conversion Hamiltonian

and $\chi^{(2)}(z)$ denotes the nonlinear coupling inside the crystal, which, for the sake of simplicity, we take to be spatially homogeneous, $\chi^{(2)}(z) = \chi^{(2)}$. This Hamiltonian bears close similarity to the Hamiltonian (A.1), which serves as the starting point for our derivation of the entangled photon pairs in appendix A. Our present derivation therefore closely follows similar calculations in the appendix, and we employ the same notation: Just like in Eq. (A.1), E_p denotes the classical pump field, and E_1 and E_2 the two quantum fields in the FC process.

For the sake of simplicity, we shall only consider the weak conversion limit, in which the output state of the FC process may be obtained perturbatively,

$$|\psi_{\text{out}}\rangle \approx |\psi_{\text{in}}\rangle - \frac{i}{\hbar} \int_{-\infty}^{\infty} dt H_{\text{FC}}(t) |\psi_{\text{in}}\rangle, \quad (7.3)$$

where, in choosing the time integration boundaries $\pm\infty$, we restrict our attention to the asymptotic state long after the interaction in the crystal. Decomposing the three fields in Eq. (7.1) in their frequency components, and integrating over t , we obtain [Christ13b, Brecht14]

$$|\psi_{\text{out}}\rangle = |\psi_{\text{in}}\rangle + H_{\text{eff}} |\psi_{\text{in}}\rangle, \quad (7.4)$$

with the effective Hamiltonian

$$H_{\text{eff}} = \int d\omega_a \int d\omega_c f(\omega_a, \omega_c) a_1(\omega_a) a_2^\dagger(\omega_c) + h.c. \quad (7.5)$$

Here, the spectral envelope $f(\omega_a, \omega_c)$ represents the amplitude for a process in which a photon with frequency ω_a is converted into a photon with frequency ω_c (and the inverse process). It is given by [Christ13b]

$$f(\omega_a, \omega_c) = \alpha A_p(\omega_c - \omega_a) \text{sinc}(\Delta k(\omega_a, \omega_c)L/2), \quad (7.6)$$

where $\alpha \propto \chi^{(2)}$ denotes the strength of the downconversion process, A_p denotes the pump field envelope, and $\Delta k(\omega_a, \omega_c)$ the phase mismatch, *i.e.* the phase between a photon with frequency ω_a propagating in E_1 , and another photon with ω_c propagating in field E_2 . Note that the phase matching function in Eq. (7.6) shows close similarities to its counterpart in downconversion, Eq. (A.6): The difference $\omega_c - \omega_a$ between the two frequencies [in contrast to their sum in Eq. (A.6)] is controlled by the pump envelope A_p . In addition, the bandwidth properties of the created photon are controlled independently by the sinc-function, in which the phase mismatch $\Delta k(\omega_a, \omega_c)$ appears.

The phase mismatch in this process may be expanded around the central frequencies of the three pulses involved, ω_p, ω_1 , and $\omega_2 = \omega_1 + \omega_p$, yielding [Christ13b]

$$\Delta k(\omega_a, \omega_c) \approx (\omega_c - \omega_1 - \omega_p)T_2/L - (\omega_a - \omega_1)T_1/L, \quad (7.7)$$

where $T_1 = (dk_p/d\omega - dk_a/d\omega)L$, $T_2 = (dk_p/d\omega - dk_c/d\omega)L$ denote the maximal time delay photons with frequencies ω_p and with ω_1 or ω_2 acquire in the course of their propagation through the nonlinear crystal (see the discussion in section A.1.1). In the following, we will use the same values for the two parameters T_1 and T_2 that we employed in

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the case of parametric downconversion in the previous chapter, *i.e.* $T_1 = 0.00007(T/fs)$ cm, and $T_2 = 0.00025(T/fs)$ cm (see chapter 4). Using the Schmidt decomposition of this phase-matching function,²

$$-\frac{i}{\hbar}f(\omega_a, \omega_c) = \sum_k r_k \psi_k(\omega_a) \phi_k^*(\omega_c), \quad (7.8)$$

we can obtain the Schmidt modes defined by the operators

$$A_k = \int d\omega_a \psi_k(\omega_a) a_1(\omega_a), \quad (7.9)$$

$$\text{and } C_k = \int d\omega_c \phi_k(\omega_c) a_2(\omega_c). \quad (7.10)$$

The electric fields may also be written in this new basis as [compare Eqs. (A.24) and (A.25)]

$$E_1(\omega) = \sum_k \psi_k^*(\omega) A_k, \quad (7.11)$$

and

$$E_2(\omega) = \sum_k \phi_k^*(\omega) C_k. \quad (7.12)$$

In the following, we focus on the scenario depicted in Fig. 7.1, where the initial state only populates field E_1 , while field E_2 is initially in the vacuum state. We may then write Eq. (7.4) as

$$|\psi_{\text{out}}\rangle = |\psi_{\text{in}}\rangle_1 + \sum_k r_k A_k |\psi_{\text{in}}\rangle_1 \otimes C_k^\dagger |0\rangle_2. \quad (7.13)$$

In general, the second term in Eq. (7.13) describes an entangled state of the two fields, as the photon annihilation A_k in a (random) mode k of field 1 determines the photon creation $C_k^\dagger$ in mode k of field 2, and it will be the main goal in the remainder of this chapter to examine, whether (and if so, how) this nonseparability of the wavefunction may show up in spectroscopic measurements. It is clear that, if the seed pulse is in a coherent state, and we may replace the annihilation operators A_k by amplitudes α_k , the second terms factorizes into the unperturbed, coherent seed pulse, and a separable single photon state,

$$|\psi_{\text{out}}^{\text{coh}}\rangle = |\psi_{\text{in}}^{\text{coh}}\rangle_1 \otimes \left(1 + \sum_k \alpha_k C_k^\dagger \right) |0\rangle_2. \quad (7.14)$$

²Using the approach employed in section A.1.3, *i.e.* by approximating the sinc-function in Eq. (7.6) by a Gaussian, we may use the identity (A.28) to find the Schmidt modes in terms of Hermite functions.

Hence, in close analogy to the situation in the two-photon absorption we discussed in section 4.1, we only observe correlations between the two fields, if the annihilation of a photon from the seed pulse changes its quantum state. The back-action of the nonlinear process of the FC process on the seed pulse is a necessary predicament to observe correlations between the two output fields.

To briefly summarize, our analysis thus shows that on a formal level, FC and down-conversion are described by very similar Hamiltonians, and their output fields may be calculated in a similar fashion. This would imply that we could employ our intuition from the previous chapters to analyze the FC output state (7.13). There is however one crucial difference: In the downconversion process, two photons are created in the vacuum, and they immediately reveal their nonclassical properties in their entangled multimode structure (We have not considered squeezed, coherent states [Scully97] in this dissertation). In the current setup however, one photon is destroyed in an initially populated mode, and a new one created in the vacuum. Therefore, the multimode nature of the FC process will create correlations between the destroyed photon, *i.e.* the “photon hole”, in the input state and the newly created photon in the third mode.

We will now examine the field correlation functions induced by the state $|\psi_{\text{out}}\rangle$, Eq. (7.13), and how they depend on the seed pulse, described by $|\psi_{\text{in}}\rangle$.

7.2. Field correlation functions

7.2.1. Two-point correlation function

This section will evaluate field correlation functions of the state (7.13). With the specification of the seed pulse $|\psi_{\text{in}}\rangle$, we can write these in terms of correlation functions of $|\psi_{\text{in}}\rangle$. In a second step, we will then discuss several exemplary input states.

We start with the two-point correlation function of the total outgoing field, $E = E_1 + E_2$,

$$\begin{aligned} & \langle \psi_{\text{out}} | E^\dagger(\omega) E(\omega') | \psi_{\text{out}} \rangle \\ &= \langle \psi_{\text{out}} | E_1^\dagger(\omega) E_1(\omega') | \psi_{\text{out}} \rangle + \langle \psi_{\text{out}} | E_2^\dagger(\omega) E_2(\omega') | \psi_{\text{out}} \rangle \\ &+ \langle \psi_{\text{out}} | E_1^\dagger(\omega) E_2(\omega') | \psi_{\text{out}} \rangle + \langle \psi_{\text{out}} | E_2^\dagger(\omega) E_1(\omega') | \psi_{\text{out}} \rangle \end{aligned} \quad (7.15)$$

The second line of Eq. (7.15) consists of the autocorrelation functions of the individual fields $\langle E_1^\dagger E_1 \rangle$ and $\langle E_2^\dagger E_2 \rangle$, and is, as such, not of interest for us. The third line, on the other hand, describes cross-correlations between the two output fields, which could be of interest for our purposes.

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Using Eq. (7.13), as well as the electric field definitions (7.11) and (7.12), we obtain

$$\langle \psi_{\text{out}} | E_1^\dagger(\omega) E_2(\omega') | \psi_{\text{out}} \rangle = \sum_{k,k'} \psi_k(\omega) \phi_{k'}^*(\omega') \langle \psi_{\text{out}} | A_k^\dagger C_{k'} | \psi_{\text{out}} \rangle \quad (7.16)$$

$$= \sum_{k,k',k''} r_{k''} \psi_k(\omega) \phi_{k'}^*(\omega') \langle \psi_{\text{in}} |_1 A_k^\dagger A_{k''} | \psi_{\text{in}} \rangle_1 \langle 0 |_2 C_{k'} C_{k''}^\dagger | 0 \rangle_2 \quad (7.17)$$

$$= \sum_{k,k'} r_{k'} \psi_k(\omega) \phi_{k'}^*(\omega') \langle \psi_{\text{in}} |_1 A_k^\dagger A_{k'} | \psi_{\text{in}} \rangle_1, \quad (7.18)$$

where in the second step, we used the fact that only the first term of Eq. (7.13) in the *bra* and the second term in the *ket* yield the only nonvanishing correlation function for the field E_2 , $\langle 0 |_2 C_{k'} C_{k''}^\dagger | 0 \rangle_2 = \delta_{k',k''}$.

Let us consider, for instance, a separable two-photon state as a seed pulse, which we write as

$$|\psi_{\text{in}}^{(1)}\rangle = \frac{1}{\sqrt{2}} \left(\sum_k c_k A_k^\dagger \right)^2 |0\rangle, \quad (7.19)$$

with $\sum_k |c_k|^2 = 1$. Using Eq. (7.19), we obtain

$$\langle \psi_{\text{in}}^{(1)} |_1 A_k^\dagger A_{k'} | \psi_{\text{in}}^{(1)} \rangle_1 = 2 \sum_k |c_k|^2 \delta_{k,k'}, \quad (7.20)$$

such that Eq. (7.18) reads

$$\langle \psi_{\text{out}} | E_1^\dagger(\omega) E_2(\omega') | \psi_{\text{out}} \rangle = 2 \sum_k r_k \psi_k(\omega) \phi_k^*(\omega') |c_k|^2. \quad (7.21)$$

Eq. (7.21) shows perfect correlations between the two fields: If the first interaction (of E_2) occurs with mode k , so does the second interaction (with E_1).

Hence, Eq. (7.21) demonstrates our initial assumption [see Eq. (7.13)] that there are correlations between the two fields, and this correlation is determined by the field correlation function $\langle \psi_{\text{in}} |_1 A_k^\dagger A_{k'} | \psi_{\text{in}} \rangle_1$ of field E_1 . Using our experience from chapter 3, one could imagine that a two-point correlation function such as Eq. (7.21) could be related to a linear absorption experiment: In section 3.6.1, we derived such an expression [see Eq. (3.146)]. However, this will not work: Eq. (3.146) is related to the correlation functions

$$\sim \langle g | V(t) V^\dagger(\tau_1) | g \rangle \langle E^\dagger(t) E(\tau_1) \rangle. \quad (7.22)$$

Hence, to see an impact of Eq. (7.21) in such an expression, the first interaction with E_2 would have to excite the system from the ground state $|g\rangle$ to some excited state $|e\rangle$, and E_1 (which, by construction, is shifted in frequency by $-\omega_p$ with respect to E_2) would have to bring the system back into the ground state. So this process cannot work due to energy conservation!

7.2.2. Four-point correlation function

Instead, we have to resort to nonlinear optical processes - especially, Raman scattering. These are related to the four-point correlation function of the field [see Eq. (3.172)],

$$\langle \psi_{\text{out}} | E_2^\dagger(\omega'_a) E_1(\omega'_c) E_1^\dagger(\omega_c) E_2(\omega_a) | \psi_{\text{out}} \rangle, \quad (7.23)$$

and we will try to obtain contributions similar to Eq. (7.21) in this higher-order correlation function.

We first evaluate the four-point correlation function for general seed pulses,

$$\begin{aligned} & \langle \psi_{\text{out}} | E_2^\dagger(\omega'_a) E_1(\omega'_c) E_1^\dagger(\omega_c) E_2(\omega_a) | \psi_{\text{out}} \rangle \\ &= \sum_{k,k'} r_k r_{k'} \langle \psi_{\text{in}} |_1 A_k^\dagger E_1(\omega'_c) E_1^\dagger(\omega_c) A_{k'} | \psi_{\text{in}} \rangle_1 \langle 0 |_2 C_k E_2^\dagger(\omega'_a) E_2(\omega_a) C_{k'}^\dagger | 0 \rangle_2 \end{aligned} \quad (7.24)$$

$$= \sum_{k,k'} r_k r_{k'} \phi_k(\omega'_a) \phi_{k'}^*(\omega_a) \langle \psi_{\text{in}} |_1 A_k^\dagger E_1(\omega'_c) E_1^\dagger(\omega_c) A_{k'} | \psi_{\text{in}} \rangle_1 \quad (7.25)$$

$$= \sum_{k,k'} r_k r_{k'} \psi_k(\omega'_a) \psi_{k'}^*(\omega_a) \sum_{k_1, k_2} \phi_{k_1}^*(\omega'_c) \phi_{k_2}(\omega_c) \langle \psi_{\text{in}} |_1 A_k^\dagger A_{k_1} A_{k_2}^\dagger A_{k'} | \psi_{\text{in}} \rangle_1 \quad (7.26)$$

Ideally, we would like to obtain a correlation function, for which the four-point correlation function factorizes as such:

$$\langle \psi_{\text{in}} |_1 E_2^\dagger E_1 E_1^\dagger E_2 | \psi_{\text{in}} \rangle_1 \propto \langle E_2^\dagger E_1 \rangle \langle E_1^\dagger E_2 \rangle, \quad (7.27)$$

which would give us a product of the two-point correlation functions obtained above. This is however not straightforward to achieve: First, we note that Eq. (7.23) is not normally ordered. This means that we will also obtain contributions from the commutator of the field E_1 , *i.e.* $[E_1(\omega'_c), E_1^\dagger(\omega_c)]$. But of course, these cannot be related to correlations between the two fields, so we will not consider them in the following. Furthermore, it is clear that any pure two-photon state of the form (7.19) cannot provide the desired factorization (7.27), since the four-point correlation function of any two-photon state factorizes as discussed in Eq. (4.34). So we will need a different seed pulse to achieve this.

In stead of a pure two-photon state, we therefore try an incoherent superposition state,

$$\varrho_{\text{incoh}} = \frac{1}{2} \sum_{k,k'} |c_k|^2 |c_{k'}|^2 A_k^\dagger A_{k'}^\dagger | 0 \rangle \langle 0 | A_k A_{k'}, \quad (7.28)$$

for which a straightforward calculation yields, using Eq. (7.26),

$$\begin{aligned} & \text{tr} \left\{ E_2^\dagger(\omega'_a) E_1(\omega'_c) E_1^\dagger(\omega_c) E_2(\omega_a) \right\} \\ &= \sum_k r_k^2 |c_k|^2 \phi_k(\omega'_a) \phi_k^*(\omega_a) \sum_{k'} |c_{k'}|^2 \psi_{k'}(\omega_c) \psi_{k'}^*(\omega'_c) \end{aligned} \quad (7.29a)$$

$$+ \sum_k r_k |c_k|^2 \phi_k(\omega'_a) \psi_k^*(\omega'_c) \sum_{k'} r_{k'} |c_{k'}|^2 \phi_{k'}^*(\omega_a) \psi_{k'}(\omega_c). \quad (7.29b)$$

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Figure 7.2.: Level scheme for the detection of FC correlations. A photon from field E_2 is transferred to field E_1 via stimulated Raman scattering off the intermediate state $|e\rangle$.

The first line, Eq. (7.29a), consists of contributions in which the two fields E_1 and E_2 (respectively, the corresponding Schmidt mode functions ψ_k and ϕ_k) are not correlated. But the second line, Eq. (7.29b), shows the same desired structure as the two-point correlation function (7.21), which correlates the two fields. In the following, we shall discuss properties of this function, and neglect Eq. (7.29a).³

7.3. Transition amplitudes

We will now demonstrate that the FC correlations may be revealed in measurements which reverse the FC process, *i.e.* which destroy a photon from field E_2 and create one in field E_1 , which can be achieved by stimulated Raman scattering. We had already discussed Raman scattering in section 3.4 with classical laser pulses, and - more importantly - in section 3.6 for general quantum fields. In the following, we will consider the simple model system depicted in Fig. 7.2, which will allow us to simplify Eq. (3.172): We recall that the Raman signal is given by two terms,⁴

$$S_{\text{Raman}}^{(3)} = \sum_{g'} \langle |T_{g'g}^{(2)}(\omega_{g'})|^2 \rangle - 2\Re \langle T_{eg}^{(1)\dagger}(\omega_e) T_{eg'}^{(3)}(\omega_e) \rangle. \quad (7.30)$$

Here, the latter term $\Re \langle T_{eg}^{(1)\dagger}(\omega_e) T_{eg'}^{(3)}(\omega_e) \rangle$ describes transitions from the ground state $|g\rangle$ to an electronic excited state $|e\rangle$. For the present study, we only consider the situation depicted in Fig. 7.2, where the electronic transition is far off-resonant with respect to

³We need to stress again that this chapter merely present preliminary work, and does not aspire to present a comprehensive study of frequency-correlated light. Eq. (7.28) merely represents a possible scenario, in which the desired structure of the four-point correlation function may be observed.

⁴In our model system, Fig. 7.2, there are no two-exciton states, and consequently, there are no TPA-pathways, Eq. (3.169).

the center frequencies of the two light fields E_1 and E_2 . This means, transitions to the excited state $|e\rangle$ may be neglected. The first term in Eq. (7.30), $\sum_{g'} \langle |T_{g'g}^{(2)}(\omega_{g'})|^2 \rangle$, describes transitions from the ground state $|g\rangle$ to another vibrational state $|g'\rangle$, and those transitions are resonant with a two-photon transition. The corresponding transition amplitude is given by Eq. (3.170), which we may write in our case as

$$T_{g'g}^{(2)}(\omega) = \frac{1}{\hbar} \int \frac{d\omega_a}{2\pi} \frac{\mu_{ge}\mu_{eg'}}{\omega_a - \omega_e + i\eta} E_1^\dagger(\omega_a - \omega) E_2(\omega_a). \quad (7.31)$$

Here, we used the fact that the frequency of field E_2 is increased by the pump frequency ω_p with respect to the seed pulse E_1 [see Eq. (7.1)]. Hence, only the process in which a photon from E_2 is absorbed, and reemitted into E_1 is resonant with the $|g\rangle \rightarrow |g'\rangle$ transition. Since the single-photon transitions are all off-resonant, we may further replace the Lorentzian by the detuning Δ of the pulses with respect to the electronic transition, and remove it from the frequency integration [see our discussion of Raman amplitudes in section 3.4.1, especially following Eq. (3.95)]. Thus, the final signal reads

$$S_{\text{Raman}}(\Gamma) = |\alpha_{g'g}|^2 \int \frac{d\omega_a}{2\pi} \int \frac{d\omega'_a}{2\pi} \langle E_2^\dagger(\omega'_a) E_1(\omega'_a - \omega_{g'g}) E_1^\dagger(\omega_a - \omega_{g'g}) E_2(\omega_a) \rangle, \quad (7.32)$$

where we defined the polarizability $\alpha_{g'g} = \mu_{ge}\mu_{eg'}/(\hbar\Delta)$, and the brackets $\langle \dots \rangle$ denote the average with respect to the output field state, with the seed pulse (7.28).

7.4. Simulations

We now simulate the frequency-resolved Raman signal (7.32) using a simple model system with four vibrational states with energies of 2,000 cm⁻¹, 2,100 cm⁻¹, 2,150 cm⁻¹, and 2,220 cm⁻¹,⁵ and which are connected to the excited electronic state with identical dipole moments (different dipole moments would only change the relative height of the corresponding resonances in the final signal). In contrast to the previous chapters, we do not include fluctuations of the energy levels, which would broaden their resonances [compare, e.g., the finite γ_e and γ_f in Eqs. (4.32) or (5.13)]. Hence, the width of the pump pulse σ_p will be the only broadening mechanism here.

In our simulations, we use the field correlation function (7.29b), where we choose a particularly simple form of the seed pulse (7.28), with $c_k = 1/\sqrt{70}$ for $k = 1 \dots 70$ and 0 otherwise⁶. Eq. (7.29b) thus take on a particularly simple form,

$$\begin{aligned} & \text{tr} \left\{ E_2^\dagger(\omega'_a) E_1(\omega'_c) E_1^\dagger(\omega_c) E_2(\omega_a) \right\} \\ &= \frac{1}{70^2} \tilde{f}(\omega_a, \omega_c) \tilde{f}^*(\omega'_a, \omega'_c), \end{aligned} \quad (7.33)$$

⁵In the present setting, we are restricted to pump frequencies ω_p for which the crystal is still transparent, *i.e.* at higher energies than its phonons. This restricts us to $\omega_p \geq 2,000$ cm⁻¹. If we were interested in smaller pump frequencies, we would need to look for different conversion processes such as four-wave mixing in a $\chi^{(3)}$ -nonlinearity.

⁶How such a seed pulse could be created shall not be our concern here. As we have seen in its derivation, its four-point correlation function shows the desired structure.

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Figure 7.3.: a) Correlation function $\tilde{f}(\omega_a, \omega_c)$, Eq. (7.34), with a pump bandwidth $\sigma_p = 10 \text{ cm}^{-1}$ and “entanglement time” $T_2 - T_1 = 10 \text{ fs}$. b) Same for $\sigma_p = 50 \text{ cm}^{-1}$ and $T_2 - T_1 = 100 \text{ fs}$.

where we defined

$$\tilde{f}(\omega_a, \omega_c) = \sum_{k=1}^{70} r_k \phi_k(\omega_a) \psi_k^*(\omega_c), \quad (7.34)$$

in which the correlations between the ψ_k ’s and the ϕ_k ’s should become most clearly observable [compare Eq. (7.8)]. The correlation function $\tilde{f}(\omega_a, \omega_c)$ is depicted in Fig. 7.3 for two different sets of parameters: Panel a) shows the correlation function with a very narrow pump pulse, $\sigma_p = 10 \text{ cm}^{-1}$, and with maximal temporal walk-off between the two photons [see Eq. (7.7)] $T_2 - T_1 = 10 \text{ fs}$.⁷ This setting creates strong *positive* correlations between the two frequencies ω_a and ω_c : If the first interaction takes place with frequency ω' , the other photon collapses onto the narrow frequency window $\omega' - \omega_p$ with the width $\sim \sigma_p$. In panel b), the same correlation function is shown with $\sigma_p = 50 \text{ cm}^{-1}$, and $T_2 - T_1 = 10 \text{ fs}$, which reduces the strength of the frequency correlations, and further reduces the marginals (*i.e.* bandwidth of each of the two frequencies). When comparing this behavior to entangled photons (Fig. A.4), we note that our two control parameters σ_p and $T_2 - T_1$ play exactly the same role in controlling the frequency correlations as did the pump bandwidth and the entanglement time in controlling the time-energy entanglement of the photon pairs (see the respective discussion in section A.3.2).

⁷ We recall that, in the case of parametric downconversion, $T = T_2 - T_1$ defined the entanglement time, see Eq. (A.11). This present situation is evidently more complicated than in the previous case, as the correlation function also depends on the seed pulse, and we refrain from using this nomenclature in the present setting.

Figure 7.4.: Raman signal (7.32) induced by the correlation function (7.33), with “entanglement time” $T_2 - T_1 = 10$ fs and pump bandwidth $\sigma_p = 10 \text{ cm}^{-1}$, 30 cm^{-1} , and 50 cm^{-1} , as indicated. The solid vertical lines indicate the vibrational state energies in the model system, $\omega_{g'} = 2,000, 2,100, 2,150$, and $2,220 \text{ cm}^{-1}$.

We now simulate the Raman signal (7.32) with the model system discussed above in Fig. 7.4. The phase mismatch, *i.e.* the pulse bandwidth, is fixed at $T_2 - T_1 = 10$ fs, and we simulate the signal for three different pump bandwidths $\sigma_p = 10 \text{ cm}^{-1}$, 30 cm^{-1} , and 50 cm^{-1} . Clearly, as could be expected from our previous discussion of the correlation function, the Raman signal resolves the different vibrational states of our model system, and the frequency resolution is determined by the pump bandwidth σ_p - and not the larger photon bandwidth.

Our previous experience with the correlation functions of entangled photons, especially our discussion in chapter 4, tells us that the broad bandwidth along the diagonal in Fig. 7.3 should correspond to good time resolution along a time axis corresponding to the Fourier transform of this frequency axis. Our simple model system cannot account for such an effect. To nevertheless lend some plausibility to our conjecture, that the observed behavior is a quantum effect, we finally depict a classical correlation function created by a coherent seed pulse populating the first seventy Schmidt modes [which thus reproduces approximately the bandwidth in Fig. 7.3a)] in Fig. 7.5. Using Eq. (7.14), the correlation function factorizes into uncorrelated summations,

$$\begin{aligned} & \text{tr} \left\{ E_2^\dagger(\omega'_a) E_1(\omega'_c) E_1^\dagger(\omega_c) E_2(\omega_a) \right\} \\ &= \sum_{k=1}^{70} \psi_k(\omega_c) \sum_{k'=1}^{70} \psi_k^*(\omega'_c) \sum_{k''=1}^{70} r_{k''} \phi_{k''}^*(\omega_a) \sum_{k'''=1}^{70} r_{k'''} \phi_{k'''}^*(\omega'_a). \end{aligned} \quad (7.35)$$

7. Frequency conversion

Figure 7.5.: a) Four-point correlation function (7.35) depicted along the frequencies ω_a and ω_c with $T_2 - T_1 = 10$ fs and $\sigma_p = 10$ cm^{-1} [corresponding to the parameters in Fig. 7.3a)]. b) Raman signal (7.32) induced by the correlation function (7.35) with $T_2 - T_1 = 10$ fs and $\sigma_p = 10, 30$, and 50 cm^{-1} (same as in Fig. 7.4). The solid vertical lines indicate the vibrational state energies in the model system, $\omega_{g'} = 2,000, 2,100, 2,150$, and $2,220$ cm^{-1} .

Hence, by simply looking at the correlation function, we may conclude that there are no quantum correlations present: A measurement of any frequency, say ω_a , does not influence the frequency distribution of the other arguments at all. This is demonstrated in Fig. 7.5a), where we depict the field correlation function (7.35) as a function of the two frequencies ω_a and ω_c , to compare it with the field correlation function (7.33) induced by the input state (7.28). The parameters for the FC process are the same as in Fig. 7.3a). Clearly, the factorization of the correlation function (7.35) into four different summations is reflected in a symmetric structure in Fig. 7.5a), and a measurement of ω_a cannot influence a subsequent measurement of ω_c .

Consequently, the Raman signal (7.32) induced by the factorizing correlation function (7.35) is determined by the larger bandwidth of the two fields E_1 and E_2 : In Fig. 7.5b), we depict the Raman signal for the same parameters of the FC process as in Fig. 7.4, *i.e.* with $T_2 - T_1 = 10$ fs and pump bandwidths $\sigma_p = 10, 30$ and 50 cm^{-1} , and clearly shows a much broader resonance structure than before. This demonstrates that the two fields do not show the same frequency correlations as before, when the seed pulse is a coherent state.⁸

⁸The bandwidth in Fig. 7.5 is not much larger than the pump bandwidth. This stems from our choice of the input state, which populates the first 70 Schmidt modes with equal strength $|\psi_{\text{in}}^{\text{coh}}\rangle = \sum_k^{70} D_k(\alpha)|0\rangle$, where D_k denotes the displacement operator in mode k [Loudon00]. Due to the large weight of Schmidt modes with large k , this state features a rather narrow distribution around its center frequency (which dominates the optical response), and long frequency tails (which are seen as

7.5. Summary

We have investigated the correlations between two fields that are mixed by a frequency conversion process. It was shown that there are no correlations in case the seed pulse is in a coherent state, but that there may be strong correlations in the case of an incident Fock state. We further demonstrated how these correlations may show up in Raman measurements, even though we have not explicitly demonstrated their time correlations. Our discussion also showed that the choice of the input state is not trivial, and we gave one possible example, which shows the cross-correlations between the two fields.

In a broader context, these results indicate that new effects arise in nonlinear optics, when the quantum character of the fields is accounted for: The present correlations between the output fields can only be observed, when the back-action of the conversion process on the seed pulse is accounted for [see Eq. (7.14)], and may not be observed, in particular, when the seed pulse is a coherent (*i.e.* classical) state [see Eq. (7.14)]. In the present preliminary study, we did not investigate whether the correlations are quantum or classical in nature. The comparison with section 4.1, where the back-action was shown to be the essential distinction between quantum and classical light in two-photon absorption processes, tempts one to assume that the correlations are indeed *quantum* correlations. This conjecture will need to be investigated in future work.

weak modulations around the central peak in panel a) of Fig. 7.5).

8. Trapped ion spectroscopy

The results presented in this chapter were obtained in collaboration with Manuel Gessner, so a similar presentation thereof can be found in [Gessner15].

So far, we have been concerned with the development of novel spectroscopic techniques to investigate the dynamics of complex quantum systems such as molecular aggregates. This final chapter will present novel protocols to obtain nonlinear spectroscopic signals in a very different setup - namely in linear chains of trapped ions.¹ The goal in this chapter is to provide a versatile toolbox to probe and to characterize the emergent complexity in such well-controlled systems. In strong contrast to the spirit of tomographic methods in quantum information, these methods do not intend to characterize the full quantum state of the system, but instead to tailor custom-fit measurement protocols to investigate desired processes or properties of the system. The crucial ingredient in this undertaking is the use of ladder diagrams, which yield the intuition necessary to estimate the information content of the created signals *beforehand*.

As possible applications, we will put our main emphasis on transport studies in such systems. Recent advances allow for the creation or annihilation of local phonons, and to monitor their spreading along the chain [Ramm14]. This opens up the possibility to study energy and heat transfer in these one-dimensional systems, and proper tools to systematically probe and analyze these transport mechanisms are required. Specifically, we shall be concerned with the question, whether quantum coherence is involved in the transport process. Furthermore, we will consider the excited state dynamics near quantum phase transitions, the detection of anharmonicities, and of steady state currents.

The chapter is structured as follows: We first introduce the Hamiltonians that we will work with, and briefly remind the reader of the construction of nonlinear measurement protocols in the impulsive limit. Then we describe possible applications in three-pulse schemes (two excitation pulses and one readout pulse), followed by five-pulse schemes.

In contrast to previous chapters, all simulations were carried out using the *Qutip* package in Python [Johansson13]. The color code employed in this chapter is shown in Fig. 8.1.

8.1. Trapped ion systems

As described earlier in section 3.4, both the electronic and the vibrational degrees of freedom of a trapped ion chain may be manipulated, and we had further derived effective

¹We trust that these protocols are equally applicable to similar synthetic quantum systems such as, e.g., cold atoms in optical lattices [Bloch08], or Rydberg atoms in optical tweezers [Saffman10, Fuhrmanek11].

8. Trapped ion spectroscopy

Figure 8.1.: Color scheme employed in this chapter. When we depict absolute values, dark blue corresponds to zero signal, otherwise to the normalized minimum value.

interaction operators for both cases. In this section, we briefly describe the Hamiltonians used in the course of this chapter.

8.1.1. Motional degrees of freedom

When a single ion is trapped in a RF-potential (see Fig. 2.9), the trap may be approximately described by a harmonic potential. When N ions are trapped in a single (linear) trap, they repel each other due to their Coulomb interaction, while still sitting in the common trap potential. As long as any displacements with respect to their equilibrium positions are small compared to their respective distances, the motional degrees of freedom of this system can be described by a tight-binding-type Hamiltonian [Porras04a]. We consider in the following the vibrations in the x-direction (*i.e.* transverse to the ion chain's axis; compare Fig. 2.9)

$$H_{\text{vib}} = \hbar \left(\sum_{k=1}^N \omega_k^{(0)} a_k^\dagger a_k + \sum_{k < l} t_{kl} (a_k^\dagger a_l + a_l^\dagger a_k) + U \sum_{k=1}^N a_k^{\dagger 2} a_k^2 \right), \quad (8.1)$$

where the site energies $\omega_k^{(0)}$ and tunnel rates, t_{kl} , between sites k and l are given by [Porras04a]

$$\omega_k^{(0)}/\nu_x = 1 - \frac{\beta_0}{2} \sum_{l \neq k} \frac{1}{|u_k - u_l|^3}, \quad (8.2)$$

$$t_{kl}/\nu_x = \frac{\beta_0}{2} \frac{1}{|u_k - u_l|^3}. \quad (8.3)$$

Here, we have defined the parameter

$$\beta_0 = \nu_z^2 / \nu_x^2. \quad (8.4)$$

It controls the validity of the Hamiltonian (8.1), which remains a suitable description as long as $\beta_0 \ll 1$. The u_k 's denote the equilibrium positions of an N -ion chain in units of

N	Equilibrium positions u_k/l_0				
2	-0.62996		0.62996		
3	-1.0772	0	1.0772		
5	-1.7429	-0.8221	0	0.8221	1.7429

Table 8.1.: Equilibrium positions of the trapped ions in units of $l_0 = (e^2/m\nu_z^2)^{1/3}$ for different numbers of ions N . The values are taken from Ref. [James98].

their average distance l_0 , which - for singly charged ions - is given by $l_0 = (e^2/m\nu_z^2)^{1/3}$ [Leibfried03]. The numerical values for the u_k 's were taken from Ref. [James98], and those used in the simulations in this chapter are listed in table 8.1. Additionally, an anharmonic correction U may be induced by a standing laser wave [Porras04a]. Due to the non-vanishing tunnel rates t_{kl} , the (vibrational) eigenstates of the ion chain consist of delocalized, collective modes. We will denote these eigenstates with one excitation in the chain, in analogy to the notation for exciton states in molecular aggregates, $|e_1\rangle, \dots, |e_N\rangle$, and their energies (in ascending order) by $\omega_1, \dots, \omega_N$. In contrast, phononic wavepackets localized on ion k will be denoted $|1_k\rangle$. Furthermore, we note that the mode ω_N with the highest energy is commonly denoted the *center-of-mass mode*, since it corresponds to a uniform motion of the entire chain in the trap potential. Similarly, ω_{N-1} is called the *breathing mode*, where the two halves of the chain oscillate in an anti-correlated manner. The anharmonicity shifts the energies of states with more than one excitation, such that products of the single excitation eigenstates $|e_j\rangle$ are not eigenstates of these higher excitation manifolds. Specifically, doubly excited states, which will be discussed extensively in the following, are denoted by $|f_1\rangle, \dots, |f_{N(N+1)/2}\rangle$.

It is possible to read out the vibrational excited state population by transferring it to a short-lived electronic state $|\xi\rangle$, and collecting the emitted fluorescence. As we discussed in section 3.4, the electronic excited-state lifetime of $|\chi\rangle$ is on the order of nanoseconds, while the phonon dynamics takes place on microsecond time scales, such that we may consider the readout as instantaneous - just like the excitation of phonons. By comparing the intensity of the electronic transition with the intensity of blue and red sidebands stemming from the annihilation (creation) of phonons, it is possible to measure the phonon population indirectly. Here, we consider the fluorescence signal after the application of a π -pulse on the red sideband, which transfers the phononic population to the short-lived electronic state $|\xi\rangle$. In summary, this amounts to measuring the observable [Gessner14c, Schlawin14a]²

$$A_j = \sum_{n_j=1}^{\infty} \sin^2\left(\sqrt{n_j}\frac{\pi}{2}\right) |n_j\rangle\langle n_j|, \quad (8.5)$$

where j denotes the readout ion. Note that the yield from states with higher vibrational excitation numbers n_j is modulated by the factor $\sin^2(\sqrt{n_j}\pi/2)$. It stems from the

²Details can be found in the dissertation of M. Gessner [Gessner15].

8. Trapped ion spectroscopy

imperfect transfer of the phonon population to the electronic excited state due to their different Rabi frequencies (which scales $\propto \sqrt{n}$).

8.1.2. Electronic degrees of freedom

The electronic states of ions in a linear chain can be restricted to the treatment of two relevant electronic states, which we denoted $|\downarrow\rangle$ and $|\uparrow\rangle$ in chapter 3. They form a local spin 1/2 degree of freedom, and the different spins only interact very weakly due to the fairly large distance ($\sim \mu m$) between them. However, the vibrational degrees of freedom may be used to engineer interactions between the electronic degrees of freedom at distinct sites [Häffner08, Cirac95, Sørensen99]. In this chapter, we will consider two seminal types of Hamiltonians that are routinely implemented in ion chains. First, we consider an Ising-type Hamiltonian with external “magnetic” field [Porras04b],

$$H_{\text{Ising}} = - \sum_{k < l} J_{kl} \sigma_x^{(k)} \otimes \sigma_x^{(l)} - B \sum_{k=1}^N \sigma_y^{(k)}, \quad (8.6)$$

$$J_{kl} = \frac{J_0}{|u_k - u_l|^\alpha}, \quad \alpha \in (0, 3). \quad (8.7)$$

where J_0 controls the coupling strength, and B denotes the strength of the magnetic field. This Hamiltonian serves as a standard toy model in solid state and statistical physics to describe ferromagnetism (but was also used in different contexts, see [Reichl09]). We therefore adopt the common solid state terminology to describe its behavior in the following. It is easy to see that the ratio between the two coupling strengths B and J_0 determines the structure of the Hamiltonian:

When the magnetic field dominates over the inter-ion interaction, $B \gg J_0$, the Hamiltonian structure is dominated by the second term of Eq. (8.6), $-B \sum_{k=1}^N \sigma_y^{(k)}$, and its ground state is given by $|\uparrow_y \cdots \uparrow_y\rangle$, where $|\uparrow_y\rangle$ denotes the eigenstate of σ_y with the eigenvalue +1. Hence, the spins align parallel to the magnetic field in the ground state, which implies that - in the terminology of solid state physics - the chain behaves like a paramagnet. In the other limit, when $B \ll |J_0|$, the interaction term $-\sum_{k < l} J_{kl} \sigma_x^{(k)} \otimes \sigma_x^{(l)}$ dominates. Depending on the sign of J_0 (and assuming for the moment that only nearest-neighbor interactions are relevant), the ground state consists of degenerate doublets³: If $J_0 > 0$, both parallel configurations $|\uparrow_x \cdots \uparrow_x\rangle$ and $|\downarrow_x \cdots \downarrow_x\rangle$ minimize the interaction. On the other hand, if $J_0 < 0$, there are two possible anti-parallel orderings, $|\uparrow_x \downarrow_x \cdots\rangle$ and $|\downarrow_x \uparrow_x \cdots\rangle$, which minimize the interaction. This means the system behaves (anti-)ferromagnetically, depending on the the sign of J_0 , in the sense that its “internal” magnetic field is oriented independently of external fields. The magnetic field merely perturbs this structure. In the following, we will focus on the ferromagnetic case with $J_0 > 0$.

³The interaction term is clearly invariant under the simultaneous flip of all the spin in the x -direction, which changes $\sigma_x^{(k)} \rightarrow -\sigma_x^{(k)}$.

Second, we discuss the Mølmer-Sørensen-interaction of two spins [Sørensen99],

$$H_{\text{MS}} = \frac{\Omega}{2} \sigma_x^{(1)} \otimes \sigma_x^{(2)}, \quad (8.8)$$

which is simply an interaction between the two spins in the x -direction. It drives the two spins into entangled Bell states: When applied for the time $t^* = \pi/2\Omega$, the Hamiltonian drives an initial product state such as $|\downarrow\downarrow\rangle$ into the entangled state $(|\downarrow\downarrow\rangle + |\uparrow\uparrow\rangle)/\sqrt{2}$.

Using strong pulses, it is possible to measure almost arbitrary spin observables locally [Häffner08]. Here, we only consider local population measurements, *i.e.* measurements of the observable

$$A_i = \sigma_z^{(i)}. \quad (8.9)$$

We remark, however, that other measurement observables may also be implemented, which may constitute an interesting extension of the present work.

8.2. Diagram construction

Here, we remind the reader of the diagram construction in the impulsive limit, phrased for the special case of effective local interactions in an ion chain. We can create local (phononic or electronic) excitations in the chain, as described in section 3.4. In the case of an electronic excitation, the coupling is provided by a direct driving of the electronic transition, and in the case of a phononic excitation by a two-photon Raman transition, as discussed in section 3.4. The diagram construction proceeds identically in both cases, so in the following, we only talk about “excitation pulses”, which may denote either of two case, and about the signal “readout”, which may refer to the fluorescence measurement of either Eq. (8.5) or of Eq. (8.9).

Since both excitation pulse and readout take place on a nanosecond time scale, it is possible to treat them as quasi-instantaneous with respect to both the phononic and the electronic dynamics in the chain. This is referred to as the *impulsive limit* [Hamm11], and allows us to neglect the explicit description of the optical fields, which merely show up as prefactors in the final interaction operator [see, e.g., Eq. (3.90)]. The density matrix induced by the interaction with M pulses is then given by (see section 3.5.5)

$$\varrho^{(M)}(t_1, \dots, t_M) = \mathcal{G}(t_M) \mathcal{V}_{i_M-} \mathcal{G}(t_{M-1}) \cdots \mathcal{G}(t_1) \mathcal{V}_{i_1-} \varrho_0, \quad (8.10)$$

where ϱ_0 denotes the initial density matrix, $\mathcal{V}_{i_j-} = \mathcal{V}_{i_j L} - \mathcal{V}_{i_j R}$ the Liouville superoperator, Eqs. (3.90) and (3.102), of the effective interaction at ion i , and after a time delay t_j , $j = 1, \dots, M$.⁴ $\mathcal{G}(t)$ denotes the free evolution as defined in Eq. (3.12). We stress again that, in contrast to our previous description of nonlinear signals, we already eliminated the explicit description of the fields in the derivation of the effective interactions, Eqs. (3.90) and (3.102). The structure of the two effective interactions was derived

⁴In the present chapter, we only consider signals in the impulsive limit. Hence, to simplify our notation, we dropped the superscript “⁽⁰⁾” for the time delays in Eq. (3.141).

8. Trapped ion spectroscopy

such that *each de-excitation of the chain carries a sign* (-1) . This will be essential in determining the relative sign of different contributions to the total signal. This convention is rather unusual, when one is used to conventional nonlinear signals in molecular spectroscopy, where each interaction on the *bra* side adds an additional minus factor [Mukamel10b]. The reason for this unusual behavior lies in the two-photon nature of the phonon excitation (see chapter 3). However, it turns out that this convention still yields identical relative signs between diagrams, for instance in the photon echo (PE) or the double quantum coherence (DQC) signals, as we shall see.

Finally, the observable, Eq. (8.5) or (8.9), is measured with respect to the excited non-equilibrium density matrix, such that the signal reads

$$S_{i_1 \dots i_M; j}^{(M)}(t_1, \dots t_M) = \text{tr} \{ A_j \mathcal{G}(t_M) \mathcal{V}_{i_M} \mathcal{G}(t_{M-1}) \dots \mathcal{G}(t_1) \mathcal{V}_{i_1} \varrho_0 \}. \quad (8.11)$$

These signals will be represented again by the Feynman diagrams introduced in chapter 3. Each effective interaction V_i is represented by the red, wiggly arrow introduced in Fig. 3.3b),⁵ and the fluorescence readout by two de-excitations, with one each on the *bra* and *ket* side (represented by a blue arrow to distinguish them from the red excitation pulses), respectively.

Note that each interaction imprints the phase of the injected laser pulse onto the signal, as can be seen from our effective interaction operators (3.90) and (3.102). The signal (8.11) therefore contains all possible combinations of phases, and may be rewritten as

$$S_{i_1 \dots i_M; j}^{(M)}(t_1, \dots t_M) = \sum_{\delta\phi} S_{i_1 \dots i_M; j}^{(M)}(\delta\phi; t_1, \dots t_M), \quad (8.12)$$

where we have the possible phase combinations

$$\delta\phi = \pm n_1 \phi_1 \pm \dots \pm n_M \phi_M, \quad \text{with } n_i = 0, 1, \dots \quad (8.13)$$

Control over these phases allows us to further select specific excitation pathways using either pulse shaping [Peifang03] or acousto-optical modulation [Tekavec07]. Here, the signal is taken repeatedly with respect to a set of fixed phases $\phi_1, \dots, \phi_M$, and the inverse Fourier transform of this signal only contains contributions from pathways with the desired phase contribution $\pm n_1 \phi_1 \dots \pm n_M \phi_M$. The phases therefore play the role of the wavevectors in the spatial phase matching scheme discussed in chapter 2. In the following, we will introduce several examples of such nonlinear signals, and use them to study non-equilibrium dynamics in various settings.

8.2.1. Diagram rules

Based on the previous discussion, and using the form of the excitation pulses, Eqs. (3.90) and (3.102), as well as the final observables, Eqs. (8.5) and (8.9), we can summarize the diagrammatic construction in the following construction rules for Feynman diagrams

⁵In case a single excitation pulse interacts multiple times with the sample (e.g. when driving two consecutive excitations in the system), it is understood that the intermediate propagators are evaluated at $t_i = 0$, and hence only yield the identity, $\mathcal{G}(0) = \mathcal{I}$. Such a scenario will be discussed in the next section.

Figure 8.2.: The four leading-order contributions to the SQC signal, see Eqs. (8.14)-(8.17).

- R1: An excitation (de-excitation) is represented by an arrow pointing right (left) on the *ket* side, and vice versa on the *bra* side.
- R2: An arrow pointing right (left) yields a phase-shift of $+\phi_i$ ($-\phi_i$).
- R3: Each de-excitation adds an additional factor -1 to the overall sign of the diagram.
- R4: The readout observable (8.5) or (8.9) is represented by de-excitations on both sides of the density matrix. Since the present observables measure populations, they yield a nonvanishing contribution, only if the pathway contains an identical number of excitations on both *ket* and *bra* sides before readout.

Besides, we employ the rotating-wave approximation, *i.e.* we discard diagrams which feature de-excitations of the ground state, for instance. Note that rule R4 pertains specifically to the observables (8.5) and (8.9), and needs to be adjusted for different signal creation.

8.3. Three-pulse schemes - Single Quantum Coherence

We first consider the simplest phase-dependent measurement: A three-pulse sequence (*i.e.* two excitation pulses and one readout pulse at ion i) with phase signature $\phi_1 - \phi_2$. Eq. (8.11) yields, for $M = 2$ excitation pulses, four different pathways, given by the diagrams in Fig. 8.2,

$$S_{i_1, i_2; j}^{\text{SQC (I)}}(t_1, t_2) = \text{tr} \left\{ A_j \mathcal{G}(t_2) D_{i_2 R} \mathcal{G}(t_1) D_{i_1 L}^\dagger \varrho_0 \right\}, \quad (8.14)$$

$$S_{i_1, i_2; j}^{\text{SQC (II)}}(t_1, t_2) = -\text{tr} \left\{ A_j \mathcal{G}(t_2) D_{i_2 L} \mathcal{G}(t_1) D_{i_1 L}^\dagger \varrho_0 \right\}, \quad (8.15)$$

$$S_{i_1, i_2; j}^{\text{SQC (III)}}(t_1, t_2) = \text{tr} \left\{ A_j \mathcal{G}(t_2) D_{i_2 L} \mathcal{G}(t_1) D_{i_1 R}^\dagger \varrho_0 \right\}, \quad (8.16)$$

$$S_{i_1, i_2; j}^{\text{SQC (IV)}}(t_1, t_2) = -\text{tr} \left\{ A_j \mathcal{G}(t_2) D_{i_2 R} \mathcal{G}(t_1) D_{i_1 R}^\dagger \varrho_0 \right\}, \quad (8.17)$$

8. Trapped ion spectroscopy

where we have employed the superoperator notation introduced in chapter 3, and the excitation operator $D_i^\dagger$ denotes either $a_i^\dagger$ in the case of phononic signals or σ_i^+ in the case of electronic signals. Depending on the initial density matrix ϱ_0 , some of these pathways may also vanish. For instance, in our first example, we will consider the system to be initialized in its motional ground state, in which case only Eq. (8.14) contributes: Diagrams (III) and (IV) feature de-excitations of the ground state, and diagram (II) evolves in the ground state after the two laser interactions (during t_2), such that the observable (8.5) vanishes [compare section 3.6.1, Eq. (3.143)].

8.3.1. Phonon transport

We now apply this measurement protocol to a five-ion chain prepared in its motional ground state $|0\rangle$. To probe transport in this system, we simulate the SQC-signal depicted in Fig. 8.3, where the first two pulses excite local (transverse vibrational) wavepackets at the leftmost ion 1, which are then probed at the central ion 3. Since the system is prepared in the ground state, only the one pathway depicted in Fig. 8.3, Eq. (8.14), contributes to the signal. Hence, by analyzing this pathway, we may readily interpret the signal: During the first time delay t_1 , the contribution to the signal with the phase signature $+\phi_1$ evolves in a coherence between the ground and a single-excited state of the vibrational degree of freedom of the chain. Its Fourier transform therefore reveals the vibrational eigenenergies ω_i of the ion chain. Similarly, during the second time interval, the contribution with phase $\phi_1 - \phi_2$ evolves in the single-excitation subspace, such that its Fourier analysis yields the frequency differences $\omega_{ij} = \omega_i - \omega_j$ between the eigenstates. These can in turn be directly related to the tunnel rates [see the Hamiltonian, Eq. (8.1)]: The probability for a phononic excitation, which is initially localized on ion k , to have transferred to ion l after time t is given by

$$p_{kl}(t) = |\langle 1_l | e^{-iH_{\text{vib}}t/\hbar} | 1_k \rangle|^2 \quad (8.18)$$

$$= \sum_{i,j} c_{ij} e^{-i\omega_{ij}t}, \quad (8.19)$$

with $c_{ij} = \langle 1_l | e_i \rangle \langle e_i | 1_k \rangle \langle 1_k | e_j \rangle \langle e_j | 1_l \rangle$. Hence, it is the difference energies ω_{ij} that determine the time scale of the excitation transfer. This justifies denoting them as the *transport rates*.

Since the measurement only probes the single-excitation subspace, anharmonic corrections U to the trap potential will not show up in the present protocol. We can only expect to see its influence when two or more excitations are present in the signal.

Fig. 8.4a) shows the SQC-signal as described in the previous section. The left panel shows a mixed time-frequency representation where the first time interval t_1 has been Fourier transformed,

$$S_{1,1;3}^{\text{SQC}}(\Omega_1, t_2) = \int dt_1 e^{i\Omega_1 t_1} S_{1,1;3}^{\text{SQC}}(t_1, t_2). \quad (8.20)$$

This representation yields the time-resolved amplitude of the excited wave packet at the readout ion. The top panel shows a cut along $\Omega_1 = \omega_5$, *i.e.* it shows the contribution

8.3. Three-pulse schemes - Single Quantum Coherence

Figure 8.3.: a) The only remaining contribution to the SQC signal, if the system is initialized in the ground state [compare Fig. 8.2 and Eqs. (8.14)-(8.17)]. b) Proposed setup to monitor phononic transport within a five-ion chain: The chain is vibrationally excited at the leftmost ion, and fluorescence is collected from the center ion.

of the center-of-mass mode at a given time delay t_2 before readout. Clearly, the oscillations cannot be explained by a single frequency alone, and call for a closer examination. Furthermore, whenever the wavepacket is localized on either side of the chain, no fluorescence is read out at the center ion, and the signal drops to zero for *any* value of Ω_1 . To guide the eye, one such instance is indicated by a black, dashed line at $t_2 \simeq 270/\nu_x$ in Fig. 8.4a). Furthermore, due to the local readout, there is no signal at ω_2 and ω_4 at all. The center ion does not participate in these collective oscillations, and thus they cannot be detected at the center ion, even though they contribute to the dynamics in the chain, as ion 1 is involved in the oscillations.

If we further Fourier transform the second time interval t_2 ,

$$S_{1,1;3}^{\text{SQC}}(\Omega_1, \Omega_2) = \int dt_1 \int dt_2 e^{i(\Omega_1 t_1 + \Omega_2 t_2)} S_{1,1;3}^{\text{SQC}}(t_1, t_2), \quad (8.21)$$

we obtain a two-dimensional frequency correlation plot reminiscent of conventional photon echo representations (see, e.g., Fig. 2.2). However, whereas the photon echo correlates exciton energies to detect couplings or transport, here we correlate the eigenenergies ω_i with the transport frequencies $\omega_{ij} = \omega_i - \omega_j$. Hence, the correlation map in the right panel of Fig. 8.4a) can tell us at which rates the excitations travel, and which eigenmodes of the system are involved in the process. The top panel again shows the cut along $\Omega_1 = \omega_5$, and now clearly demonstrates that its dynamics is governed by two frequencies. By diagonalizing the Hamiltonian, they may be easily identified as ω_{53} and ω_{51} .

So far, we have only monitored the coherent propagation of (transverse vibrational) wave packets along the chain. In the absence of any dissipation, this behavior may also be derived from simple linear spectroscopy, since the level structure is simple enough to be clearly resolved, and determines the spreading of any wave packet. The addition of a local dissipative environment, which may be induced artificially [Poyatos96, Myatt00, Barreiro11], may further enrich the picture: Coherent transport now has to compete with

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Figure 8.4.: The absolute value of the SQC-signal (8.14) for a five-ion chain initially in the motional ground state. a) The left bottom panel depicts $\text{arcsinh}|S_{1,1;3}^{\text{SQC}}(\Omega_1, t_2)|$, and the right panel $\text{arcsinh}|S_{1,1;3}^{\text{SQC}}(\Omega_1, \Omega_2)|$. The arcsinh-scaling is employed to highlight small features. The top panels show cuts along the center-of-mass mode $\Omega_1 = \omega_5$ and the breathing mode $\Omega_1 = \omega_4$. b) Same signal for dissipative dynamics with local dephasing, see Eq. (8.23). Each plot is normalized between 0 and 1 (see also Fig. 8.1).

incoherent, environment-induced transport. We model the environment by a Lindblad

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equation [Breuer02], where we have to use the Liouville space propagator⁶

$$\mathcal{G}(t) = \exp[\mathcal{L}t], \quad (8.22)$$

$$\text{with } \mathcal{L}\varrho = -\frac{i}{\hbar}H_{\text{vib},-}\varrho + \sum_i \left(L_{iR}^\dagger L_{iL}\varrho - (L_i^\dagger L_i)_+\varrho \right), \quad (8.23)$$

where $L_i = \sqrt{\gamma}a_i^\dagger a_i$ for $i = 1, \dots, 5$, and we choose $\gamma = 0.01\nu_x$. The resulting SQC-signal is shown in Fig. 8.4b). In the mixed time-frequency representation $S_{1,1;3}^{\text{SQC}}(\Omega_1, t_2)$, we observe that the coherent oscillations, which are similar to the previous coherent case for short times, slowly die out, as the system equilibrates, thus broadening the resonances in the frequency representation. Furthermore, the local dephasing incoherently couples the delocalized eigenmodes of the chain. This is reflected in the appearance of signals at $\Omega_1 = \omega_4$ and at ω_2 : When these two eigenmodes are initially populated, they cannot be detected at the center ion due to their symmetry. But with increasing t_2 , their populations may be incoherently transferred to one of the other modes, at which point they create a signal. This incoherent transport can be conveniently read off in the frequency representation by the emergence of two new resonances labelled a and b at $\Omega_2 = 0$ (the appearance of the signal at $\Omega_2 = 0$ being indicative of its incoherent character). We further note that the decay also allows to detect coupling between the modes ω_2 and ω_4 (labelled c and d in Fig. 8.4). Hence, the phase-coherent excitation which generates the S^{SQC} signal allows us to monitor both coherent and incoherent energy transport along the chain, and to distinguish the two cases.

8.3.2. Steady state currents

We now turn to a situation in which a three-ion chain is initialized in a state different from its motional ground state. To this end, we couple the system to two heat baths with different temperatures on both sides of the chain (the mean occupation number of the bath is $\bar{n}_1 = 0.0$ on the leftmost ion, and $\bar{n}_3 = 0.5$ on the right ion), such that the temperature gradient establishes a steady-state current between the two sides. We model this with another Lindblad equation [Breuer02],

$$\begin{aligned} \mathcal{L}\varrho = & -\frac{i}{\hbar}H_{\text{vib},-}\varrho + \gamma \sum_i (\bar{n}_i + 1) \left(a_{iR}^\dagger a_{iL}\varrho - (a_i^\dagger a_i)_+\varrho \right) \\ & + \gamma \sum_i \bar{n}_i \left(a_{iR} a_{iL}^\dagger \varrho - (a_i a_i^\dagger)_+\varrho \right), \end{aligned} \quad (8.24)$$

where $\bar{n}_i$ denotes the mean occupation number of the local heat bath (not of the vibrational mode of the system itself!) at ion i . With a rate $\bar{n}_i\gamma$, it creates an excitation at ion i , and destroys one with the rate $(\bar{n}_i + 1)\gamma$. In contrast to the dephasing master equation (8.23), it thus alters the number of excitations in the system. To numerically initiate the system in the non-equilibrium steady state, we first propagate the density

⁶For the Liouville space notation, see section 3.2.

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Figure 8.5.: SQC-signals $S_{1,1;2}^{\text{SQC}}(\Omega_1, \Omega_2)$ (top) and $S_{33;2}^{\text{SQC}}(\Omega_1, \Omega_2)$ (center), Eqs. (8.14)-(8.17), for a three-ion chain connected to two thermal reservoirs (8.24) with mean photon numbers $\bar{n}_1 = 0.0$, $\bar{n}_3 = 0.5$, and dephasing rate $\gamma = 0.01\nu_x$. Bottom: Difference signal ΔS^{SQC} , Eq. (8.25). The signals are normalized between -1 (blue) and $+1$ (red), and the absolute value plot between 0 and 1 (see also Fig. 8.1).

matrix using the Lindblad equation (8.24), until the density matrix no longer changes. Then we start our measurement protocol.

In the absence of currents (*i.e.* in our present setting, of balanced reservoirs), the ion chain is symmetric with respect to its center. This is reflected in the Hamiltonian (8.1), where the ions k and $N - k$ feel exactly the same external potential. As a direct consequence, nonlinear measurements with local interactions also share this symmetry: For instance, in a three-ion chain the SQC signals $S_{1,1;2}^{\text{SQC}}$ and $S_{3,3;2}^{\text{SQC}}$ are identical. Hence, we propose the difference between two such signals as a sensitive probe for a steady-state current which should break this symmetry due to the asymmetric steady state:

$$\Delta S^{\text{SQC}} = S_{1,1;(N-1)/2}^{\text{SQC}} - S_{N,N;(N-1)/2}^{\text{SQC}}. \quad (8.25)$$

8.3. Three-pulse schemes - Single Quantum Coherence

Simulations of the resulting signals are shown in Fig. 8.5. Note that, due to the nonequilibrium steady-state, initial populations are present in the chain, and hence all four contributions to the SQC signal, Eqs. (8.14)-(8.17), need to be taken into account. To interpret the plots in Fig. 8.5, it is instructive to first consider the single-excitation subspace of the vibrational Hamiltonian (8.1), which reads in the local basis of the three-ion chain considered in this example

$$H = \begin{pmatrix} \nu_x - t_{12} - t_{13} & t_{12} & t_{13} \\ t_{12} & \nu_x - 2t_{12} & t_{12} \\ t_{13} & t_{12} & \nu_x - t_{12} - t_{13} \end{pmatrix}. \quad (8.26)$$

Through its diagonalization, we obtain the eigenenergies $\omega_1 = (\nu_x - 3t_{12})$, $\omega_2 = (\nu_x - t_{12} - 2t_{13})$, and $\omega_3 = \nu_x$. Hence, the transport frequencies ω_{ij} (see the previous section), which can be observed during the t_2 -time, are given by combinations of the tunnel rates t_{kl} .

In both signals $S_{1,1;2}^{\text{SQC}}$ and in $S_{3,3;2}^{\text{SQC}}$, we observe strong resonances at $\Omega_1 = \omega_1$ and ω_3 . These consist of incoherent peaks at $\Omega_2 = 0$, and coherent transport resonances at $\Omega_2 = \pm\omega_{31} = 3t_{12}$. Furthermore, a weak resonance at $\Omega_1 = \omega_2$ indicates environment-induced transport (see our discussion of the previous section). However, at first glance both plots look very similar. Only when we look at their difference in the bottom row of Fig. 8.5, we observe that indeed the transport rates are either shifted with respect to one another or exhibit slightly different heights, thereby creating the difference signal ΔS^{SQC} .

We first note the strong role of the coherent resonances, indicating the importance of coherence in this transport process. This may be understood by the strong “coherent” couplings t_{ij} in comparison to the coupling to the heat bath. Once a local excitation is created, it spreads coherently along the chain. Furthermore, resonances at $\Omega_2 = \pm\omega_{21}$, *i.e.* pertaining to the breathing mode, are strongly pronounced, even though they can be hardly observed in the single SQC-plots. This may be understood as a consequence of the breaking of the chain’s symmetry by the steady state current, which couples the breathing mode to the center ion.

8.3.3. (Quantum) Phase transitions

In chapter 2, we already saw that nonlinear spectroscopy provides a convenient tool to probe couplings between excited states in atomic systems. Here, we demonstrate how this property may be utilized to investigate phase transitions in an ion chain. It also represents our first example of nonlinear measurements probing the electronic degrees of freedom in such chains.

To this end, we assume that the Ising chain Hamiltonian (8.6) has been induced in an ion chain, and the electronic degrees of freedom of the chain are prepared in their ground state. As described earlier in this chapter, the Hamiltonian features a transition from a ferromagnetic to a paramagnetic state depending on the relative strength of the two control parameters J_0 and B . This can be clearly identified in the spectrum of the

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Figure 8.6.: a) Normalized energy spectrum of the Ising Hamiltonian (8.6) for $N = 5$ ions, as a function of the ratio B/J_0 of its two order parameters. The spectrum is normalized such that the lowest-energy eigenstate is set to $E_0 = 0$, and the highest eigenenergy is $E_{\max} = 1$. The vertical red lines indicate the parameter settings of the SQC simulations below: b) SQC signal $S_{11;1}^{\text{SQC}}(\Omega_1, \Omega_2)$ in the ferromagnetic regime, with $B/J_0 = 0.1$, c) in the critical regime, $B/J_0 = 1$, and d) in the paramagnetic regime, $B/J_0 = 30$.

Hamiltonian, which we show in Fig. 8.6a) (normalized to the highest energy eigenstate $E_{\max}$, and the lowest eigenstate E_0 set to zero). In the crossover region where $B/J_0 \sim 1$, a discontinuous change of the ground state properties in the thermodynamic limit (*i.e.* $N \rightarrow \infty$) signifies a so-called quantum phase transition [Sondhi97]. In the finite-sized chain which we consider here, a clear signature of this transition may still be observed [Gessner14a]: When the ratio $B/J_0 \ll 1$, the ground state consists of a degenerate doublet, since the first term $-\sum_{k < l} J_{kl} \sigma_x^{(k)} \otimes \sigma_x^{(l)}$ in Eq. (8.6) dominates. This term is invariant with respect to a collective spin flip of all the spins in the chain, and is minimized by the state $|\downarrow_x \downarrow_x \cdots \downarrow_x\rangle$, as well as by $|\uparrow_x \cdots \uparrow_x\rangle$. With increasing ratio B/J_0 , this degenerate doublet splits up due to the symmetry breaking induced by the second term of the Hamiltonian. But besides, it is quite apparent from Fig. 8.6a) that dramatic changes also take place in the excited states: While the Hamiltonian features well-separated manifolds both for $B/J_0 \gg 1$ and $B/J_0 \ll 1$, all the manifolds strongly mix in the intermediate region.

In Figs. 8.6b)-d), we simulate the SQC-signals $S_{1,1;1}^{\text{SQC}}$ of a five-ion chain, where the laser interaction induces a local spin-flip at ion 1, see Eq. (3.102), and the signal is created by

the measurement of $\sigma_z^{(1)}$, see Eq. (8.9). Our three choices reflect the different asymptotic limits: ferromagnetic behavior ($B/J_0 \ll 1$) in panel b), paramagnetic behavior ($B/J_0 \gg 1$) in panel d), and critical behavior near the phase transition ($B \sim J_0$) in panel c). In the regular regimes, b) and d), the spectra are dominated by one strong resonance coupling the ground state to the first excited manifold. This can be understood as a consequence of the symmetry imposed by the dominating terms in the Hamiltonian. For instance, when $B \gg J_0$, the ground state is - to a very good approximation - given by $|\uparrow_y \cdots \uparrow_y\rangle$. The first excited state manifold is composed of states with one of the N spins pointing in the opposite direction, the second excited manifold has two spins pointing downwards, and so forth. Each such spin flip effectively behaves like a bosonic quasiparticle [Jurcevic14] - akin to the Frenkel excitons encountered earlier in molecular aggregates (for details on the bosonization procedure, see, e.g., [Cazalilla11] for a general review or [Jurcevic14] for the present model system), and due to the additional weak interaction term, they spread along the chain. Hence, a single spin flip can only couple two adjacent manifolds, but leaves the other states largely unaffected. Weaker resonances along the diagonal in panel b) and one strong off-diagonal peak in panel d) stem from weaker couplings to higher-excited states, originating from the respective weaker term in Eq. (8.6) - the second term in the ferromagnetic, and the first term in the paramagnetic regime. In stark contrast to this spectrally ordered regime, the spectrum at the phase transition [panel c)] features an enormous number of resonances distributed over the entire spectrum. The large number of off-diagonal resonances further illustrates the coupling between the resonances.

This behavior may be rationalized in the framework of quantum chaos. In fact, the broadly distributed energy levels and their strong couplings in the form of avoided crossings are very generic for critical behavior [Madrero06]. Just like in the present case, these phenomena typically indicate competing symmetries (here caused by B and J_0) of similar strength, where the absence of macroscopic order may be already observed in such relatively small systems [Kolovsky04, Venzl09]. The absence of good quantum numbers in this regime implies that any perturbation of the system generically couples a large number of eigenstates, as demonstrated in the simulations.

8.3.4. Multiple excitations in the SQC signal

As a final remark on three-pulse schemes, we note that the present scheme is not restricted to measuring single excitations, as was the case in our examples so far. By selecting the phase $n\phi_1 - n\phi_2$, it is possible to also probe the multiple (electronic or phononic) excitation sector of the ionic Hamiltonian. In these signals each pulse interacts multiple times (*i.e.* with multiple absorptions or emissions) with the ion chain, which brings about one complication: As shown in Fig. 8.7a), for the case of two interactions with phase $2\phi_i$, there are two indistinguishable processes which have to be taken into account. Two excitations on the *ket* side of the density matrix promote the system from, e.g., the ground state to the desired two-excitation space. However, when the chain is not prepared in the ground state, there is also the possibility of inducing an excitation on the *ket*, and a de-excitation on the *bra* side of the density matrix. Both

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Figure 8.7.: a) Two different processes with identical phase signature $+2\phi_i$. b) The two diagrams which contribute to the signal with phase signature $2\phi_1 - 2\phi_2$, in case the system is initialized in the ground state, and subject to two excitation pulses with phases ϕ_1 and ϕ_2 , respectively. Selecting the Fourier component $2\phi_1 - 2\phi_2$ implies that each pulse has to interact twice with the ion chain.

processes carry the same phase signature, such that they both need to be taken into account. Hence, the SQC-like signal with phase signature $2\phi_1 - 2\phi_2$ starting from the ground state consists of two pathways depicted in Fig. 8.7b) - and not only diagram (Ia), as one might expect naively. This means that for the phase signature $n\phi_i$, we need to consider n indistinguishable processes contributing to the signal.

Keeping this complication in mind, the generalization to multiple interactions with each laser pulse is straightforward (as long as the impulsive limit approximation, section 3.5.5, that we employed in this chapter remains valid).

8.4. Five-pulse schemes - Double Quantum Coherence and Photon Echo

We now turn to more complicated measurement schemes involving four excitation- and the readout pulses. These signals bear close similarity with four-wave mixing signals in conventional ultrafast spectroscopy, and we will employ them to study related phenomena - anharmonicities (here: of the trap potential) and population decay in the presence of a dissipative heat bath. Both applications will again focus on the vibrational degrees of freedom of the ion chain, as described by their Hamiltonian, Eq. (8.1).

8.4.1. Detection of anharmonicities

To study anharmonic corrections to the trap potential, accounted for by the factor U in Eq. (8.1), we propose the fluorescence-based analogon to the *double quantum coherence*

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Figure 8.8.: Diagrams with phase signature $\phi_1 + \phi_2 - \phi_3 - \phi_4$, which constitute the DQC signal when the ion chain is initialized in its vibrational ground state.

(DQC) signal in molecular spectroscopy [Li08, Kim09b]. As discussed in chapter 2, in optical spectroscopy this signal constitutes a sensitive probe of interactions between electronic excited states, since non-interacting components do not yield a signal in this specific phase matching direction. Unfortunately, this is no longer true in general for fluorescence-based optical signals, which may not be described in terms of a nonlinear polarization [Mukamel99] (*i.e.* in terms of stimulated, “classical” emission, see chapter 3). However, as we will show in the following, the DQC signal still presents a formidable tool to investigate anharmonic corrections and phonon interactions.

We define the DQC signal by five-pulse pathways with the phase signature $\phi_1 + \phi_2 - \phi_3 - \phi_4$. For the sake of simplicity, we once again consider a system which has been prepared in the motional ground state.⁷ In this case, the DQC signal is given by the three diagrams in Fig. 8.8. The first two pulses excite the system into a coherence between a doubly excited state $|f\rangle$ and the ground state $|g\rangle$ (hence *double* quantum coherence), and the other two excitation pulses promote the system either into a single excitation population (DQC₁ and DQC₂) or into a doubly-excited population (DQC₃). As control parameters, we have the specific choice of the excitation and readout ions, $i_1, \dots, i_4$ and j , and the variable four time delays $t_1, \dots, t_4$, respectively. The final time delay t_4 constitutes the major difference to related fluorescence-based measurement schemes in molecular systems [Tekavec07, Lott11, Hildner11, Hildner13], where the radiative lifetime of the excited populations is typically much longer than the dynamics of interest, and t_4 thus has to be integrated over at the detector to generate sufficient signal.

Using the diagram rules of section 8.2, the correlation functions which pertain to the

⁷Our following discussion may also be applied to systems in thermal equilibrium, for instance. One simply needs to take additional diagrams into account, just like in our discussion of multiple excitations in the previous section 8.3.4.

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Figure 8.9.: a) Absolute value of the DQC signal, $|S_{1,1,1,1;1}^{\text{DQC}}(\Omega_1, t_2 = 0, \Omega_3, t_4 = 0)|$, of a pair of trapped ions in a perfectly harmonic potential, *i.e.* $U = 0$. b) The same signal for $U = -0.025\nu_x$.

diagrams in Fig. 8.8 read

$$S_{i_1, i_2, i_3, i_4; j}^{\text{DQC}_1}(t_1, t_2, t_3, t_4) = -\text{tr} \left\{ A_j \mathcal{G}(t_4) D_{i_4 R} \mathcal{G}(t_3) D_{i_3 L} \mathcal{G}(t_2) D_{i_2 L}^\dagger \mathcal{G}(t_1) D_{i_1 L}^\dagger \rho_0 \right\}, \quad (8.27)$$

$$S_{i_1, i_2, i_3, i_4; j}^{\text{DQC}_2}(t_1, t_2, t_3, t_4) = -\text{tr} \left\{ A_j \mathcal{G}(t_4) D_{i_4 L} \mathcal{G}(t_3) D_{i_3 R} \mathcal{G}(t_2) D_{i_2 L}^\dagger \mathcal{G}(t_1) D_{i_1 L}^\dagger \rho_0 \right\}, \quad (8.28)$$

$$S_{i_1, i_2, i_3, i_4; j}^{\text{DQC}_3}(t_1, t_2, t_3, t_4) = \text{tr} \left\{ A_j \mathcal{G}(t_4) D_{i_4 R} \mathcal{G}(t_3) D_{i_3 R} \mathcal{G}(t_2) D_{i_2 L}^\dagger \mathcal{G}(t_1) D_{i_1 L}^\dagger \rho_0 \right\}. \quad (8.29)$$

Note that, if we set $t_1 = t_3 = 0$, *i.e.* if the first two and the last two interactions stem from the same pulse, we recover the signal previously discussed in Fig. 8.7b), keeping in mind that only one of the two diagrams DQC_1 and DQC_2 must be taken into account, since otherwise diagram (Ia) in Fig. 8.7 would be counted twice. And in fact, it is also possible to detect anharmonicities with this simpler scheme. However, as we will demonstrate in the following, the greater information content due to additional time delays t_1 and t_3 may be used to identify excitation pathways, as well as interaction-induced symmetry breaking.

We simulate the DQC signal of the simplest nontrivial example - of a chain of $N = 2$ ions - in Fig. 8.9. All laser pulses interact with the same ion, we Fourier transform the first and third time delay, t_1 and t_3 , and set the other two t_2 and t_4 equal to zero, thereby obtaining the signal $|S_{1,1,1,1;1}^{\text{DQC}}(\Omega_1, t_2 = 0, \Omega_3, t_4 = 0)|$. In this example, the chain is not coupled to an environment, such that the width of the resonances stems solely from the finite propagation length during the free time evolutions. With regard to the diagrams in Fig. 8.8, we can see that the pathways evolve in an $e - g$ coherence between single excited and ground state during t_1 , such that its Fourier transform reveals the single excitation eigenenergies of the chain, ω_1 and ω_2 . Similarly, during t_3 the pathways evolve either again in a $e - g$ coherence (DQC_1) or in a $f - e$ coherence between doubly

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and single excited states (DQC₂ and DQC₃). Hence, their Fourier transform can reveal anharmonicities by shifts of the $f - e$ with respect to the $e - g$ resonances.

Figure 8.10.: DQC signal $|S_{i_1, i_2, i_3, i_4; j}^{\text{DQC}}(t_1 = 0, \Omega_2, t_3 = 0, \Omega_4)|$, see Eqs. (8.27) - (8.29), of a three-ion chain is simulated for a) $i_1 = \dots = i_4 = j = 1$ and $U = 0$, b) $i_1 = i_2 = 1, i_3 = i_4 = j = 2$ and $U = 0$, c) $i_1 = \dots = i_4 = j = 1$ and $U = -0.01\nu_x$, and d) $i_1 = i_2 = 1, i_3 = i_4 = j = 2$ and $U = -0.01\nu_x$. The top panels sketch the respective excitation and readout schemes. The red arrows in panels c) and d) highlight a weak anharmonic resonance, which is hidden in the setup in the left column, but can be uncovered using the setup in the right column.

Fig. 8.9a) shows these features for a perfectly harmonic potential with $U = 0$. The axes show the single excited state energies ω_i along Ω_1 , and the $f - e$ transition frequencies $\omega'_{fe} = \omega_f - \omega_e$ along Ω_3 (the notation is introduced to distinguish them from the $e_i - e_j$ frequencies ω_{ij} in the discussion of the SQC signal, see section 8.3.1). In this harmonic

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regime, we have three doubly excited states with energies $f_1 = 2e_1$, $f_2 = e_1 + e_2$, and $f_3 = 2e_2$. Hence, the transition between f_2 and e_2 , for instance, matches the eigenenergy of state $|e_1\rangle$, and therefore the resonances ω'_{22} and ω'_{11} pertaining to $f_2 - e_2$ and $f_1 - e_1$, respectively, are degenerate. The Feynman diagrams in Fig. 8.8 allow for a direct interpretation of each resonance in the two-dimensional plane: The position along Ω_1 indicates the single excited state, through which an f -state gets excited, since both the single and the double excitation evolve along the *ket* side. Therefore, we cannot observe a peak at (ω_1, ω'_{31}) , for instance, since $f_3 = 2e_2$ may not be excited via $|e_1\rangle$. The various $f - e$ resonances along Ω_3 cannot yield information on excitation pathways, since they stem from uncorrelated interactions on the *ket* or *bra* side, respectively.

When anharmonicity is introduced to the system in Fig. 8.9b), two effects can be observed: Degeneracies are lifted due to energy shifts in the f -manifold, such that the transition frequencies ω'_{11} and ω'_{22} discussed above may be distinguished. Even though their splitting is not directly proportional to the interaction strength U (in particular for larger values of U) the splitting between these resonances may still be unambiguously related to the value of U , thus providing a convenient way to measure its strength. But besides, the appearance of additional peaks in the spectrum, such as at (ω_1, ω'_{31}) , further indicates the breaking of the symmetry of the vibrational eigenstates due to the anharmonicity. In second quantization, we may say that the anharmonicity corresponds to an interaction term between the eigenmodes $|e_i\rangle$. The state $|f_3\rangle$ then changes from a product state $|f_3\rangle = a_2^{\dagger 2}|g\rangle/\sqrt{2}$ to an entangled state $|f_3\rangle = \sum_{i,j} b_{ij} a_i^{\dagger} a_j^{\dagger} |g\rangle$, where $a_i^{\dagger}$ denotes the creation operator of an excitation in the phononic eigenmode $|e_i\rangle$. In this sense, this new peak may be interpreted as a direct signature of interaction-induced entanglement between phonon pairs [Mukamel10a] (and their entanglement could, in principle, be analyzed using the apparatus summarized in appendix A for the case of photons).

8.4.2. Multi-exciton transport

We mentioned earlier (see our discussion on page 206) how the SQC signal with multiple excitations may be recovered by setting $t_1 = t_3 = 0$. Similarly to our previous discussion of the SQC signal, we will now use the current DQC setup to investigate tunnel rates in the double-excitation sector of the vibrational Hamiltonian (8.1). From the diagrams in Fig. 8.8, it is clear that the Fourier transform of t_2 will reveal the vibrational eigenenergies in the double-excitation sector. During t_4 , the pathways evolve either in a $f - f'$ or an $e - e'$ coherence, such that its Fourier transform will show the tunnel rates, as well as the possible impact of the bosonic character of the phonons on transport along the chain (for instance, whether the presence of other phonons enhances or suppresses the tunneling from one site to another).

Fig. 8.10 shows this signal $|S_{i_1 i_2 i_3 i_4; j}^{\text{DQC}}(t_1 = 0, \Omega_2, t_3 = 0, \Omega_4)|$ for a three-ion chain. We compare harmonic ($U = 0$) and anharmonic cases ($U = -0.01\nu_x$), as well as two different local excitation and readout schemes. In the left column, we excite and read out at the leftmost ion in the chain, thereby resolving all the eigenstates of the chain.

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Figure 8.11.: Fourth-order diagrams with phase signature $-\phi_1 + \phi_2 + \phi_3 - \phi_4$ which represent the *photon echo* (PE) signal of an ion chain initialized in its ground state. Historically, the diagrams are labelled (from left to right) *ground state bleach* (GSB), Eq. (8.30), *excited state emission* (ESE), Eq. (8.31), and *excited state absorption* (ESA), Eqs. (8.32) and (8.33).

This can already be seen in panel a), which features a wealth of resonances of different intensities. Adding anharmonicity further complicates a clear assignment of the peaks in panel c), as the breaking of degeneracies in the harmonic system further increases the number of resonances which contribute to the signal. One strategy to resolve this problem and still reliably measure the anharmonicity in the chain is to exploit the local addressability of each individual ion in the chain. Exciting at the center ion, for instance, we can “turn off” the population of the breathing mode, and thereby filter the obtained spectrum. As can be seen in panels b) and d), combining an excitation at ion 1 with a second excitation and readout at ion 2 suppresses most of the resonances, and allows for a clean measurement of the anharmonicity. Instead of all six f -states along Ω_2 , only three states ($|f_1\rangle, |f_3\rangle$, and $|f_6\rangle$) contribute to this signal. In the presence of anharmonicity, state $|f_4\rangle$ gains some overlap with the readout ion, and can also be observed. The strong peaks overshadowing the marked resonance in Fig. 8.10c) are entirely removed in d), such that the resonance can be clearly identified - even in the presence of line-broadening due to environmental fluctuations. This suppression is the exact double-excitation analogue of the suppression of the single excitons $|e_2\rangle$ and $|e_4\rangle$ in the single excitation manifold in Fig. 8.4. Varying the time delay t_3 would further enable to monitor environment-induced excitation transport in the multi-excitation sector, and investigate multi-particle quantum transport [Walschaers15] in this setting.

8.4.3. Population decay

As a final example of possible applications of multidimensional signals for linear ion chains, we now consider the analog of the seminal photon echo signal, which was also discussed in some detail in chapter 2. Assuming that the system is again initialized in the ground state, the signal is given by the four Feynman diagrams in Fig. 8.11, with phase signature $-\phi_1 + \phi_2 + \phi_3 - \phi_4$. They translate into the following correlation functions:

$$S_{i_1, i_2, i_3, i_4; j}^{\text{GSB}}(t_1, t_2, t_3, t_4) = -\text{tr} \left\{ A_j \mathcal{G}(t_4) D_{i_4 R}^\dagger \mathcal{G}(t_3) D_{i_3 L} \mathcal{G}(t_2) D_{i_2 R} \mathcal{G}(t_1) D_{i_1 R}^\dagger \varrho_0 \right\}, \quad (8.30)$$

$$S_{i_1, i_2, i_3, i_4; j}^{\text{ESE}}(t_1, t_2, t_3, t_4) = -\text{tr} \left\{ A_j \mathcal{G}(t_4) D_{i_4 R}^\dagger \mathcal{G}(t_3) D_{i_3 R} \mathcal{G}(t_2) D_{i_2 L} \mathcal{G}(t_1) D_{i_1 R}^\dagger \varrho_0 \right\}, \quad (8.31)$$

$$S_{i_1, i_2, i_3, i_4; j}^{\text{ESAa}}(t_1, t_2, t_3, t_4) = -\text{tr} \left\{ A_j \mathcal{G}(t_4) D_{i_4 L}^\dagger \mathcal{G}(t_3) D_{i_3 L} \mathcal{G}(t_2) D_{i_2 L} \mathcal{G}(t_1) D_{i_1 R}^\dagger \varrho_0 \right\}, \quad (8.32)$$

$$S_{i_1, i_2, i_3, i_4; j}^{\text{ESAb}}(t_1, t_2, t_3, t_4) = \text{tr} \left\{ A_j \mathcal{G}(t_4) D_{i_4 R}^\dagger \mathcal{G}(t_3) D_{i_3 L} \mathcal{G}(t_2) D_{i_2 L} \mathcal{G}(t_1) D_{i_1 R}^\dagger \varrho_0 \right\}. \quad (8.33)$$

Traditionally, they are named *ground state bleaching* (GSB), *excited state emission* (ESE), and *excited state absorption* (ESA).⁸ In contrast to heterodyne-detected nonlinear signals, the ESA contribution is composed of two diagrams, due to the fluorescence readout (the final interaction can either de-excite the system into an e -population or promote it to an f -population). Note also that ESAb does not contain any de-excitations, whereas the other three pathways each have one. Therefore, the pathway contributes with opposite sign to the total signal. The so-called *coherence times* t_1 and t_3 , during which the pathways evolve in either $g - e$ (t_1) or $e - g$ and $f - e$ (t_3) coherences, are Fourier transformed to obtain two-dimensional frequency correlation plots. The final delay t_4 will be set to zero in our example, and the *population* or *transport time* t_2 will be varied to monitor transport and decay processes.

We aim to investigate the loss of populations into a thermal reservoir, which is modeled by the Lindblad equation (8.24) introduced in section 8.3.2 [Breuer02]. In the present example, we consider a three-ion chain, in which each atom is coupled to a thermal reservoir with mean phonon number $\bar{n}_i = 0.1$ and dissipative coupling strength $\gamma = 0.01\nu_x$ [see Eq. (8.24)]. Hence, due to the small mean phonon number, we expect to see predominantly decay into the environment, and - with much smaller probability - incoherent local excitation of the chain by the environment. To be able to observe these decay processes, we need to be able to spectrally distinguish the $g - e$ from the $e - f$ transitions. Therefore, we shift the doubly-excited states by the anharmonic amplitude $U = -0.03\nu_x$.

Fig. 8.12 shows the real part of the PE signal taken at the center ion, for three different population times t_2 . For $t_2 = 0$, it features four strong peaks at the single-excitation resonance energies at $\omega_1 \approx 0.88\nu_x$ and $\omega_3 = \nu_x$. Due to the local readout at the center ion, the intermediate single excitation frequency ω_2 is not accessible. In addition to these $e - g$ resonances, two additional $f - e$ transitions (labelled A and B) may be identified.

⁸In optical signals, GSB and ESE pathways show up as positive resonances and ESA as a negative contribution (compare chapter 5). Here, the signs are reversed, but their relative signs remain the same. We employ the terminology for the pathways developed in Ref. [Lott11].

Figure 8.12.: Real part of the photon echo signal [given by the sum of Eqs. (8.30)-(8.33)] is shown for $t_4 = 0$ and a) $t_2 = 0$, b) $t_2 = 1.275\gamma$, and c) $t_2 = 2.55\gamma$. The system is coupled to a heat bath, Eq. (8.24), which causes population to leak out of the system. The bath parameters are set to the mean occupation number $\bar{n} = 0.1$, and the coupling strength $\gamma = 0.01\nu_x$. All interactions are probed at the center ion.

As can be seen in panels b) and c), these two peaks lose intensity with increasing t_2 , and in addition new peaks appear in the signal. The two strongest ones are labelled C and D in Fig. 8.12b).

To rationalize this behavior, we need to examine the behavior of the four pathways that contribute to the PE (Eqs. (8.30) - (8.33) and Fig. 8.11): Three diagrams (ESE, ESAa, and ESAb) evolve in the single-excitation subspace during t_2 , and are therefore susceptible to decay, as t_2 increases. When a decay process takes place, it predominantly de-excites the system $e \rightarrow g$. In this case, ESE and ESAa vanish, since they represent the evolution of the chain in the ground state during t_4 , which does not contribute to the total signal. ESAb may also decay, but due to the final two excitations still produces a signal. Finally, GSB evolves in the ground state during t_2 , such that it is not affected by decay. Hence, we expect to see GSB and ESAb contributions to the total signal to become stronger relative to the other two pathways. This is reflected in the signals: For small t_2 , the peaks C and D are cancelled by destructive interference between ESAa and ESAb. But with increasing time, the intermediate state in ESAb may decay such that the resonance shifts from $\Omega_3 \approx 0.85\nu_x$ to $0.88\nu_x$, while ESAa vanishes, and the peaks C and D emerge.

8.5. 2D lineshapes

So far, we have not debated the lineshapes of the multidimensional signals we simulated. It is well known in nuclear magnetic resonance as well as in molecular spectroscopy that it is possible to distinguish homogeneous and inhomogeneous broadening in the rephasing photon echo [Ernst90, Mukamel99]. In a similar spirit, we explore the lineshapes to distinguish different environmental couplings. We simulate the evolution induced by

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the Mølmer-Sørensen Hamiltonian (8.8) of two trapped ions with incoherent coupling to either local dephasing, described by the operator

$$L_i = \sqrt{\gamma}\sigma_z^{(i)}, \quad i = 1, 2 \quad (8.34)$$

or collective dephasing,

$$L = \sqrt{\gamma}\sigma_z^{(1)} \otimes \sigma_z^{(2)}. \quad (8.35)$$

We employ the SQC signal $S_{1,1;1}^{\text{SQC}}$ to obtain the two-dimensional lineshapes of a two-ion chain initialized in its electronic ground state. Diagonalizing the Hamiltonian, it is straightforward to see that the SQC signal yields resonances at $(\Omega_1, \Omega_2) = \pm(0, \Omega)$ and $\pm(\Omega, \Omega)$ [Gessner14c]. We only depict the resonance at $+(\Omega, \Omega)$ in Fig. 8.13a), as a single peak is fully sufficient for our current analysis.

For local dephasing, the resonance is broadened equally along both frequency axes, whereas it is only broadened along Ω_1 for collective dephasing. Hence, in the latter case the SQC signal reveals that the system evolves in a decoherence-free subspace [Lidar98] during t_2 . Furthermore, the peak widths also allow to directly quantify the reliability of entanglement creation: The purpose of a Mølmer-Sørensen gate is to entangle the two qubits by application of the Hamiltonian for the time $t^* = \pi/(2\Omega)$, leading to the creation of a Bell state for perfectly unitary dynamics (see our discussion on page 193; $U_{\text{MS}}|\downarrow\downarrow\rangle$ is a maximally entangled (Bell) state). The reliability of this protocol is usually quantified with the *fidelity* [Nielsen10],

$$\mathcal{F} = \sqrt{\langle\downarrow\downarrow|U_{\text{MS}}^\dagger\varrho(t^*)U_{\text{MS}}|\downarrow\downarrow\rangle}, \quad (8.36)$$

where $U_{\text{MS}} = \exp[-iH_{\text{MS}}\pi/(2\Omega\hbar)]$, and $\varrho(t^*)$ denotes the density matrix obtained under the dissipative dynamics. $\mathcal{F} = 1$ then corresponds to perfect entanglement creation. Reliable quantum computing requires fidelities well above $\mathcal{F} \geq 99\%$ [Benhelm08]. In Fig. 8.13b) we show that for small dephasing rates γ , the full-width half-maximum of the resonance is directly proportional to the error probability $1 - \mathcal{F}$.

Hence, by analyzing the two-dimensional lineshape of the SQC signal, it is possible to assess the strength of environmental couplings, and determine whether these are detrimental for a desired task at all. Decoherence-free subspaces may be identified this way.

8.6. Summary

We have established a versatile formalism to obtain nonlinear spectroscopic signals from linear chains of ions. Our formalism is based on three important ingredients: the local creation and annihilation of (phononic or electronic) excitations, the signal readout by fluorescence detection, and phase cycling. While the former two have already been demonstrated experimentally [Monroe96, Jurcevic14], phase cycling constitutes - to the best of our knowledge - a novel tool in trapped ion experiments, whereas it is widely used

in chemical or solid state physics. In comparison to multidimensional NMR methods, which also employ phase cycling protocols, our perturbative approach offers greater flexibility, as it is also capable of describing signals of, e.g., coupled, anharmonic oscillators, in which a nonperturbative treatment of the interaction with the light pulses is no longer feasible.

Three-pulse schemes are able to distinguish coherent and incoherent phononic transport - a unique feature, that relies on the single site addressability of trapped ion systems, and that cannot be achieved in typical sample systems in chemical or solid state physics. Furthermore, these protocols are able to detect and analyze steady state currents, and to monitor critical behavior near phase transitions. Excitation schemes with five pulses can access the multi-excitation sector of the system Hamiltonian. This allowed us to devise measurement protocols that can measure the anharmonicities in the system, and detect population decay into surrounding environments. Finally, in close analogy to the situation in chemical physics, the analysis of the two-dimensional lineshapes allows for the distinction between different environmental coupling mechanisms.

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Figure 8.13.: a) Two-dimensional resonance in the Mølmer-Sørensen interaction, Eq. (8.8), coupled to either local dephasing (left panel) or collective dephasing (right panel). The coupling is described by time-independent Lindblad equations with Lindblad operators for local dephasing (8.34), and the operator (8.35) for collective dephasing. The small panels on top and on the left depict cuts along either $\Omega_1 = \Omega$, or $\Omega_2 = \Omega$, respectively. b) Full-width-half-maximum (FWHM) of the resonance in panel a) along Ω_1 plotted vs. the fidelity (8.36) of entanglement creation using the Mølmer-Sørensen gate for local dephasing. The FWHM is given in units of the driving strength Ω of the Mølmer-Sørensen Hamiltonian (8.8).

9. Conclusions and Outlook

In this dissertation, we explored the application of nonclassical light sources developed in the quantum optics community as nonlinear spectroscopic tools, as well as the application of measurement protocols developed in nonlinear spectroscopy to quantum-optical sample systems. We will discuss the two topics separately: *novel sources* and *novel samples*.

Novel Sources In the first part of this dissertation, we developed nonlinear optical signals based on a fully quantum-mechanical description of both the sample system *and* the electromagnetic field, which allowed us to develop a perturbative theory to assess the impact of the interaction with complex sample systems on arbitrary observables of the field.

This theory led us to investigate the excited state distributions induced by the absorption of quantum light in multilevel quantum systems subject to dissipation. The main take-away message of this part of the dissertation may be formulated as follows:

In multiphoton processes, the combined time and frequency resolution of classical light is fundamentally limited by the Fourier uncertainty. *Quantum light is not subject to the same uncertainty relations!*

Combined time and frequency resolution constitutes a *genuine quantum advantage* that cannot - not even in principle - be achieved with classical light sources. While the structure of the time-frequency correlations responsible for the enhancement were of course known, it is the main result of this dissertation to point out how they are reflected in said multiphoton processes. Of course, the crucial question to be answered is how - and under what circumstances - this enhancement may be exploited in experiments.

We could give partial answers in two cases: Our more thorough discussion of this property of quantum light focusses on the most prominent example of nonclassical light - entangled photon pairs - where the combined resolution shows up in two-photon absorption events. We however pointed out in chapter 7 that the multimode structure of the parametric downconversion process creating the entangled photons is actually generic for parametric processes involving broadband pulses and so are nonclassical time-frequency properties - provided the parametric processes take place in a regime in which the quantum nature of the light becomes relevant. For the case of frequency conversion, we could propose a possible scheme to detect these correlations in measurements of Raman scattering.

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The nonclassical time and frequency resolution of entangled photon pairs can be used to induce excited state distributions that are not accessible with classical laser sources: The two-exciton distributions in the bacterial RC of *Blastochloris viridis* may be controlled with frequency anti-correlated entangled photon pairs. The frequency correlations allow to target specific f -states, whereas the broad bandwidth of each individual photon allows to access all the possible excitation pathways leading to the state. In the absence of dissipation, we could show that the same f -state distribution may be obtained with *correlated, yet separable* two-photon states, where the time-frequency entanglement of the entangled photon pair is replaced by a classical frequency distribution with classical frequency *correlations*. This situation changes dramatically when the system is coupled to a dissipative environment. Due to the quasi-simultaneous arrival of the two photons, intermediate dissipation between the two absorption events can be suppressed. This suppression of intermediate population transport facilitates the theoretical description of the nonlinear optical response to entangled photons in this parameter regime, since it allows for the calculation of the signal as if there was no coupling to the environment. Hence, it is sufficient to propagate a wavefunction instead of the full density matrix, thus greatly reducing the computational requirements for the simulation of nonlinear optical signals in this parameter regime.

The variation of the entanglement time, which controls the time delay between photon absorption events, provides a novel tool to probe the relaxation dynamics with femtosecond resolution - without the technical difficulties involved in the use of femtosecond pulses. Furthermore, due to the frequency resolution in the two-exciton manifold, together with the possibility to selectively excite specific f -states, a given choice of pulse parameters only reveals the excitation pathways leading to this specific state. Hence, transport processes within the subset of states that are connected to the f -state may be selected, which is not possible in conventional multidimensional spectroscopy. We showed that clear signatures of the excited wavepackets and of the transport processes can be observed in the two-photon induced fluorescence signal.

Similar findings could be reported in chapter 5, where we calculated the frequency-dispersed absorption spectrum created by the interaction with entangled photons. In contrast to the two-photon induced fluorescence spectra, this signal contains strong contributions from Raman pathways, which complicate the interpretation of the signal and often cover the weaker two-photon absorption resonances. But at the same time, the signal also contains more information than its fluorescence counterpart: While the greater number of Feynman diagrams that were used to simulate the signals evidently complicate their interpretation, they also define additional excitation pathways which can probe the sample. This greater number of excitation pathways allows to resolve the $g \leftrightarrow e$ and the $e \leftrightarrow f$ transitions separately, which is not possible in the fluorescence signal above.

The absorption signals show the same strong signatures of time-energy entanglement that were observed before in the direct simulation of wavepackets. In comparison to classical signals, it was shown that the two-photon absorption pathways have stronger weight in the final signal, when the signal is created by entangled photons. This feature

could be traced back to the strong correlations in the arrival time of entangled photon pairs. Hence, entangled-photon spectroscopy may further be beneficial to enhance weak two-exciton resonances, regardless of relaxation processes in the sample.

Yet another possible use of entangled photons in spectroscopy was proposed in chapter 6, where we discussed spectroscopic signals in an interferometric setup. Only one of the two entangled beams interacts with the sample, while the other one is detected in coincidence, and acts as a reference to filter the signal. While this scheme is already used to reduce signal fluctuations in noisy samples, here we showed how it can be used in a pump-probe-like setup. The time-frequency correlations shared between the photons may be employed as a frequency filter to enhance or suppress certain parts of the resulting spectrum.

In short, we elaborated a genuine advantage of quantum light in terms of its simultaneous time and frequency resolution under certain conditions, and we proposed several experimental scenarios to make use of it in spectroscopic applications. We could also point out that this advantage is not restricted to the well-known entangled photon pairs. It stems from the multimode nature of the parametric process which underlies their creation, and is therefore rather generic to similar processes in nonlinear optics. It would therefore be highly interesting to further explore quantum correlations in other parametric processes such as Bragg scattering etc, where they may have been overlooked so far. Furthermore, our current proposed setups all represent phase-incoherent setups in the sense that no pathway selection is used. However, as pointed out in Ref. [Raymer13], acousto-optical modulation shows a path to implement phase cycling protocols, and hence pathway selectivity even on a single-photon level. Given the tremendous success of phase-coherent optical spectroscopy in recent years, it will be highly exciting to explore this possibility for quantum light as well.

Novel Samples The second part of this dissertation concerned the development of multidimensional spectroscopic signals for quantum-optical systems - and in particular for linear chains of trapped ions. We derived effective excitation and readout schemes for both the vibrational and the electronic degrees of freedom of such chains. These proposed schemes are based on current trapped ion technology combined with phase cycling (which is well established in optical spectroscopy), and fluorescence readout. In contrast to the rather unorthodox signals that we simulated in the first part of this dissertation, the measurement protocols bear close resemblance to conventional signals in nonlinear optical spectroscopy in that the time delays between pulses are varied and Fourier transformed to obtain frequency correlation maps. In contrast to fluorescence-based signals in molecular spectroscopy, however, the fluorescence signals here may be induced externally, adding an new dimension to the protocols. Furthermore, the large spacing between ions allows for the local excitation and readout of signals, giving us even greater flexibility in the design of our measurement protocols.

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The vibrational degrees of freedom of the ion chain can be mapped on a Bose-Hubbard-type model, and we could show that nonlinear spectroscopy constitutes a convenient tool to explore its rich physics. Specifically, we developed measurement protocols that can distinguish coherent (“wave-like”) and incoherent (diffusive) energy transport along the chain. This is made possible by the unique feature to address ions individually, and is not possible in molecular or semiconductor samples. Similar protocols can sensitively probe steady-state currents, and analyze them spectrally. Four-pulse schemes can be used to measure anharmonicities in the trap potential, which appear - for instance - near so-called “zig-zag” phase transitions [Shimshoni11, Ulm13, Pyka13], or to detect population decay into heat baths.

The electronic degrees of freedom, whose description we restricted to only two relevant levels, may form spin chains, where the interaction can be controlled experimentally. Here, we specifically investigated the phase transition between a paramagnetic and a ferromagnetic phase in such a spin chain. We showed that, again, multidimensional spectroscopy constitutes a convenient tool to investigate the phase transition, and identify critical behavior in the absence a dominant order parameter. As a more direct application to quantum information, we demonstrated how the two-dimensional line-shapes of nonlinear spectra can reveal different couplings to dissipative environments, and showed that the width of the resonances can be related to the fidelity of Bell state preparation in the Mølmer-Sørensen gate.

In short, it is fair to say that nonlinear spectroscopy holds great promise in the investigation of nonequilibrium dynamics in artificial quantum systems, and its full potential has yet to be explored. The plethora of Hamiltonians that may readily be implemented in trapped ion systems can already be probed using the presented formalism. In the near future, the next necessary step will be the adaption of this formalism to other quantum-optical systems - most prominently to Rydberg atoms trapped in optical tweezers and to ultracold atoms in optical lattices. In a broader context, the adaption of the phase cycling method for pathway selection, that has proven to be so tremendously successful, from NMR to optical spectroscopy, will hold great promise in quantum optics as well, as the experimentally realized systems increase in size and complexity. Similar steps were also undertaken in Refs. [Knap13, Serbyn14], yet they do not go beyond two-pulse schemes. The missing key element is the representation of signals in terms of Feynman diagrams, which create great intuition for the processes creating the signal within the sample. This intuition facilitates the development of new measurement protocols designed for the observation of specific phenomena, as we have here demonstrated.

A. Parametric downconversion

This appendix develops the theory of entangled beams created by parametric downconversion. The following derivation closely follows the presentation in Refs. [Christ11, Christ13a, Christ13b]. As described in chapter 2, we consider type-II downconversion in a birefringent crystal, where entangled photon pairs are created by the interaction of a pump pulse with a $\chi^{(2)}$ -nonlinearity. Our derivation is restricted to collinear propagation of all the involved fields. It simplifies the notation, and captures all the essential physics. We will point out, in the course of this appendix, under which circumstances and how non-collinear downconversion would affect the correlation functions.

This model was chosen for two main reasons. First, its great flexibility: As we will see in the following, it allows us to derive analytical expressions for arbitrary field correlation functions both in the time and in the frequency domain. Even in situations where we can no longer find closed expressions for the matter propagator - for instance, due to time-dependent dephasing rates [Fischer13] - one can use the time domain representation of our model, and numerically propagate the matter-field correlation function in optical signals. On the other hand, in the case of frequency-dispersed signals (see, e.g., chapter 5), the frequency domain representation may allow for quicker evaluation of the signal.

The model's second big advantage lies in the fact that it allows us to simulate the multi-photon regime, where overlapping photon pairs lead to the measurement of random coincidences in two-photon counting measurements. It provides us with the means to assess the trade-off between greater photon flux (larger signal) and the degradation of certain quantum effects in the high-intensity regime.

A.1. Hamiltonian and analytical approximations

In a collinear setup, in which all the fields propagate along the same axis, the interaction Hamiltonian between the fields within the nonlinear crystal reads [Christ13b]

$$H_{\text{PDC}}(t) = \epsilon_0 \int_{L/2}^{L/2} dz \chi^{(2)}(z) E_p(z, t) E_1^\dagger(z, t) E_2^\dagger(z, t) + h.c. \quad (\text{A.1})$$

where we write the fields inside the crystal,

$$E_i(z, t) = i \sqrt{\frac{\pi \hbar \omega_i}{\epsilon_0 c A_0}} \int \frac{d\omega}{2\pi} e^{i(k(\omega)z - \omega t)} a_i(\omega). \quad (\text{A.2})$$

In contrast to the fields in free space [Eq. (3.5)], we here explicitly take the spatial dependence into account. The wave vector inside the medium $k(\omega)$ depends nonlinearly

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on the frequency of the field, we assume, however, that it is far off-resonant from any resonance within the crystal. Thus, we neglect absorption, and the wave vector $k(\omega)$ becomes a real function. The second-order susceptibility $\chi^{(2)}(z)$ describes the strength of the parametric process inside the crystal. In the following, we consider a spatially homogenous crystal, *i.e.* a constant nonlinearity $\chi^{(2)}(z) = \chi^{(2)}$. $a_i(\omega)$ denotes the photon annihilation operator in field i . We further remark that, in type-II downconversion, the two fields may be distinguished by their polarization degree of freedom. The length of the crystal in propagation direction is denoted L .

We consider the most relevant case of driving by a strong, coherent pump pulse, which allows us to treat the pump field E_p in Eq. (A.1) classically. The Hamiltonian (A.1) then turns into a quadratic Hamiltonian in the quantum fields, and can be solved analytically. Since we are interested in the final state after propagation through the crystal, we can send time $t \rightarrow \infty$ without affecting the result, and write the action of Eq. (A.1) as

$$U_{\text{PDC}} = \mathcal{T} \exp \left[-\frac{i}{\hbar} \int_{-\infty}^{\infty} d\tau H_{\text{PDC}}(\tau) \right], \quad (\text{A.3})$$

Neglecting four-photon processes, which amounts to neglecting the time-ordering in Eq. (A.3) [Christ13b], the action of Eq. (A.1) onto an initial field $|\varphi_{\text{in}}\rangle$ can be written as the transformation¹

$$U_{\text{PDC}} = \exp \left[-\frac{i}{\hbar} H_{\text{eff}} \right], \quad (\text{A.4})$$

$$\text{with} \quad H_{\text{eff}} = \int d\omega_a \int d\omega_b \Phi(\omega_a, \omega_b) a_1^\dagger(\omega_a) a_2^\dagger(\omega_b) + h.c. \quad (\text{A.5})$$

such that the output state is given by $|\varphi_{\text{out}}\rangle = U_{\text{PDC}}|\varphi_{\text{in}}\rangle$. In this dissertation, we always consider the initial state to be the vacuum, $|\varphi_{\text{in}}\rangle = |0\rangle$. The so-called two-photon amplitude is given by [Christ13b]

$$\Phi(\omega_a, \omega_b) = \alpha A_p(\omega_a + \omega_b) \text{sinc} \left(\frac{\Delta k(\omega_a, \omega_b)L}{2} \right). \quad (\text{A.6})$$

Here, A_p denotes the normalized envelope of the pump pulse, and $\text{sinc}(\Delta kL/2)$ is the phase-matching function, which stems from the integration along the z -direction in the initial Hamiltonian (A.1). $\Delta k(\omega_a, \omega_b) = k_p(\omega_a + \omega_b) - k_1(\omega_a) - k_2(\omega_b)$ is the phase mismatch between the fields' wavevectors. α is a constant containing the second-order susceptibility of the crystal, the quantization area of the fields, the dielectric constant, as well as the crystal length. Since these properties strongly depend on the experimental setup, they will not be specified in this dissertation. But in addition to these given constants, α also depends on the pump beam intensity. Hence, we can take the constant α to be proportional to the downconversion rate, and later in this appendix we will show how to gauge it to a measured photon number.

¹The effective Hamiltonian defined in Eq. (A.5), in fact, has the dimension of an action $[\hbar]$, since we carried out the time integration in its derivation as described above.

A.1.1. Phase mismatch

To continue in our derivation of the entangled beams, we first need to examine the phase mismatch function Δk . It is usually sufficient to expand the wavevector in a Taylor series around the central frequencies of the beams,²

$$k_i(\omega) \approx k_{i0} + \left. \frac{dk_i}{d\omega} \right|_{\omega=\omega_i} (\omega - \omega_i) + \dots \quad (\text{A.7})$$

We can identify the first derivative with the inverse of the group velocity of the wavepacket, $1/v_i = dk_i/d\omega$. We assume that phase-matching at the central frequency is exact, *i.e.* we have $\omega_p = \omega_1 + \omega_2$, such that $k_{p0} - k_{10} - k_{20} = 0$. In type-II downconversion, we have $v_1 \neq v_2$, and the linear approximation yields

$$\Delta k(\omega_a, \omega_b) = \left(\frac{1}{v_p} - \frac{1}{v_1} \right) (\omega_a - \omega_1) + \left(\frac{1}{v_p} - \frac{1}{v_2} \right) (\omega_b - \omega_2). \quad (\text{A.8})$$

The phase mismatch appears in a product with the length of the nonlinear crystal L , thus defining two time scales

$$T_1 = \left(\frac{1}{v_p} - \frac{1}{v_1} \right) L, \quad (\text{A.9})$$

$$T_2 = \left(\frac{1}{v_p} - \frac{1}{v_2} \right) L, \quad (\text{A.10})$$

which define the time difference between a wavepacket traveling with the group velocity of the pump pulse and one traveling with the group velocity of beam 1 or 2, respectively. This is the only situation where non-collinear propagation would influence the correlation function: If the two beams are collected in angles θ_1 and θ_2 with respect to the pump axis, the beams traverse a different length within the crystal, and we have to replace the length L by the adjusted propagation length inside the crystal $L \cos(\theta_i)$ [Joobeur94]. This also implies that the time scales may be varied independently to some extent, even though this property will not be explored in this dissertation.

For spectroscopic applications such as two-photon absorption, the time delay between beams 1 and 2 is the most relevant quantity. This motivates the definition of the *entanglement time*,

$$T = T_2 - T_1 \quad (\text{A.11})$$

(where we assume, without loss of generality, $T_2 > T_1$). Since entangled photon pairs are created spontaneously at a random position within the crystal, the entanglement time represents an upper bound for the time delay between such pairs. Note that depending on

²This approximation is very similar to the slowly varying envelope approximation employed in the definition of the field operators. It again assumes that the treatment of the fields may be restricted to optical frequencies, which are far detuned from any resonance of the nonlinear crystal. This assumptions can limit the validity of the presented theory under some circumstances.

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the phase matching condition, T_1 may be smaller than zero. For instance, Ref. [Grice01] reports group velocities for a BBO-crystal pumped at 800 nm, where indeed $T_1 < 0$. The same crystal pumped at 395 nm [Jennewein09], on the other hand, has $T_1 > 0$. This has important consequences, for only the case $T_1 < 0$ allows for positive frequency correlations, as we will show later in this appendix. In this dissertation, we will consider two possible sets of parameters,

$$T_1 = \pm 0.00007(T/fs) \text{ cm}, \quad (\text{A.12})$$

$$T_2 = 0.00025(T/fs) \text{ cm}, \quad (\text{A.13})$$

where T denotes the entanglement time in femtoseconds. $T_1 > 0$ corresponds to the set of parameters taken for the BBO crystal pumped at 395 nm [Jennewein09], and will be used whenever we discuss frequency anti-correlations. $T_1 < 0$ corresponds to a theoretical situation, which will be used to simulate positive frequency correlations.

A.1.2. Schmidt decomposition

The Hamiltonian (A.5) can be diagonalized using the Schmidt decomposition of the two-photon wavefunction (A.6) [Law00, McKinstrie13a, McKinstrie13b],

$$-\frac{i}{\hbar}\Phi(\omega_a, \omega_b) = \sum_k r_k \psi_k^*(\omega_a) \phi_k^*(\omega_b). \quad (\text{A.14})$$

The functions $\{\psi_k\}$ and $\{\phi_k\}$ both form orthonormal bases, the Schmidt modes, and their contribution to the PDC process is determined by the mode weights $\{r_k\}$, which may be chosen positive by absorbing the phase into one of the bases. Defining the mode operators

$$A_k = \int d\omega_a \psi_k(\omega_a) a_1(\omega_a), \quad (\text{A.15})$$

$$\text{and } B_k = \int d\omega_b \phi_k(\omega_b) a_2(\omega_b), \quad (\text{A.16})$$

the transformation (A.4) reads

$$U_{\text{PDC}} = \exp\left(-\frac{i}{\hbar} H_{\text{eff}}\right) \quad (\text{A.17})$$

$$= \exp\left(\sum_k r_k A^\dagger B_k^\dagger - h.c.\right), \quad (\text{A.18})$$

To simulate nonlinear optical signals, we need to evaluate multi-point correlation functions of the electromagnetic fields after the interaction with the nonlinear crystal. It will be most convenient to calculate these correlation functions in the Heisenberg picture with respect to the downconversion Hamiltonian, since the effect of Eq. (A.18) on the

A.1. Hamiltonian and analytical approximations

Schmidt mode annihilation operators can be expressed by simple input-output relations [Christ11]

$$A_k^{\text{out}} = \cosh(r_k)A_k^{\text{in}} + \sinh(r_k)B_k^{\dagger\text{in}}, \quad (\text{A.19})$$

$$B_k^{\text{out}} = \cosh(r_k)B_k^{\text{in}} + \sinh(r_k)A_k^{\dagger\text{in}}, \quad (\text{A.20})$$

where the operators A_k^{in} etc denote the initial operators at the time before the pump pulse passes through the crystal, and A_k^{out} the final operators at the output side of the crystal, *i.e.* after the pump passage. $\psi_k(t)$ and $\phi_k(t)$ denote the Fourier transforms of the Schmidt mode envelopes in Eq. (A.14),

$$\psi_k(t) = \int \frac{d\omega}{2\pi} \psi_k(\omega) e^{i\omega t}. \quad (\text{A.21})$$

The electromagnetic fields after transmission through the crystal can now be expressed in terms of the Schmidt modes. We drop the spatial dependence and the normalization constants to simplify our notation (keeping in mind that these constants are then absorbed into the dipole moments in their interaction with matter systems), and obtain

$$E_1(t) = \int \frac{d\omega}{2\pi} e^{-i\omega t} a_1^{\text{out}}(\omega) \quad (\text{A.22})$$

$$= \int \frac{d\omega}{2\pi} \int d\omega' \sum_k \psi_k(\omega) \psi_k^*(\omega') e^{-i\omega' t} a_1^{\text{out}}(\omega) \quad (\text{A.23})$$

$$= \sum_k \psi_k^*(t) A_k^{\text{out}}, \quad (\text{A.24})$$

where we inserted the representation of the delta-function in the Schmidt basis, *i.e.* $\sum_k \psi_k(\omega) \psi_k^*(\omega') = \delta(\omega - \omega')$, and the definition (A.21) of $\psi_k(t)$. Similarly, we obtain for the second field

$$E_2(t) = \sum_k \phi_k^*(t) B_k^{\text{out}}. \quad (\text{A.25})$$

We stress again that we have propagated the annihilation operators in the Heisenberg picture. Hence, these output fields act on the initial state $|\varphi_{\text{in}}\rangle$ of the fields.

A.1.3. Analytical decomposition

Using the Schmidt decomposition (A.14), we have formally diagonalized the Hamiltonian, and, using Eqs. (A.24) and (A.25), we may calculate arbitrary field observables in terms of the Schmidt modes. However, with the form of the Hamiltonian (A.6) and the phase mismatch (A.8), it is not possible to find a closed form for the spectral shape of the Schmidt modes. One simple approximation however allows to do just that. Neglecting the minor maxima of the sinc-function, we approximate it by a Gaussian envelope [U'Ren03, Grice01, Maurer09]

$$\text{sinc}\left(\frac{\Delta k(\omega_a, \omega_b)L}{2}\right) \approx \exp\left[-\gamma(\Delta k(\omega_a, \omega_b)L)^2\right], \quad (\text{A.26})$$

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with the fitting factor $\gamma = 0.04822$. Using also a (normalized) Gaussian envelope for the pump pulse,

$$A_p(\omega_a + \omega_b) = \frac{1}{\sqrt{2\pi\sigma_p^2}} \exp \left[-\frac{(\omega_a + \omega_b - \omega_p)^2}{2\sigma_p^2} \right], \quad (\text{A.27})$$

the two-photon amplitude (A.6) is given by Gaussian functions. This allows us to decompose them in terms of Hermite functions H_n [U'Ren03, Grice01],

$$-\frac{i\alpha}{\hbar\sqrt{2\pi\sigma_p^2}} \exp[-ax^2 - 2bxy - cy^2] = \sum_{n=0}^{\infty} r_n H_n(k_1x) H_n^*(k_2y), \quad (\text{A.28})$$

where we have $a = 1/(2\sigma_p^2) + \gamma T_1^2$, $b = 1/(2\sigma_p^2) + \gamma T_1 T_2$, and $c = 1/(2\sigma_p^2) + \gamma T_2^2$. The Hermite functions are given by

$$H_n(k_i x) = \sqrt{\frac{k}{\sqrt{\pi} 2^n n!}} e^{i\frac{3\pi}{8} - (k_i x)^2} h_n(k_i x), \quad (\text{A.29})$$

and h_n denotes the n -th Hermite polynomial [Reed81]. The Hermite functions are normalized, such that

$$\int dx |H_n(kx)|^2 = 1. \quad (\text{A.30})$$

The real value of the Hermite functions (A.29) is plotted in Fig. A.1 for $n = 1, \dots, 4$. We need to point out two features: With increasing n , the Hermite functions become strongly oscillatory, and their variance increases as $\sqrt{n}$. This poses an apparent difficulty for their use in numerical simulations, since we often have to take more than fifty modes into account. However, we will see later in this appendix that the final correlation functions are always non-oscillatory [reflecting the Gaussian distributions on the left side of Eq. (A.14)] - unless we terminate the summation in Eq. (A.28) too early!

The factors a and c in Eq. (A.28) define the spectral width of the photon wavepackets, and b quantifies their correlations. When $b > 0$, we have frequency anti-correlations, as discussed in most of the dissertation. When $b < 0$, we have positive frequency correlations, and the downconversion process creates uncorrelated wavepackets for $b = 0$. This can only happen, when either T_1 or T_2 is negative, and since we defined earlier that $T_2 > T_1$, it can only happen when $T_1 < 0$. Defining further

$$\mu = \frac{-\sqrt{ac} + \sqrt{ac - b^2}}{b}, \quad (\text{A.31})$$

A.2. Multipoint correlation functions of entangled photons

Figure A.1.: Real part of the Hermite functions $H_n(x)$ (A.29) for $n = 1$ (blue, solid), $n = 2$ (red, dashed), and $n = 3$ and 4 (yellow and green, dot-dashed).

the remaining constants in Eq. (A.28) read

$$r_n = \frac{\alpha}{\hbar} \sqrt{\frac{1 + \mu^2}{4ac\sigma_p^2}} \mu^n, \quad (\text{A.32})$$

$$k_1 = \sqrt{\frac{2a(1 - \mu^2)}{1 + \mu^2}}, \quad (\text{A.33})$$

$$k_2 = \sqrt{\frac{2c(1 - \mu^2)}{1 + \mu^2}}. \quad (\text{A.34})$$

At this point, it is worth noting that $\mu < 1$. Hence, as can be seen from Eq. (A.32), the closer μ approaches unity, the more modes obtain appreciable weight, and therefore the stronger the two-photon wavepackets are entangled.

Time domain expressions

We finally remark that Hermite functions are eigenfunctions of the Fourier transform to the eigenvalue $(-i)^n$. If we have the frequency domain spectral function $H_n(k(\omega_a - \omega_1))$, we know that its time domain representation is given by $H_n(t/k) \exp(-i\omega_1 t)$. Hence, the analytical approximation described in the previous section A.1.3 enables us to obtain analytical expressions for arbitrary time and frequency domain correlation functions.

A.2. Multipoint correlation functions of entangled photons

In order to discuss properties of the downconverted light, we need to first calculate its multipoint correlation functions. As shown in chapter 3, they also form the basis for

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the simulation of optical signals. Our discussion will focus on frequency domain expressions, however, as pointed out in the preceding section, the time domain representation may be obtained straightforwardly. We explicitly calculate the two- and the four-point correlation functions; higher-order correlation functions may be obtained similarly.

A.2.1. Two-point correlation function

Here, we derive the two-point correlation function in detail. Other combinations of the two fields E_1 and E_2 may be calculated analogously. Using the definition (A.24) of the Schmidt decomposition of the field, and the input-output relation (A.19), the correlation function of E_1 is given by

$$\begin{aligned} \langle E_1^\dagger(\omega') E_1(\omega) \rangle &= \sum_{k,k'} \psi_k(\omega') \psi_{k'}^*(\omega) \\ &\times \langle 0 | \left(\cosh(r_k) A_k^\dagger + \sinh(r_k) B_k \right) \left(\cosh(r_{k'}) A_{k'} + \sinh(r_{k'}) B_{k'}^\dagger \right) | 0 \rangle. \end{aligned} \quad (\text{A.35})$$

Clearly, only the term $\propto B_k B_{k'}^\dagger$ may yield a signal, such that we arrive at

$$\begin{aligned} \langle E_1^\dagger(\omega') E_1(\omega) \rangle &= \sum_k \sinh^2(r_k) \psi_k(\omega) \psi_k^*(\omega') \\ &\equiv g_1(\omega, \omega'). \end{aligned} \quad (\text{A.36})$$

In the second line of Eq. (A.36), we defined the function $g_1(\omega, \omega')$. Note that $g_1(\omega, \omega)$ is the power spectrum of field 1. Similarly, we have, of course,

$$g_2(\omega, \omega') = \sum_k \sinh^2(r_k) \phi_k(\omega) \phi_k^*(\omega'). \quad (\text{A.37})$$

A.2.2. Four-point correlation function

The four-point correlation function may be calculated analogously. The final result reads

$$\begin{aligned} &\langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle \\ &= (f_{12}(\omega'_a, \omega'_b) + f_{21}(\omega'_a, \omega'_b)) (f_{12}^*(\omega_a, \omega_b) + f_{21}^*(\omega_a, \omega_b)) \end{aligned} \quad (\text{A.38a})$$

$$+ (g_1(\omega_a, \omega'_a) + g_2(\omega_a, \omega'_a)) (g_1(\omega_b, \omega'_b) + g_2(\omega_b, \omega'_b)) \quad (\text{A.38b})$$

$$+ (g_1(\omega_a, \omega'_b) + g_2(\omega_a, \omega'_b)) (g_1(\omega_b, \omega'_a) + g_2(\omega_b, \omega'_a)), \quad (\text{A.38c})$$

where we defined

$$f_{12}(\omega_a, \omega_b) = \sum_k \cosh(r_k) \sinh(r_k) \psi_k(\omega_a) \phi_k(\omega_b), \quad (\text{A.39})$$

and f_{21} is obtained by exchanging ψ_k and ϕ_k in Eq. (A.39). Fig. A.2 shows how the frequency correlations in Eq. (A.39) arise due to the sum over the Schmidt modes, by

A.3. Properties of entangled two-photon states

plotting the real part of $f_{12}(\omega, \omega)$ for different values N , after which we terminate the sum in Eq. (A.39),

$$f_{12}(\omega_a, \omega_b) \approx \sum_{k=1}^N \cosh(r_k) \sinh(r_k) \psi_k(\omega_a) \phi_k(\omega_b). \quad (\text{A.40})$$

If we terminate the sum after the first Schmidt mode, f_{12} shows the broad spectral envelope of the first Hermite function. As we increase the number of Schmidt modes, the bandwidth decreases substantially. However, strong oscillations with frequency also emerge, and only after we have converged (solid, green plot), these oscillations are averaged out, such that we obtain a well-behaved result.

To interpret the different terms (A.38a)-(A.38c), we note that the first line stems from correlated interactions with both fields, whereas the other two lines are given by uncorrelated products of correlation functions of the two fields. This motivates the following nomenclature: Eq. (A.38a) will be denoted the *coherent* contribution, and the other two lines *incoherent* contributions.

Note also that for weak pump intensities ($\alpha/\hbar \ll 1$), when different entangled pairs do not overlap temporally, the mode weights r_k are very small, *i.e.* $r_k \ll 1$. This allows us to expand the sinh and cosh functions to leading order, and obtain $\sinh(r_k) \cosh(r_k) \propto r_k$, as well as $\sinh^2(r_k) \propto r_k^2$. Hence, for weak downconversion, the second and third line scale as $\sim r_k^4$, and may be neglected, such that the four-point correlation function is given by Eq. (A.38a). This coincides with the result obtained by only considering a two-photon state as input [Branning99]. Hence, the entire four-point correlation function scales as $\sim r_k^2$ at low intensities. Note that this is the same scaling behavior as the two-point correlation function. This is the formal origin of the linear scaling behavior of two-photon absorption signals of entangled photons as discussed in chapters 2 and 4.

As a word of caution, it should be noted that our current approach, which neglects the time-ordering of the Dyson series in the derivation Eq. (A.5) (four-, six, eight-, .. photon processes),³ is not capable to describe the influence of very high pump intensities on the Schmidt mode structure, as was investigated, for instance, for frequency conversion in Ref. [Reddy13]. Hence, our present model may be applied with full confidence for moderately high gain only, where such multi-photon processes may be neglected.

A.3. Properties of entangled two-photon states

In the preceding two sections, we have presented the necessary formalism to calculate the output fields of the nonlinear crystal driven by a strong pump pulse. However, the rather abstract Schmidt mode decomposition does not endow one with intuition for the fields. Hence, before turning to the full four-point correlation function, we first discuss properties of entangled two-photon states, their entanglement properties, and frequency correlations.

³An in-depth discussion of the discrepancies due to multiphoton processes can be found in Ref. [Christ13b].

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Figure A.2.: Real part of the of the correlation function $f_{12}(\omega, \omega)$ for degenerate entangled photons with $\omega_p = 22,000 \text{ cm}^{-1}$, $\sigma_p = 100 \text{ cm}^{-1}$, and $T = 10 \text{ fs}$. The dashed lines correspond to a termination of the sum in Eq. (A.39) after $N = 1, 10, 20, 30, 40$ and 50 , respectively. The solid green line corresponds to $N = 60$.

A.3.1. Mode entanglement

We start again with the two fields E_1 and E_2 being in the ground state. When the downconversion is weak, *i.e.* $r_k \ll 1$, we can expand the exponential (A.18), and obtain to leading order the un-normalized twin photon state

$$|\psi\rangle \propto \sum_k r_k A_k^\dagger B_k^\dagger |0\rangle. \quad (\text{A.41})$$

Normalizing the state, $\langle\psi|\psi\rangle = 1$, we have

$$|\psi\rangle = \sum_k \tilde{r}_k A_k^\dagger B_k^\dagger |0\rangle. \quad (\text{A.42})$$

The weights $\tilde{r}_k$ are plotted in Fig. A.3a) for two different sets of control parameters. In the strongly entangled case (blue), many modes have appreciable weight, and need to be included in the description, whereas in the weakly entangled case (red), fewer modes with larger weight dominate.

This motivates the definition of the entanglement entropy in terms of the weights $\tilde{r}_k$,

$$E(\psi) = - \sum_k \tilde{r}_k^2 \ln \tilde{r}_k^2. \quad (\text{A.43})$$

If ψ is separable, we have $\tilde{r}_1 = 1$, and all other weights vanish. Hence, $E(\psi) = 0$. Otherwise $E(\psi)$ is larger than zero.

We now present calculations for phase-matching with parameters $T_1 < 0$, as described at the beginning of this chapter. Using Eq. (A.32), we may calculate the entanglement

A.3. Properties of entangled two-photon states

Figure A.3.: a) Distribution of the mode weights $\tilde{r}_k$ [Eq. (A.42)] in the analytic approximation for degenerate downconversion with pump bandwidth $\sigma_p = 100 \text{ cm}^{-1}$, and entanglement times $T = 10 \text{ fs}$ (blue), and 100 fs (red). b) Entanglement entropy, Eq. (A.43), plotted vs. the pump bandwidth σ_p and the entanglement time T .

entropy straightforwardly. It is shown in Fig. A.3b) as a function of the the pump pulse bandwidth σ_p and the entanglement time T . For small values of either of the two variables, and most remarkably when they both are small, we observe strong entanglement. The entanglement then decreases, goes through a minimum, and then starts to increase again for large values of the two variables. As we will show with more detailed figures, this behavior may be understood by a crossover in frequency correlations between the photons: When σ_p is much smaller than $1/T$, the bandwidth of the individual photons is given by the inverse entanglement time. However, the sum of the photon frequencies is distributed with width σ_p . Hence, the two photon frequencies are strongly anti-correlated. In the opposite regime, when $\sigma_p \ll 1/T$, the two frequencies are positively correlated. Thus, there has to be an intermediate, weakly correlated regime, when the photons pass from one extreme to the other. This is precisely what we see in Fig. A.3. Note also that the entanglement entropy increases without bound, when either $T \rightarrow 0$ or $\sigma_p \rightarrow 0$. In the former case, the bandwidth of the photon wavepackets in this regime is roughly given by $1/T$, and therefore diverges. The latter case may be rationalized by noting that it requires an infinite number of Schmidt modes to represent the cw-limit pump envelope $\delta(\omega_a + \omega_b - \omega_p)$.

A.3.2. Frequency (anti-)correlations

In the previous section, we have mentioned the frequency correlations associated with parameter regimes with strong entanglement. These are shown more explicitly in Fig. A.4 where we depict the absolute value of the coherent correlation function $f_{12}(\omega_a, \omega_b)$ for different exemplary values: Fig. A.4a) represents the strongly anti-correlated regime,

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Figure A.4.: Absolute value of the coherent correlation function $f_{12}(\omega_a, \omega_b)$, Eq. (A.39), of degenerate, entangled photon pairs with a) $\sigma_p = 100 \text{ cm}^{-1}$, $T = 18 \text{ fs}$, b) $\sigma_p = 100 \text{ cm}^{-1}$, $T = 450 \text{ fs}$, and c) $\sigma_p = 400 \text{ cm}^{-1}$, $T = 900 \text{ fs}$.

where we observe a strong resonance line along the antidiagonal. It provides a clear interpretation: If we measure ω_a first, its value is picked randomly from the broad distribution, which is given by the marginal of f_{12} with respect to the ω_a -axis. But after measuring the value $\omega_1 - \delta x$, the value for the measurement of ω_b collapses onto a narrow distribution around $\omega_2 + \delta x$. Hence, the two values are anti-correlated. With regard to the form of the downconversion Hamiltonian, Eq. (A.6), this regime is characterized by $\sigma_p \ll 1/T$, and the frequency correlations are therefore created by the pump amplitude A_p .

Panel A.4b) shows the weakly correlated intermediate regime. Here, the measurement of ω_a does not affect the distribution along ω_b as strongly as before. However, as can be seen in Fig. A.3b), the complete absence of correlations is very hard to achieve. In fact, this is an actively pursued field in quantum information theory, since perfect Bell states in the polarization degree of freedom require spectrally uncorrelated photons [Grice97].

Finally, panel A.4c) presents an example of positive frequency correlations. When the first photon is detected at $\omega_1 - \delta x$, the second photon has increased probability to be detected at $\omega_2 - \delta x'$. It corresponds to the regime where $\sigma_p \gg 1/T$, and the correlations are therefore created by the phase-matching function, while the pump envelope merely represents a broad background. Due to the structure of the Δk , the two frequencies do not show perfect correlations, but we rather have $\delta x' \sim \delta x \times |T_1/T_2|$.

A.4. High-intensity regime

So far, we have only been concerned with properties of the two-photon state created by parametric downconversion. However, when the pump intensity increases, different photon pairs start to overlap in time, and uncorrelated coincidences may occur in optical signals. This is described by the additional terms (A.38b) and (A.38c) in the four-point

correlation function. Here, we will discuss this transition, and how it affects properties of the entangled states.

A.4.1. Photon number distributions

The photon number in field 1 (field 2 can be treated analogously, of course) at time t is given by [Eqs. (A.24) and (A.25)]

$$n_1(t) = \langle E_1^\dagger(t) E_1(t) \rangle \quad (\text{A.44})$$

$$= \sum_{k,k'} \psi_k(t) \psi_{k'}^*(t) \langle 0 | \left(\cosh(r_k) A_k^\dagger + \sinh(r_k) B_k \right) \times \left(\cosh(r_{k'}) B_{k'}^\dagger + \sinh(r_{k'}) A_{k'} \right) | 0 \rangle \quad (\text{A.45})$$

$$= \sum_k \sinh^2(r_k) |\psi_k(t)|^2. \quad (\text{A.46})$$

The time-integrated photon number is therefore given by

$$n_1 = \int dt n_1(t) = \sum_k \sinh^2(r_k). \quad (\text{A.47})$$

To interpret this formula, note that

$$\sinh^2(r_k) = r_k^2 + \frac{1}{3} r_k^4 + \dots \quad (\text{A.48})$$

As one can easily verify, the first term r_k^2 gives the contribution of the two-photon state (A.41). Consequently, the second term stems from four-photon contributions, and so forth. When $n_1 \ll 1$, we know that it is therefore safe to restrict calculations to the coherent contributions of the correlation function. We recall that in our definition of the field, Eq. (A.24), we have neglected the field normalization.

A.4.2. Coherent and incoherent contributions to correlation functions

When discussing the transition between the behavior of the full four-point correlation function $\langle E^\dagger(\omega'_a) E^\dagger(\omega'_b) E(\omega_b) E(\omega_a) \rangle$ in the high-intensity regime, we immediately encounter one obvious problem: Whereas it was sufficient to plot two-dimensional correlation plots in the two-photon case, since only two frequencies ω'_a and ω'_b (or ω_a and ω_b) were correlated, here, all four frequencies are correlated! To still give some intuition to the full correlation function, we depict three-dimensional surfaces of the full four-dimensional frequency space in Fig. A.5 at different pump intensities. The red surfaces correspond to the equipotential surface at 80 % of the maximum value, and the sides depict projections onto the corresponding two-dimensional subspaces.

Panel a) shows the surface for very small mean photon number, $\bar{n} = 0.03$, in which case the two fields are still well approximated by the two-photon state. The equipotential surface is cigar-shaped, reflecting the strong anti-correlations between ω_a and ω_b . The

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third dimension ω'_a is peaked narrowly around $11,000 \text{ cm}^{-1}$. This is because we have set the fourth frequency $\omega'_b = 11,000 \text{ cm}^{-1}$, and due to the strong correlations between those two frequencies, our projection along ω'_a is peaked around $\omega_p - \omega'_b$.

With increasing photon number [panels b) - d)], the incoherent contributions to the field correlation function create ball-shaped contributions, which add to the cigar shape, until, at high photon numbers, the correlated part can hardly be noticed any more.

A.4.3. Quadrature squeezing

Field quadrature fluctuations are not discussed in the present dissertation. For the sake of completeness and since it may constitute an interesting field for further investigations, we finally point out how the quantum correlations between the two fields manifest themselves in correlated fluctuations.

While energy-time entanglement may not be observed anymore in the strong pump regime, another peculiar feature shows up: The squeezing of correlated fluctuations of the two beams. To see this, let us first define the quadratures of Schmidt mode k ,

$$X_k = \frac{1}{2} (A_k + B_k + A_k^\dagger + B_k^\dagger), \quad \text{and} \quad Y_k = \frac{1}{2i} (A_k^\dagger + B_k^\dagger - A_k - B_k). \quad (\text{A.49})$$

Note that these are quadratures of the combined field $E_1 + E_2$. One can easily verify by straightforward calculation of $\langle n_i^2 \rangle$ that each individual field shows chaotic fluctuation statistics. However, for these combined fluctuations, we obtain

$$\langle X_k^2 \rangle = \frac{1}{2} e^{2r_k}, \quad (\text{A.50})$$

$$\langle Y_k^2 \rangle = \frac{1}{2} e^{-2r_k}. \quad (\text{A.51})$$

Hence, the fluctuations in Y_k are squeezed, as the mode weights r_k increase with the pump intensity. The fluctuations in X_k , on the other hand, increase exponentially, such that we always have $\langle X_k^2 \rangle \langle Y_k^2 \rangle = 1/4$.

Figure A.5.: Four-point field correlation functions of degenerate downconverted beams, $\langle E^\dagger(\omega'_a)E^\dagger(\omega'_b = 11,000 \text{ cm}^{-1})E(\omega_b)E(\omega_a) \rangle$, with pump frequency $\omega_p = 22,000 \text{ cm}^{-1}$ and bandwidth $\sigma_p = 100 \text{ cm}^{-1}$. The entanglement time is set to $T = 30 \text{ fs}$, and the average photon number is indicated in the panels. It corresponds to a) $\alpha/\hbar = 0.001$, b) 0.0025 , c) 0.005 , and d) 0.01 in Eq. (A.6). The red surfaces are equipotential surfaces with 80 % of the maximum value

B. The bacterial reaction center of *Blastochloris viridis*

Here, we provide the details of the Hamiltonian and of the secular Redfield equation which has been used in chapters 4 to 6. As described in Ref. [Fingerhut12], it is based on a tight-binding formulation of the Hamiltonian using the X-ray data from Ref. [Deisenhofer95], Protein Data Bank code 1PRC. The site energies are taken from Ref. [Won88], the coupling between the special pair was chosen to be 852 cm^{-1} to reproduce experimental data, and the other couplings were calculated in the dipole approximation. Transport rates between the excitons were simulated by coupling the sites to five harmonic bath modes using a generalized Redfield rate equation.

We will not discuss details of the derivation of the model, but rather state its final form.

B.1. Hamiltonian

As discussed in much detail in the course of this dissertation, the electronic excited states - the excitons - group into manifolds, which are defined by the number of excitons, *i.e.* the number of excited electron-hole pairs. The Hamiltonian of the system thus reads

$$H_{\text{el}} = H_g \oplus H_e \oplus H_f \oplus \cdots, \quad (\text{B.1})$$

where the dots denotes higher-excited manifolds which are not included in the model. H_g denotes the ground state, H_e the single exciton, and H_f the two-exciton manifold.

The 12 single exciton energies are given in table B.1, and dipole moments connecting the ground state with the single exciton manifold are given in table B.2. In contrast to the original model, we do not take the vector nature of the electromagnetic field into account, and instead use the absolute value of the dipole vectors of Ref. [Fingerhut12].¹ The dipole moments are given in units of *Debye* ($1D = 3.33564 \times 10^{-30} \text{ Cm}$ in SI units), which provides the advantage that they are on the order of one.² The excitons consist of correlated electron-hole pairs. Depending on the wavefunction of their constituents, excitons are conventionally categorized into two groups: *molecular excitons* (ME), when

¹This approach oversimplifies the problem to some extent, as it is not able to properly account for the relative angle between different dipoles, which is only included via their interaction in the two-exciton manifold. However, as noted throughout this dissertation, we do not attempt to provide an in-depth analysis of the bacterial RC, but rather take it as a realistic example to demonstrate features of the interaction of quantum light with a complex quantum system.

²For comparison, a proton and an electron separated by one Angstrom create a dipole moment of $4.8 D$.

B. The bacterial reaction center of *Blastochloris viridis*

both electron and hole reside predominantly on the same site, and *charge separated* (CS) states, when they reside on different sites (chromophores). Of course, due to the dipole interaction between distinct sites, wavefunctions can sometimes span different chromophores, in which case the above definition becomes somewhat ambiguous (even though this is not the case in our present model), and it is more precise to talk of “states with strong CS (ME) character” [Romero14]. One way to determine their character is by the size of their dipole moment: The attraction between electron and hole in a CS state is shielded by the presence of many other bound electrons in the aggregate. Hence, CS states have a very small dipole moment compared to ME states.

Exciton	$ e_1\rangle$	$ e_2\rangle$	$ e_3\rangle$	$ e_4\rangle$	$ e_5\rangle$	$ e_6\rangle$
Energy / cm^{-1}	9,458.75	9,628.46	9,794.6	10,036.4	10,245	11,908.3
Exciton	$ e_7\rangle$	$ e_8\rangle$	$ e_9\rangle$	$ e_{10}\rangle$	$ e_{11}\rangle$	$ e_{12}\rangle$
Energy / cm^{-1}	12,185.2	12,278.9	12,585.9	12,936.8	15,639.3	16,372.8

Table B.1.: Single exciton energies of the model of the bacterial RC are given in wavenumbers (cm^{-1}) [Fingerhut12].

As can be seen from the magnitude of the dipole moments in table B.2, excitons $|e_1\rangle - |e_4\rangle$, $|e_{11}\rangle$ and $|e_{12}\rangle$ are CS states. Due to the electronic shielding of their charges by the environment, their dipole moment is only weak, and they can only be populated via the decay of molecular excitons. Since this decay takes place on the order of several hundred of fs, we do not encounter it in our simulations of the RC, and only deal with the much faster energy transport to the special pair. The dominant overlap of the ME states ($|e_5\rangle - |e_{10}\rangle$) with the chromophores of the RC is depicted in Fig. B.1. States $|e_9\rangle$ and $|e_{10}\rangle$ reside almost exclusively on the two electron-accepting bacteriopheophytins, states $|e_7\rangle$ and $|e_8\rangle$ reside on the outer bacteriochlorophylls (even though these states already have substantial overlap with special pair chromophores), and the lowest-energy eigenstates $|e_5\rangle$ and $|e_6\rangle$ are both delocalized over the special pair.

The 41 two-exciton energies in the model are given in table B.3, and the 492 dipole moments connecting them to the single exciton states are listed at the end of the appendix.

B.2. Secular Redfield equation

The coupling to the environment is accounted for by a secular Redfield equation, which describes the simplest form of environmental coupling [Abramavičius09]: While the off-diagonal elements of the density matrix (in the exciton eigenbasis) decay exponentially, the populations of the single-exciton manifold undergo relaxation governed by a Pauli rate equation. Two-exciton transport is not taken into account.

The elements of the Green’s function for the coherence between ground state and single-exciton manifold reads

$$\mathcal{G}_{eg}(t) = e^{-i\omega_{eg}t - \gamma_{eg}t}, \quad (\text{B.2})$$

B.2. Secular Redfield equation

Exciton	Dipole moment μ_{eg}/D
$ e_1\rangle$	0.0220001
$ e_2\rangle$	0.219537
$ e_3\rangle$	0.00866293
$ e_4\rangle$	0.450375
$ e_5\rangle$	6.55105
$ e_6\rangle$	2.83608
$ e_7\rangle$	6.32903
$ e_8\rangle$	2.56476
$ e_9\rangle$	3.50193
$ e_{10}\rangle$	4.03867
$ e_{11}\rangle$	0.051421
$ e_{12}\rangle$	0.0563672

Table B.2.: Dipole moments connecting the ground state with the single exciton manifold are given in units of *Debye* [Fingerhut12].

Exciton	$ f_1\rangle$	$ f_2\rangle$	$ f_3\rangle$	$ f_4\rangle$	$ f_5\rangle$	$ f_6\rangle$	$ f_7\rangle$
Energy / cm^{-1}	20548.7	20728	20883.7	21127.6	21652.8	21696.6	21711.3
Exciton	$ f_8\rangle$	$ f_9\rangle$	$ f_{10}\rangle$	$ f_{11}\rangle$	$ f_{12}\rangle$	$ f_{13}\rangle$	$ f_{14}\rangle$
Energy / cm^{-1}	21872	21986	22052.3	22160.8	22195	22288.2	22395.4
Exciton	$ f_{15}\rangle$	$ f_{16}\rangle$	$ f_{17}\rangle$	$ f_{18}\rangle$	$ f_{19}\rangle$	$ f_{20}\rangle$	$ f_{21}\rangle$
Energy / cm^{-1}	22437.5	22506.2	22565.2	22604.3	22731.3	22831.2	22973.1
Exciton	$ f_{22}\rangle$	$ f_{23}\rangle$	$ f_{24}\rangle$	$ f_{25}\rangle$	$ f_{26}\rangle$	$ f_{27}\rangle$	$ f_{28}\rangle$
Energy / cm^{-1}	23182.3	24109	24166.8	24467.8	24496.7	24773.5	24845.5
Exciton	$ f_{29}\rangle$	$ f_{30}\rangle$	$ f_{31}\rangle$	$ f_{32}\rangle$	$ f_{33}\rangle$	$ f_{34}\rangle$	$ f_{35}\rangle$
Energy / cm^{-1}	24862.1	25123.4	25214.1	25522.6	26618.4	27808	27887.6
Exciton	$ f_{36}\rangle$	$ f_{37}\rangle$	$ f_{38}\rangle$	$ f_{39}\rangle$	$ f_{40}\rangle$	$ f_{41}\rangle$	
Energy / cm^{-1}	28225	28305.1	28575.9	28635.9	29309.5	32092.3	

Table B.3.: Two-exciton energies of the model are given in wavenumbers (cm^{-1}) [Fingerhut12].

B. The bacterial reaction center of *Blastochloris viridis*

Figure B.1.: Spatial distribution of the eigenstates. The table on the right labels the eigenstates in ascending energy, distinguishes molecular excitons (ME) and charge separated states (CS), and identifies the dominant sites that contribute to the state [Fingerhut12], e.g. the state $|e_5\rangle$ is - to a good approximation - a balanced superposition of the two special-pair sites ${}^P\text{BCl}_L$ and ${}^P\text{BCl}_M$.

where the first two indices denote the final matrix element, and the last two indices its initial element. Similarly, we have

$$\mathcal{G}_{fe}(t) = e^{-i\omega_{fe}t - \gamma_{fe}t}, \quad (\text{B.3})$$

$$\mathcal{G}_{ee';ee'}(t) = e^{-i\omega_{ee'}t - \gamma_{ee'}t}, \quad \text{for } e \neq e'. \quad (\text{B.4})$$

In the course of this dissertation, we used the values $\gamma_{eg} = \gamma_{ef} = \gamma_{ee'} = 200 \text{ cm}^{-1}$, which yields the appropriate line broadening to be expected in such a molecular aggregate (see the linear absorption signal in Fig. 4.6). The population transport is described by a Pauli rate equation [Breuer02]

$$\mathcal{G}_{e'e';ee} = \exp[Kt]_{e',e}, \quad (\text{B.5})$$

where K denotes the transport matrix (given in table B.4). It can be diagonalized as

$$\mathcal{G}_{e'e';ee} = \sum_{p=1}^{12} \frac{\chi_{e'p}^R \chi_{pe}^L}{D_p} e^{-\lambda_p t}, \quad (\text{B.6})$$

where $\chi^L(\chi^R)$ denote the left (right) eigenvectors of K , λ_p their common eigenvalues, and $D_p = \chi_{pe}^L \cdot \chi_{ep}^R$ (see Ref. [Abramavičius09] for details).

[illegible]

Table B.4.: Population transport matrix K , Eq. (B.5), describing single-exciton transport [Fingerhut12].

B. The bacterial reaction center of *Blastochloris viridis*

The following list provides the dipole moments connecting the single and the two-exciton states (from Ref. [Fingerhut12]). All values are again given in units of Debye.

Double exciton transition dipoles:	3	4	0.03313771780446113
e f dipole moment / D	4	4	5.093107690647137
1 1	0.20388974339914695	5	4 0.15276604243862574
2 1	0.02237699257720751	6	4 0.08220299978632166
3 1	0.9761266315832182	7	4 0.029900680029383946
4 1	0.02983054149050265	8	4 0.01827620763633692
5 1	0.02075608130675923	9	4 0.0008427979604068582
6 1	0.008680444398567161	10	4 0.0007742195758983623
7 1	0.00908128619777072	11	4 0.004001343558081585
8 1	0.004163182924085849	12	4 0.00024470147668841314
9 1	0.018670116777358303	1	5 1.6544364000855398
10 1	0.0000798248918988933	2	5 0.20464293166430156
11 1	0.002612445729213145	3	5 0.1390785427323712
12 1	0.021218866149068854	4	5 0.03796755897415056
1 2	0.014766892472761492	5	5 0.03714540184061683
2 2	0.1560344701860778	6	5 0.004789492917874397
3 2	0.08879863217420637	7	5 0.041143832369413526
4 2	0.8155576526483275	8	5 0.01123168646991626
5 2	0.11967591372437313	9	5 0.020106642073245348
6 2	0.06944736967243323	10	5 0.00003680426429654585
7 2	0.06592711835036096	11	5 0.003349823001458435
8 2	0.0279209304944606	12	5 0.03280246437688638
9 2	0.010220362487287867	1	6 2.1359634168414496
10 2	0.0005534679357963206	2	6 0.0630993040435471
11 2	0.01596492023606958	3	6 0.1929310667037582
12 2	0.003999768065212782	4	6 0.11904281838299571
1 3	1.0422143354617608	5	6 0.015030997769366776
2 3	0.12250986261521968	6	6 0.004387738998094576
3 3	5.0238677812941095	7	6 0.012169254296258255
4 3	0.004504381038066828	8	6 0.006036398909134485
5 3	0.006167072778863567	9	6 0.002483630263953353
6 3	0.006973664835113601	10	6 0.00012270058911863463
7 3	0.0007159251720962184	11	6 0.0004922783316430249
8 3	0.00157674803518032	12	6 0.004419570758316071
9 3	0.0010726032722406032	1	7 4.330924255017629
10 3	0.00006482539417300986	2	7 0.11017331093259383
11 3	0.000559200251192719	3	7 0.2095853273678289
12 3	0.002526783040112467	4	7 0.03601478999647228
1 4	0.03824191216749498	5	7 0.019173611325042552
2 4	0.8737345928650186	6	7 0.006605844592786679

B.2. Secular Redfield equation

7	7	0.010105053489745663	2	11	0.30617211482105944
8	7	0.022580050002158986	3	11	0.0029101188827736916
9	7	0.007386141666770276	4	11	0.4387328344813504
10	7	0.00002178900281105127	5	11	8.242650688305371
11	7	0.0015357863670217937	6	11	2.0711390291694567
12	7	0.015443855923030233	7	11	1.7613678949115088
1	8	0.019245724081117344	8	11	0.6784771656290284
2	8	5.105672553709256	9	11	0.06127570879379609
3	8	0.016905148610955774	10	11	0.05772150274865078
4	8	0.12330135360108582	11	11	0.05085842866674117
5	8	0.05069754971583538	12	11	0.0003788220701199443
6	8	0.03521297227640546	1	12	0.7065299373909147
7	8	0.09539604298050366	2	12	3.7431806030321324
8	8	0.18203939463754132	3	12	0.02899455896301925
9	8	0.0034507678280674	4	12	0.027863902179746828
10	8	0.0014115418334619064	5	12	0.24993207886505883
11	8	0.00034948862265029456	6	12	0.07943219266475023
12	8	0.0005896486264970351	7	12	0.048843102076859324
1	9	0.007888526322159292	8	12	0.07688574235582044
2	9	0.03253126565179412	9	12	0.1953931456502157
3	9	1.4538622099181202	10	12	0.0022318308877206624
4	9	0.19464029004214414	11	12	0.001995878347400963
5	9	0.036660756391581714	12	12	0.002197663132989676
6	9	0.017293173997690533	1	13	0.0025608279263982184
7	9	0.027972297169692736	2	13	0.05594772075700046
8	9	0.007039015747283138	3	13	0.011775247768794506
9	9	0.002925604084458456	4	13	4.701257456500334
10	9	0.0000350248853831872	5	13	0.15345792969717922
11	9	0.0008472908719684167	6	13	0.08976765701047343
12	9	0.013560170174736009	7	13	0.1660171365228383
1	10	0.058371271854037926	8	13	0.360027927488808
2	10	0.013914785502572434	9	13	0.002951884533442323
3	10	4.488471491933529	10	13	0.0005047156590883227
4	10	0.06102318803168186	11	13	0.0012734744613776125
5	10	0.015999173473767322	12	13	0.00008791770919570187
6	10	0.005992698631084329	1	14	4.022384841505845
7	10	0.00903212339727071	2	14	0.007920557032248426
8	10	0.009282527904360384	3	14	0.005807320852063281
9	10	0.0010227928878331135	4	14	0.00010834054518530908
10	10	0.00006852688735532937	5	14	0.0014737619301336835
11	10	0.0002647148992839089	6	14	0.0004154754077796182
12	10	0.004356119709634826	7	14	0.0012144502552064289
1	11	0.023065449019986584	8	14	0.00034360214477683346

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9	14	0.0008641512214723126	4	18	3.7796190092654838
10	14	0.021948541683321467	5	18	0.1274257607492692
11	14	0.00001669266161374213	6	18	0.0268216140822304
12	14	0.00019957022801850982	7	18	0.06572822199772409
1	15	0.025514804087235315	8	18	0.049558650792131134
2	15	0.07834202921784705	9	18	0.40051806470450246
3	15	0.006771486349517364	10	18	0.0004437372394620474
4	15	0.3087959826066395	11	18	0.00017055199439684076
5	15	3.950265636131829	12	18	0.0017545500200293522
6	15	1.7524724928272053	1	19	0.005231465828044374
7	15	5.427968113678643	2	19	0.0006390509359705297
8	15	2.1788651830172148	3	19	4.013101651879877
9	15	0.03249704035277674	4	19	0.006695925550040413
10	15	0.017347383560386533	5	19	0.0009288694761407547
11	15	0.015538828016375624	6	19	0.000041499330665084225
12	15	0.00047531831255065275	7	19	0.00017828204781715964
1	16	0.004431841648058288	8	19	0.000130304140084995
2	16	0.04442600977020669	9	19	0.0023995054424683767
3	16	0.0026280869044384737	10	19	0.008671161458011263
4	16	0.06624982476150408	11	19	5.556967664945421*~6
5	16	3.665256419924805	12	19	0.00010458302817575135
6	16	1.4229504464095015	1	20	0.03555249081766283
7	16	2.32697524019852	2	20	0.03048689803079349
8	16	5.524665539376644	3	20	0.03493785676975336
9	16	0.004138135849378196	4	20	0.058321065044201655
10	16	0.015476166227913165	5	20	3.493610486445219
11	16	0.010783021850951617	6	20	0.039007178196578125
12	16	0.00006347693762101398	7	20	0.06906099947647731
1	17	0.006206700501683644	8	20	0.044854008073303774
2	17	4.0376624035325195	9	20	6.5251346658180935
3	17	0.0006711649955121617	10	20	0.0015150491020098989
4	17	0.005040176340410025	11	20	0.0005851523055545112
5	17	0.004249122230587866	12	20	0.0015490617891297945
6	17	0.002748321101953154	1	21	0.00015816613639540544
7	17	0.0015176228754697262	2	21	0.004488867601085601
8	17	0.0038633222447805207	3	21	0.004486663559929583
9	17	0.0007433377618209467	4	21	4.029271284148165
10	17	0.21827045804222545	5	21	0.004187753236035882
11	17	0.00012452434958424799	6	21	0.002377726032986349
12	17	0.00004435139562052698	7	21	0.00044266210247320703
1	18	0.0060090286909241	8	21	0.0013090366550822783
2	18	0.006609694380151022	9	21	0.001442637677400407
3	18	0.49316714677035206	10	21	0.4488993641026907

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11	21	0.00004705040966431642	6	25	0.6421163698107999
12	21	0.000025577206035704915	7	25	5.972305178641243
1	22	0.00036607779080000195	8	25	2.4044409889371376
2	22	0.002882489009010539	9	25	0.33415973384435477
3	22	0.00030055755317025387	10	25	0.04926797639542343
4	22	0.0028933605570505725	11	25	0.0017179763149057091
5	22	4.039834974027528	12	25	0.004056064133048195
6	22	0.040562431644071834	1	26	0.01310941160499967
7	22	0.02211809404044797	2	26	0.00906225776442405
8	22	0.01903739604364263	3	26	0.013476283193959675
9	22	0.0010228233073727837	4	26	0.016228080306323972
10	22	6.532859744620725	5	26	0.026127583035460818
11	22	0.0007615123841763835	6	26	3.4332138859966186
12	22	0.000015833716591754447	7	26	0.1513555597463552
1	23	0.0029872598433624753	8	26	0.48922830540556417
2	23	0.04455755146752681	9	26	2.4999135354025745
3	23	0.003902501488707083	10	26	0.004029360187382235
4	23	0.09102914674930443	11	26	0.0004020602054580881
5	23	0.2627760948654957	12	26	0.015994753861388426
6	23	5.188252356712808	1	27	0.009030648590710415
7	23	2.8612633602725217	2	27	0.002859393290759598
8	23	1.264547002296178	3	27	0.008343794965505804
9	23	0.22735418237413182	4	27	0.0023123467768663072
10	23	0.005635857666451487	5	27	0.0022851390421730054
11	23	0.003543397881215148	6	27	0.2671996958443802
12	23	0.0017218759130355474	7	27	3.868078958836802
1	24	0.0007635424341419147	8	27	0.8092695046991454
2	24	0.009192640767880794	9	27	6.025384762992319
3	24	0.0002991410302749524	10	27	0.023759584324015433
4	24	0.009933773063066219	11	27	0.00021514351942924053
5	24	0.22906551635473202	12	27	0.05345962057572051
6	24	5.005231434229591	1	28	0.00013241300082624061
7	24	1.5661474546456347	2	28	0.0004465867338031885
8	24	2.9389564060171085	3	28	0.00012699829977436708
9	24	0.024033513359525693	4	28	0.0006936440251739793
10	24	0.05176710869586981	5	28	0.011967854716949066
11	24	0.0029148690510209887	6	28	4.044663367871299
12	24	0.0003911105986610437	7	28	0.05028807698152714
1	25	0.0019110900026817156	8	28	0.14772338232643098
2	25	0.008443018009633759	9	28	0.05512633701353646
3	25	0.002247784152991563	10	28	2.708733203565829
4	25	0.01827908802594528	11	28	0.00007817341291737236
5	25	0.11715142583216646	12	28	0.00008606147870772381

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1	29	0.004876645125965185	8	32	0.005165990660410775
2	29	0.0030158312791482554	9	32	4.011785370143821
3	29	0.0032017091723435783	10	32	3.519881101415217
4	29	0.0038810145755306044	11	32	3.801803618427497* ⁻⁶
5	29	0.006162835870180546	12	32	0.00036584477459572934
6	29	0.15253303988080746	1	33	0.026454960086740708
7	29	0.5571897867890258	2	33	0.003922118646307503
8	29	3.5388845718508537	3	33	0.01499961274093768
9	29	2.615469431454514	4	33	0.005213621878483325
10	29	0.0348524552991163	5	33	0.05674273578617796
11	29	0.0001054284158934867	6	33	0.0005594565007558675
12	29	0.022798359086758854	7	33	0.003158063829906546
1	30	0.00005769941168131613	8	33	0.0015906642900615452
2	30	0.00029199630861293435	9	33	0.0019630404155605153
3	30	0.00008892571259641386	10	33	0.000037385116787299194
4	30	0.00015440987717710937	11	33	0.000038913312189167345
5	30	0.004203608862518491	12	33	6.406753433312546
6	30	0.048724182508586025	1	34	0.0008328332760048676
7	30	4.044559500715127	2	34	0.017948066994038663
8	30	0.3523045251909206	3	34	0.0005855864604970047
9	30	0.027765012865332873	4	34	0.004151968435618672
10	30	6.341715511891399	5	34	0.0032202678611777
11	30	0.00004823107609655418	6	34	0.011752620987800978
12	30	0.0007083331821946505	7	34	0.05053042623241961
1	31	0.000024321620424274777	8	34	0.009612413014482889
2	31	0.00021658398610862809	9	34	0.0012127014946465599
3	31	0.00003041416380274164	10	34	0.00010279930083473331
4	31	0.00005240985163980242	11	34	6.209967863648651
5	31	0.0029422972313000602	12	34	0.000138737882263353
6	31	0.0979810626284998	1	35	0.00018539321370667806
7	31	0.32318919496858184	2	35	0.004610269232921653
8	31	4.162348081516009	3	35	0.0001476572504581133
9	31	0.01260930184007822	4	35	0.0011595520408711462
10	31	2.3918594565193416	5	35	0.003145733461203921
11	31	0.00019334380504813182	6	35	0.012803797307150717
12	31	0.000334392275917447	7	35	0.012186316974910837
1	32	0.00014648877682744163	8	35	0.04988666021703597
2	32	0.00004033228589941934	9	35	0.00041537556475438274
3	32	0.00008798313391749636	10	35	0.0006387310739340931
4	32	0.000022538450021685166	11	35	3.973594710872763
5	32	0.0003050869760133985	12	35	0.000049187627461994955
6	32	0.0012904834150635179	1	36	0.0029641280200053775
7	32	0.01305173306966933	2	36	0.003532576815308621

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3	36	0.0007348653255012105	3	39	0.001915487665552039
4	36	0.0007800119865758474	4	39	0.0003712875229807891
5	36	0.00028783172522731055	5	39	0.0001590838004011722
6	36	0.0004440106532524304	6	39	0.0016479285640354682
7	36	0.0008892423742141398	7	39	0.022704399767271982
8	36	0.0005392475666009073	8	39	0.0518682003282358
9	36	0.05192748711472567	9	39	0.0007630186440405569
10	36	9.81081382142501* ⁻⁶	10	39	0.00003630610664158304
11	36	3.493186555625107	11	39	0.00008877435338412779
12	36	0.0007501357594689111	12	39	4.658430709981635
1	37	0.008945645509693529	1	40	0.0001503589052220267
2	37	0.001914728936992388	2	40	0.000027649156972184524
3	37	0.010210595701064654	3	40	0.00006367423381907394
4	37	0.001962906083539913	4	40	8.289867131028097* ⁻⁶
5	37	0.0006696583265046437	5	40	8.503897226154606* ⁻⁷
6	37	0.054354092319990034	6	40	0.00007340422987778021
7	37	0.01642694980226396	7	40	0.00028642368723232373
8	37	0.005663175167086041	8	40	0.00018907002189511694
9	37	0.0005699599520220697	9	40	0.0003226532324668234
10	37	0.000050089751596109955	10	40	0.056294495450532285
11	37	0.0011648454088993955	11	40	7.522798504766163* ⁻⁷
12	37	2.6611727207379836	12	40	4.0163207575112825
1	38	0.000025525535544722664	1	41	0.00022506873881507846
2	38	0.00011094477692694246	2	41	0.00016048658071022635
3	38	7.876467420227166* ⁻⁶	3	41	0.0002420942006110225
4	38	0.000026204687385277084	4	41	0.0000618369856680652
5	38	0.0002794686498185619	5	41	0.000011237309992720677
6	38	0.00012966164865333156	6	41	8.35559250762027* ⁻⁶
7	38	0.00021628703920949588	7	41	0.000022703423951653195
8	38	0.000469266461308498	8	41	0.000012090557187594789
9	38	7.71209416465463* ⁻⁶	9	41	7.591713569183772* ⁻⁶
10	38	0.05195746676984935	10	41	3.284571349464188* ⁻⁷
11	38	4.045795268733206	11	41	0.05589642484399159
12	38	0.000015352916157056287	12	41	0.05128719082919243
1	39	0.0025230712107677422			
2	39	0.0005088843876982275			

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Publications

The following publications are based on the present dissertation:

- *Manipulation of two-photon induced fluorescence spectra of chromophore aggregates with entangled photons: A simulation study*
F. Schlawin, K.E. Dorfman, B.P. Fingerhut and S. Mukamel
Physical Review A **86**, 023851 (2012).
- *Suppression of population transport and control of exciton distributions by entangled photons*
F. Schlawin, K.E. Dorfman, B.P. Fingerhut and S. Mukamel
Nature Communications **4**, 1782 (2013).
- *Photon Statistics of Intense Entangled Photon Pulses*
F. Schlawin and S. Mukamel
Journal of Physics B **46**, 175502 (2013).
- *Two-photon spectroscopy of excitons with entangled photons*
F. Schlawin and S. Mukamel
Journal of Chemical Physics **139**, 244110 (2013).
- *Matter correlations induced by coupling quantum light*
F. Schlawin and S. Mukamel
Physical Review A **89**, 013830 (2014).
- *Nonlinear Spectroscopy of controllable Many-Body Quantum Systems*
M. Gessner, F. Schlawin, H. Häffner, S. Mukamel, and A. Buchleitner
New Journal of Physics **16**, 092001 (2014).
- *Nonlinear Spectroscopy of Trapped Ions*
F. Schlawin, M. Gessner, S. Mukamel, and A. Buchleitner
Physical Review A **90**, 023603 (2014).
- *Pump-probe spectroscopy using quantum light with two-photon coincidence detection in preparation*
F. Schlawin, K. E. Dorfman, and S. Mukamel