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Nonlinear Spectroscopy and Quantum Interferometry

Towards Nonlinear Entangled-Photon Spectroscopy

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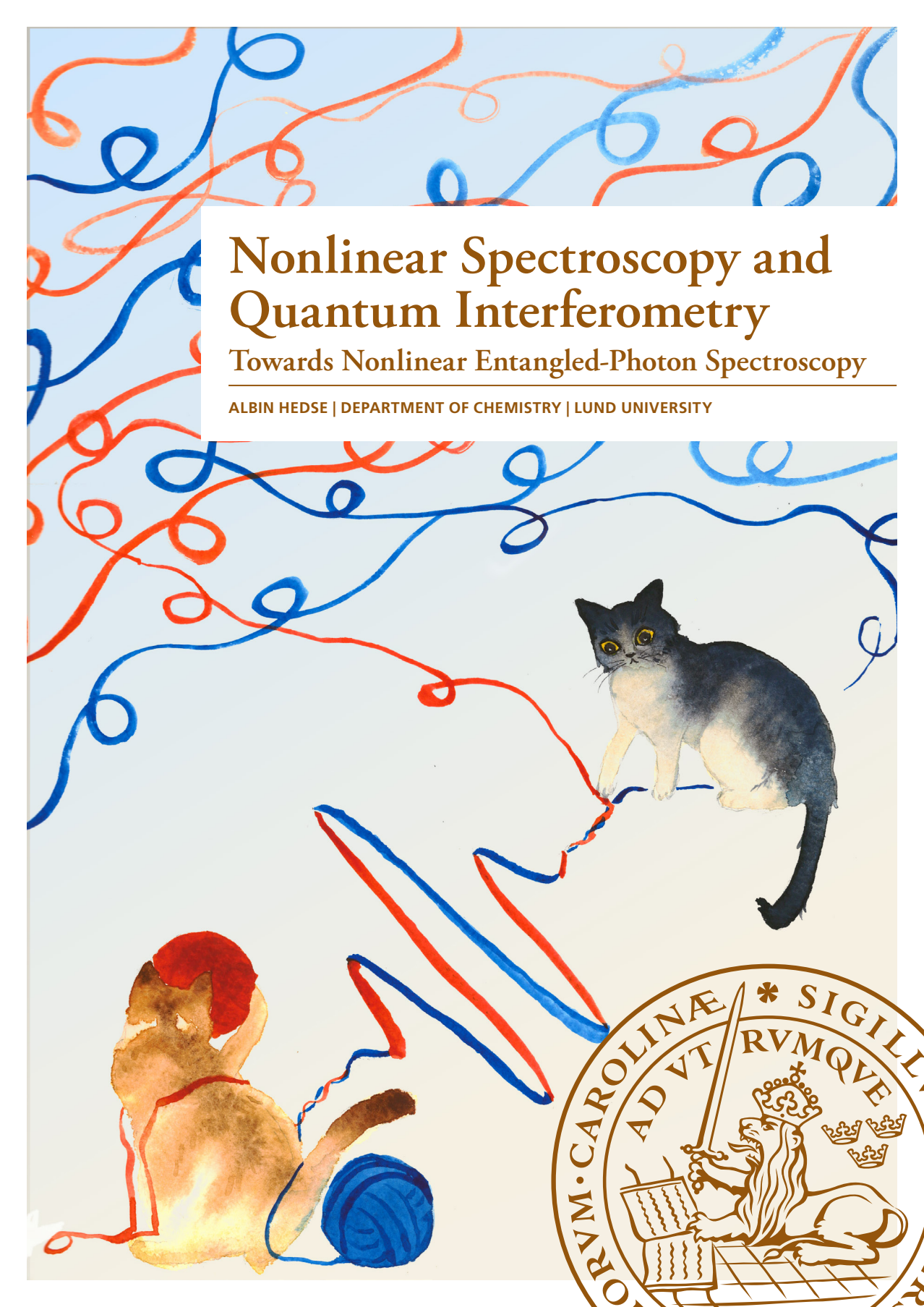
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Nonlinear Spectroscopy and Quantum Interferometry

Towards Nonlinear Entangled-Photon Spectroscopy

ALBIN HEDSE | DEPARTMENT OF CHEMISTRY | LUND UNIVERSITY



Nonlinear Spectroscopy and Quantum Interferometry

Towards Nonlinear Entangled-Photon Spectroscopy

Nonlinear Spectroscopy and Quantum Interferometry Towards Nonlinear Entangled-Photon Spectroscopy

by Albin Hedse



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Thesis for the degree of Doctor of Philosophy
Thesis advisors: Prof. Tõnu Pullerits, Prof. Andreas Wacker
Faculty opponent: Prof. Markus Kowalewski

To be presented, with the permission of the Faculty of Science of Lund University, for public criticism at **KC:F (Kemicentrum)** at the Department of Chemistry on Friday, the 30th of October 2026 at 09:00.

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Abstract Nonlinear spectroscopy is a powerful method for measuring complex systems with significant inter-state correlations. Even methods such as these are, however, still vulnerable to spectral congestion. One of the proposed methods to enhance the resolution of this already powerful technique is to harness the strong correlations of photon-frequency entanglement. This is easier said than done of course, but this doctoral thesis presents work in nonlinear spectroscopy and towards practical implementations of entangled-photon spectroscopy. Initially, we present some theoretical analysis of problems which may arise in nonlinear spectroscopy when pulse overlap is an issue. This is carried out in Paper I, which also numerically quantifies a fundamental theoretical limitation that pulse overlap presents, especially for short-lived signals. We then go on to experimental data analysis of the origins of coherent beatings and the size-dependence of primarily biexciton binding energies in CdSe quantum dots. These are covered in Papers II and III respectively. Finally, we perform an investigation of the possible upper bounds of an entangled-two photon absorption cross-section. Claims of strong quantum advantages in low-flux regimes have warranted further observation, and in examining them we are taking the first steps towards nonlinear entangled spectroscopy. This is done through use of a Franson interferometer, used here in a novel way by performing delay-dependent coincidence measurements for the purpose of obtaining an upper bound on entangled two-photon absorption cross-sections. This work is covered in Paper IV. We then discuss possible future directions for entangled-photon spectroscopy and the forms it can take.			
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Nonlinear Spectroscopy and Quantum Interferometry Towards Nonlinear Entangled-Photon Spectroscopy

by Albin Hedse



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A doctoral thesis at a university in Sweden takes either the form of a single, cohesive research study (monograph) or a summary of research papers (compilation thesis), which the doctoral student has written alone or together with one or several other author(s).

In the latter case the thesis consists of two parts. An introductory text puts the research work into context and summarizes the main points of the papers. Then, the research publications themselves are reproduced, together with a description of the individual contributions of the authors. The research papers may either have been already published or are manuscripts at various stages (in press, submitted, or in draft).

Cover illustration front: Artistic rendition of entanglement, Franson interference and Schrödinger cats by Maria Åkesson, watercolor and digital.

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Be yourself, no matter what they say
-Sting, 'Englishman in New York'

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List of publications

This thesis is based on the following publications, referred to by their Roman numerals:

I Pulse overlap artifacts and double quantum coherence spectroscopy

A. Hedse, A. A. S. Kalaei, A. Wacker, T. Pullerits
J. Chem. Phys. **158**, 0021-9606 (2023)

I performed the data analysis and wrote a large part of the manuscript.

II Beating signals in CdSe quantum dots measured by low-temperature 2D spectroscopy

Z. Wang, A. Hedse, E. Amarotti, N. Lenngren, K. Židek, K. Zheng, D. Zigmantas, T. Pullerits
J. Chem. Phys. **157**, 0021-9606 (2022)

I performed the data analysis and wrote a majority of the manuscript.

III Direct Visualization of Confinement and Many-Body Correlation Effects in 2D Spectroscopy of Quantum Dots

Z. Wang, E. Amarotti, A. Hedse, N. Lenngren, K. Židek, K. Zheng, D. Zigmantas, T. Pullerits
Adv. Optical Mater. **12**, 2302968 (2024)

I was involved in discussions of the data analysis and contributed to the writing of the manuscript.

IV Franson-Interferometric Bounds on Entangled Two-Photon Absorption

A. Hedse, S. Ramesh, L. Matheis, S. Gstyr, A. Wacker, G. Weihs, R. Keil, Q. Shi, A. Sahu, T. Pullerits
arXiv:2608.27157, (2026)

I designed and built the extension of the setup that allows for two-photon absorption to be measured, in addition to the pump setup, and carried out the measurements. I also performed the data analysis and wrote the majority of the manuscript.

Papers I, II and III are reproduced under CC BY 4.0. Paper IV is reproduced with the permission of the authors.

Publications not included in this thesis:

v **Excited States and Their Dynamics in CdSe Quantum Dots Studied by Two-Color 2D Spectroscopy**

Z. Wang, N. Lenngren, E. Amarotti, A. Hedse, K. Židek, K. Zheng, D. Zigmantas, T. Pullerits,

J. Phys. Chem. Lett. **13**, 1266-1271, (2022)

Popular scientific summary

In nature, there are many complicated, interconnected systems which may contain useful information to us. One example of these systems are chlorophylls in plants, which are in charge of the absorption of sunlight. Together with other molecules, they then transport the absorbed energy from the sunlight into molecules that convert this energy into a form that the plant can use. Processes such as these are broadly understood, but a more in-depth knowledge of the chemical and physical can have interesting implications when it comes to things such as solar cells. One major problem facing solar cells is in fact not a lack of efficiency in absorbing light, but rather lacking an efficient transfer of the absorbed light-energy into a useful electric current. There is potential for studying different complex systems which solve these problems in their own ways which could be of use in designing solutions to our problems.

There are today very powerful techniques for studying these complex objects but these are still limited when looking at highly interconnected systems. When there are too many things occurring too close to one another, it can become hard to resolve individual processes and make any sense of one's measurements. This is up until now performed with extremely fast laser pulses, which are very useful, but which, in addition to the problems listed above may also damage the very systems we intend to study. As a possible solution to both the 'congestion' problem and the photo-damage problem, we then suggest the use of entangled light, to enhance resolution and to reduce the required power of the light used.

Entanglement is a quantum-mechanical phenomenon which states that two or more objects which somehow become 'entangled' can affect each other even when separated a great distance from one another. Put a bit more precisely, it means that one cannot fully describe and measure one entangled particle without taking all 'entangled partners' into account as well. This much-discussed property of quantum mechanical objects is today harnessed mainly within quantum computing and quantum cryptography, but has potential for other applications as well.

In this work we take steps towards using entangled light for the purpose of spectroscopy, i.e. the study of matter through use of light. The unique properties of entangled light allow it to (partially) circumvent some of the restrictions that the laws of physics impose on regular laser pulses which could potentially give significant advantages to this quantum light.

Populärvetenskaplig sammanfattning på svenska

I naturen finns det många komplicerade, hög sammankopplade system som kan innehålla en mångfald med användbar information. Ett sådant exempel är klorofyller i växter, som låter dem absorbera solljus. Klorofyllerna, tillsammans med andra molekyler transporterar sedan den absorberade energin och omvandlar den till kemisk energy som växterna kan använda som näring. Processer som dessa är förstådda på ett allmänt sett, men en djupare förståelse av de kemiska och fysiska processerna kan ge kunskap inom andra områden, som t.ex. utvecklingen av solceller. Ett av de största problemen som solceller stöter på är inte att de inte kan absorbera tillräckligt med ljus, utan snarare att de inte kan transportera och utvinna energin från solljuset på ett effektivt sätt. Genom att studera dessa komplexa system så finns det potential för att hitta lösningar till dessa problem som naturen redan löst.

I nuläget finns det väldigt sofistikerade tekniker för att undersöka dessa svårförstådda system, men vi har fortfarande begränsningar när det gäller en hög grad komplexitet. När för mycket händer i ett litet utrymme blir det svårt att upplösa allt samtidigt. Tills nu så används extremt snabba laserpulser som är användbara för denna sorts undersökningar, men dessa har begränsningar utöver de som listats redan. De kan exempelvis skada systemen som vi försöker undersöka. Vi föreslår då användandet av kvantsammanflätat ljus för att öka vår möjliga upplösning och att minska skadan som kan orsakas under mätningar eftersom vi då kan minska mängden ljus vi använder.

Kvantsammanflätning är ett kvantmekaniskt fenomen som innebär att två eller flera föremål har 'sammanflätats' och därför kan påverka varandra, även på stora avstånd. En mer precis formulering hade varit att det inte går att beskriva de sammanflätade föremålen fullt ut utan att beskriva dem alla tillsammans. Denna väldiskuterad egenskap som tillhör kvantmekanikens värld är idag huvudsakligen utnyttjad inom kvantberäkning och kvantkryptografi, men har tillämpningsområden inom flera fält.

I denna avhandling så tar vi steg mot att använda sammanflätat ljus inom spektroskopi, det vill säga materialforskning som använder sig av ljus. Kvant-sammanflätat ljus har unika egenskaper som tillåter det att delvis undkomma vissa grundläggande begränsningar som påverkar vanliga laserpulser, vilket kan ge starka fördelar åt kvantljus inom fältet.

Nonlinear Spectroscopy and Quantum Interferometry

1 Introduction

Spectroscopy is, put simply, investigating matter through use of light. This can be done either by looking at the effect a material has on light that reaches it, or the light emitted by a material when under illumination. This yields information based on how the spectrum of the light is affected by the light-matter interaction, or the spectrum of light emitted by the material, which in turn reveals information about the material itself. Spectroscopy is a broad field with multiple techniques of varying degrees of complexity and information that is possible to extract with them. The simplest type of spectroscopy is steady-state spectroscopy, which uses a single, relatively weak light field to observe the absorption or emission properties of a material under constant lighting. These types of measurements are easy to perform and require relatively simple experimental setups, which are widely commercially available. Techniques that can give more information, such as the time-resolved absorption/emission spectra of the material require more complex experiments in exchange for this additional information. Therefore, spectroscopy is in some ways a balancing act; weighing the information one wishes to extract against the necessary complexity of the experiment required. The ends must justify the means, so to say. As an example, a technique like action-detected two-dimensional electronic spectroscopy (A-2DES) is highly complex and would be completely unjustifiable to use for the above-mentioned type of steady-state spectroscopy. Not because the technique is incapable of extracting the desired information, but rather that the effort and time required for the appropriate measurement would be significantly more than that of conducting the same experiment with a standard commercial steady-state absorption spectrometer. However, in the case where one wishes to observe beatings or couplings between different excited states in a quantum dot (useful for studying e.g. energy transport in a system on the nanoscale), a steady-state spectrometer would be incapable of producing any relevant results, and A-2DES would be a viable option. Nonlinear spectroscopy, such as A-2DES, will be discussed more in-depth in Chapter 2.

The exact complexities, both in describing results theoretically and the experimental considerations, vary widely with different techniques. Making use of entangled photons, for example, can be experimentally simple, depending on the requirements one has on the photon properties themselves. However, they can depend on using complex theoretical modeling to yield any advantage relative to established methodologies using classical light. First though, we will discuss entanglement briefly. Broadly speaking, entanglement is a non-local phenomenon where two seemingly separate systems have a measurable correlation in some physical property which make the outcome of a measurement of one

system affect the other, i.e. the measurement of one system ‘determines’ the outcome of the second measurement. As an example, a process which outputs two polarization-entangled photons only requires the measurement of the polarization of one photon to reveal the polarizations of both, provided the measurement is made in the same measurement basis as the entanglement. For a horizontal-vertical polarized photon pair, the polarization measurement must then be in the horizontal-vertical basis to yield a definitive outcome. When only considering a single experiment in this way, however, there appears to functionally be no difference between the entangled case and a case where the polarization of the two particles is simply determined on emission. To be able to distinguish between these two cases, one must perform a statistical analysis of the correlations between the particles, using something known as the Bell inequality. This will be discussed more in Chapter 3. The aim of this thesis project is to move closer to a practical application of entangled photons within nonlinear spectroscopy. With regards to practical application, we will also briefly cover some material properties of quantum dots, which were investigated through nonlinear spectroscopy techniques in Chapter 4. The goal being to trade some of the infamous experimental ‘trickiness’ of nonlinear spectroscopy with the demands of high-quality spectral entanglement and non-dissipative measurements that instead burden entangled-photon spectroscopy. In Chapter 5, as a practical starting point we also discuss entangled two-photon absorption, which is alleged to have a ‘quantum advantage’ in the low-flux regimes. Simply put, at low photon fluxes entangled photon streams are predicted to have an advantage (due to linear absorption scaling) relative to classical two-photon absorption which scales quadratically with the photon flux. The outcomes of experiments on this topic remain dubious, in part due to difficulties quantifying time-frequency entanglement as a non-binary entangled state, unlike the relatively simple polarization entanglement states, which can be measured in binary bases and was used to demonstrate, statistically, the existence of entanglement by Alain Aspect et al^[1].

While the topics may seem sprawling, we can distill them down to some key questions which we intend to answer here: While multidimensional spectroscopy is a powerful technique, how reliable is it at detecting short-lived, weak correlations? Secondly, what can we learn about systems of research interest, such as quantum dots and many-body correlations, using this multidimensional technique? Finally, can we then find a use for quantum light that allows us to find new ways to harness this technique at low fluxes while remaining at a high resolution? The first of these questions is investigated in Paper I, with a focus on fundamental limitations. The second question is the topic of Papers II and III, and the third is tackled in Paper IV.

2 Spectroscopy, linear to nonlinear

To get started with spectroscopy, we need to first consider what we expect our signal to be in a given situation, to be able to draw any conclusions from it. In order to do this, we need to set up a description of both the light and matter involved.

2.1 Pure states and wavefunctions

To start, we then consider a simple description of real-valued time-dependent electric field at a given position in space^[2], which we write as:

$$E_r(t) = E'(t) \cos(\omega t), \quad (2.1)$$

where $E'(t)$ is the time-dependent amplitude of the field, and ω refers to the angular frequency of the field. This expression ignores the orientation of polarization, the phase of the field at a given time and the position in space for the sake of simplicity.

Then, treating the interaction with matter semiclassically, i.e. leaving the electric field in its classical description, but treating the electronic states of our matter-system quantum mechanically, we describe the energy in the electric field-dipole interaction with the operator:

$$\hat{V}(t) = -\hat{\mu}E_r(t). \quad (2.2)$$

Here $\hat{\mu}$ is the dipole operator of the system. We assume that the external electric field is completely aligned with the dipole of the system so we do not have to incorporate vectors. The Hamiltonian of our system then consists of two components: $\hat{H}_0$, which represents the energy of the electronic states of our system (be it atomic, molecular, etc.) independent of any external interaction, which would be time-dependent, and the time-dependent interaction term $\hat{V}(t)$, so that the Hamiltonian is $\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$. Our Hamiltonian is Hermitian, as our observable.

Then, to describe the time-evolution of the system, here represented by the wavefunction $|\Psi\rangle$ ^[3], we use the time-dependent Schrödinger equation

$$\frac{\partial}{\partial t}|\Psi\rangle = -\frac{i}{\hbar}\hat{H}|\Psi\rangle. \quad (2.3)$$

Where $\hbar$ is the reduced Planck constant. Since $\hat{H}_0|n\rangle = E_n|n\rangle$, where $|n\rangle$ are the eigenstates of $\hat{H}_0$, and E_n are its eigenvalues, corresponding to the relative

energy levels of the electronic states. Then we get, in the case where no external electric pulse is present:

$$|\Psi\rangle = \sum_n c_n e^{-iE_n t/\hbar} |n\rangle. \quad (2.4)$$

When an electric field, such as a laser pulse, is introduced, the coefficients in Equation 2.4 also become time-dependent. Then, reintroducing this into the time-dependent Schrödinger equation, as seen in Equation 2.3, we get:

$$\frac{\partial}{\partial t} c_m(t) = -\frac{i}{\hbar} \sum_n c_n e^{-i(E_n - E_m)t/\hbar} \langle m | \hat{V}(t) | n \rangle, \quad (2.5)$$

which provides a time-dependent description of the energy-level populations in our matter-system that are under consideration (generally terms that are on- or close-to-resonance with the electric field). Here, the transition dipole moment $\langle m | \hat{\mu} | n \rangle$ becomes important, as it has no time-dependent effect on the outcome of the measurement when $n = m$, and its magnitude directly correlates to how strongly a given transition will be affected by an applied electric field. Before we move on it becomes prudent to introduce the density matrix, as in reality we are generally not dealing with pure states (as represented by the wave function), but rather statistical ensembles. Both of which can be represented by the density matrix, which for a pure state:

$$\rho \equiv |\Psi\rangle \langle \Psi|, \quad (2.6)$$

and the individual elements of which are given by:

$$\rho_{nm} = c_n c_m^* \quad (2.7)$$

Now that we have a simple description of our system, we may ask the question of how to extract our desired information from it experimentally. To do this, we need some kind of observable, typically in the form of the macroscopic polarization which is induced by interaction with an external electric field. We describe the polarization of our system as the expectation value of our dipole operator $\hat{\mu}$:

$$P(t) = \langle \Psi(t) | \hat{\mu} | \Psi(t) \rangle = \sum_m c_m^* \sum_n c_n \langle m | \hat{\mu} | n \rangle = \sum_{mn} \rho_{nm} \mu_{mn} \equiv \text{Tr}(\hat{\rho} \hat{\mu}). \quad (2.8)$$

Then, assuming that we are operating in a two-level system, with the entire population in the ground state initially (before an external electric field is applied). Then we assume that our system is in a linear superposition of the constant-component eigenstates after the interaction, where $c_0 \gg c_1 > 0$. This gives us, after the interaction:

$$|\Psi(t)\rangle = c_0 e^{-iE_0 t/\hbar} |0\rangle + i c_1 e^{-iE_1 t/\hbar} |1\rangle, \quad (2.9)$$

where the coefficients are not time-dependent, as the interaction with the electric field is over, with the i being introduced from Equation 2.5 during the (short) period of interaction with the electric field, with the complex component of c_0 assumed to be negligible as $c_0 \gg c_1$. Here, the transition dipole moment is additionally baked into the coefficients as well, so that all real terms are collected inside $c_{n=0,1}$. We then take the expectation value of the macroscopic polarization and insert Equation 2.9 to get:

$$P(t) = \langle \mu \rangle = c_0 c_1 \langle 0 | \mu | 1 \rangle \sin(\omega_{01} t) + c_0^2 \langle 0 | \mu | 0 \rangle + c_1^2 \langle 1 | \mu | 1 \rangle. \quad (2.10)$$

Where $\omega_{01} = \frac{E_1 - E_0}{\hbar}$, since the second and third term are time-independent, we can choose to ignore them as they do not contribute to the field emitted by the system, which is what is measured experimentally. Since the coefficients $c_0 \approx 1$ and $c_1 \propto \mu_{01}$, we can then see that:

$$P(t) \propto \mu_{01}^2 \sin(\omega_{01} t). \quad (2.11)$$

This tells us two important things: that our polarization amplitude is proportional to the square of the transition dipole moment between the relevant levels, and that the polarization oscillates with the frequency ω_{01} . The oscillating polarization in turn gives rise to the field emitted by the system, which also oscillates with the same frequency. This emitted field is the signal which we measure in a basic spectroscopic experiment.

2.2 Mixed states and pathways

In reality, we are not working with single systems which are perfectly coherent in pure states. To move closer to reality then, we use the property of the density matrix (which it does not share with the wavefunction!) that it can be used to describe a statistical mixture of states. In this case, the density matrix is expressed as:

$$\rho = \sum_s P_s |\Psi_s\rangle \langle \Psi_s|, \quad (2.12)$$

where $P_s \geq 0$ is the probability that our system ensemble is in a given state $|\Psi_s\rangle$. Normalizing our system then also gives:

$$\sum_s P_s = 1. \quad (2.13)$$

Conveniently, this definition of the density matrix maintains the earlier relationship between the expectation value of the operator. Since we are also interested in extracting more information than the energetic difference between the electronic

energy levels of our system, we will also be using multiple pulses. We mathematically mediate these through repeated application of the transition dipole moment operator, as described by Equation 2.2. As we touched on earlier, we treat the diagonal matrix elements of our transition dipole moment as zero and additionally make no distinction between 'equivalent' off-diagonal elements, that is we say $\mu_{nm} = \mu_{mn}$ where $m \neq n$. We then need to start to consider the time propagation of the density matrix. Here we treat the density matrix as though it were treating a pure state, the main difference being that in the case of a statistical mixture the end result will include an additional term which deals with relaxation and dephasing. Here we instead treat these phenomenologically as treating them rigorously is beyond our scope here. Then, for a density matrix describing a pure state:

$$\frac{d}{dt}\rho = \left(\frac{d}{dt}|\Psi\rangle\right)\langle\Psi| + |\Psi\rangle\left(\frac{d}{dt}\langle\Psi|\right). \quad (2.14)$$

We can then simply apply the time-dependent Schrödinger equation (2.3), and for the wavefunction's complex conjugate:

$$\frac{d}{dt}\langle\Psi| = +\frac{i}{\hbar}\langle\Psi|\hat{H}, \quad (2.15)$$

which then gives us:

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}\left(\hat{H}|\Psi\rangle\langle\Psi| - |\Psi\rangle\langle\Psi|\hat{H}\right) = -\frac{i}{\hbar}\left(\hat{H}\rho - \rho\hat{H}\right) = -\frac{i}{\hbar}[\hat{H}, \rho]. \quad (2.16)$$

This is known as the Liouville-von Neumann equation. Then, in order to be able to easily treat interactions with the light field, we make the mostly reasonable assumption about our Hamiltonian that $\hat{H}_0 \gg \hat{V}(t)$. This means that we assume that the external electric field is never strong enough to disturb the energy levels of our system and we can treat the time-dependent component of our Hamiltonian perturbatively^[4]. We can then insert the full Hamiltonian into the Liouville-von Neumann equation (2.16) along with a phenomenological term to treat dephasing, we get:

$$\frac{d}{dt}\rho_{nm} = -\frac{i}{\hbar}[\hat{H}_0, \rho]_{nm} - \frac{i}{\hbar}[\hat{V}(t), \rho]_{nm} - \rho_{nm}/T_d, \quad (2.17)$$

where T_d is our homogeneous dephasing term. Since $E_n - E_m = \hbar\omega_{mn}$, we can quickly get:

$$\frac{d}{dt}\rho_{nm} = -(i\omega_{mn} + 1/T_d)\rho_{nm} - \frac{i}{\hbar}[\hat{V}(t), \rho]_{nm} \quad (2.18)$$

Since this is our system before interaction with the field, we call it our "zero-order" density matrix. As it is before any interaction, we also set our off-diagonal

elements to zero (no coherences are formed yet) such that $\rho_{nm}^{(0)} = 0$ if $n \neq m$. We can now introduce this into the "first-order", i.e. the density matrix after one light pulse, to get:

$$\frac{d}{dt}\rho_{nm}^{(1)}(t) = -(i\omega_{mn} + 1/T_d)\rho_{nm}^{(1)}(t) - \frac{i}{\hbar}[\hat{V}(t), \rho^{(0)}]_{nm}, \quad (2.19)$$

we then integrate this expression in terms of relative time delays (such as delays between light pulses...) to give us:

$$\rho_{nm}^{(1)}(\tau) = \frac{i}{\hbar} \int_0^\infty [\hat{V}(\tau - \tau_1), \rho^{(0)}]_{nm} e^{-(i\omega_{mn} + 1/T_d)\tau_1} d\tau_1. \quad (2.20)$$

Then, we can decompose $\hat{V}(t)$ using the Euler formula to split the electric field into two complex terms, though the end result is still real-valued:

$$\hat{V}(t) = -\hat{\mu}E'(t) \cos(\omega t) = -\hat{\mu} \frac{E'(t)}{2} (e^{-i\omega t} + e^{i\omega t}) = -\hat{\mu} \frac{(E(t) + E^*(t))}{2}. \quad (2.21)$$

Where $E(t), E^*(t)$ represent the negative and positive oscillations of the field and their magnitudes, respectively. We then plug this back into our expression in Equation 2.20 to get, using that $\hat{\mu}, \rho_{nm}^{(0)}$ are time-independent when $n \neq m$ and assuming our light field is resonant with the electronic transition $\omega = \omega_{nm}$:

$$\begin{aligned} \rho_{nm}^{(1)}(\tau) = & -\frac{i}{\hbar}(\rho_{mm}^{(0)} - \rho_{nn}^{(0)})\mu_{nm} \left(e^{-i\omega\tau} \int_0^\infty E'(\tau - \tau_1) e^{-\tau_1/T_d} d\tau_1 \right. \\ & \left. + e^{i\omega\tau} \int_0^\infty E'(\tau - \tau_1) e^{-\tau_1/T_d} e^{-2i\omega\tau_1} d\tau_1 \right). \end{aligned} \quad (2.22)$$

We can then take the rotating wave approximation to remove the second term, as it will oscillate rapidly and average out to zero. Then using the above, we can get for the first-order macroscopic polarization $P^{(1)}(t) = \langle \mu(t) \rangle = \text{Tr}(\mu\rho^{(1)}(t))$. Then to get higher orders, we have to keep adding terms in the way we did in Equation 2.22. An important note to keep in mind here, is that as the first-order density matrix includes an interaction with the light field (through the μ -term in Equation 2.22), the expression for the first-order macroscopic polarization actually contains two interactions with the light field! What this means in practice, is that after one interaction with the external light field, the system itself emits a light field which originates from the macroscopic polarization, as a system response.

Then, using established properties of the density matrix and the trace, we get of an n:th order macroscopic polarization:

$$P^{(n)}(t) = \langle \hat{\mu}\rho^{(n)}(t) \rangle \quad (2.23)$$

which we can insert into our recursive expression to get (doing the actual recursion step-by-step is left as an exercise for the reader):

$$P^{(n)}(t) = - \left(-\frac{i}{\hbar} \right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \dots E(\tau_1) \langle \hat{\mu}(t) [\hat{\mu}(\tau_n), [\hat{\mu}(\tau_{n-1}), \dots [\hat{\mu}(\tau_1), \rho(t_0)] \dots]] \rangle. \quad (2.24)$$

Here the times $\tau_n, \dots, \tau_1$ represent the interaction times and t_0 can be set to some arbitrary limit, such as $-\infty$, for the sake of convenience. We then define what we call the n :th order "response function" ^[5] as the product of the complex prefactor and the expectation value inside the integral in Equation 2.24, so that the first order, or linear, response function is:

$$\begin{aligned} R^{(1)}(t) &= \frac{i}{\hbar} \langle \hat{\mu}(t) [\hat{\mu}(0), \rho(-\infty)] \rangle \\ &= \frac{i}{\hbar} (\langle \hat{\mu}(t) \hat{\mu}(0) \rho(-\infty) \rangle - \langle \rho(-\infty) \hat{\mu}(0) \hat{\mu}(t) \rangle), \end{aligned} \quad (2.25)$$

where we have set $\tau_1 = 0$ and $t_0 = -\infty$. We have made use of the cyclic invariance of the trace to make it extra visible that the second term is simply a complex conjugate of the first, as all the operators are Hermitian. When the positive and negative oscillations of the electric field are taken into account, this makes a total of four terms in the first-order polarization. However, as before we can disregard half of these terms per the conditions of the rotating wave approximation, again reducing the amount of terms to two. All these terms, canceled or not, are what we refer to as "pathways" that the system takes to reach the end state, which depend on the order of interactions and the relative direction to the density matrix. This is generally illustrated in an intuitive way through what is known as double-sided "Feynman diagrams" ^[6] (not to be mistaken with the ones employed in particle physics) shown in Figure 2.1. Of note is that the two uncanceled terms are complex conjugates of one another, meaning that they are functionally identical in an experiment, and as such one of the two is typically disregarded, depending on convention.

There are a number of implicit rules for Feynman diagrams (for reference, look at Figure 2.1), which are drawn from the algebra itself, that we will make explicit here for ease of reading ^[2]:

1. The left and right sides of the diagram represent the ket and bra of the density matrix, respectively, which together give the relevant matrix element at a given point.
2. The arrows represent interactions between the system and the external light field. By convention the final interaction (e.g. the $\hat{\mu}(t)$ -factor in

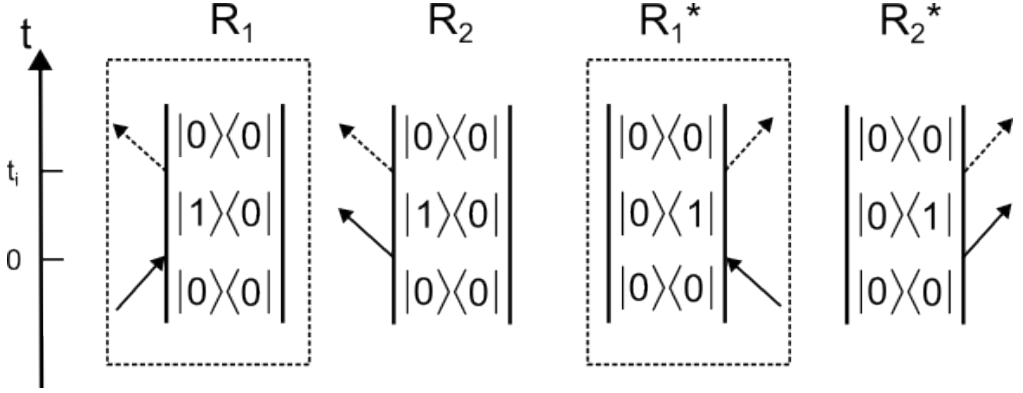


Figure 2.1: All possible double-sided Feynman diagrams for the linear system response, from Equation 2.25. The numbers represented inside the bra and ket illustrate the elementwise pathway the system takes through the interactions. The arrows represent interactions with the electric field, where the solid arrows refer to interactions with the external electric field and the dashed arrows refer to the system response (emission). The two left-side diagrams originate from the first term in Equation 2.25 and the right-side diagrams originate from the second term. The two diagrams inside the dashed boxes refer to the terms which survive the rotating wave approximation.

Equation 2.25), which is not part of the commutator, is marked with a dashed arrow and is always an emission since it represents the system *response*. That is, the final interaction gives us the *coherent signal* that we measure in an experiment. The convention in the field is to only display plots with emission from one side, since terms with emissions from the opposite side are simply complex conjugates and add no information to the outcome.

3. The sign of a given diagram is given by $(-1)^n$, where n represents the number of non-'final emission' interactions on the right side of the density matrix. This originates from the commutator and can be seen by comparing the left and right terms in Equation 2.25 to their respective Feynman diagrams in Figure 2.1. The rule remains true for higher-order interactions as well.
4. The direction of the arrow represents the sign of the oscillating term of the electric field, so that arrows pointing to the right $\Rightarrow e^{-i\omega t}$ and arrows pointing to the left $\Rightarrow e^{+i\omega t}$. The emitted signal then has the frequency which is the sum of the input frequencies (i.e. excluding the final emission, the signal) with signs taken into account. This is also true for wavevectors/phase, but we do not treat these explicitly here yet.
5. Arrows pointing toward the density matrix represent an interaction which excites the system, whereas arrows pointing away represent a de-excitation. This is a consequence of the rotating wave approximation.

6. The last interaction ends in a population state $|n\rangle\langle n|$. This is justified physically: if our system is not in a population state, it is not yet at rest and has not 'finished responding' by emitting a signal yet.

As can be seen, due to the nature of the nested commutators, the amount of terms will increase greatly with each order, but a few key assumptions can reduce the amount somewhat and simplify our calculations. The first of these is that the electric pulse is short enough relative to the system processes that we can treat it impulsively. This essentially allows us to treat our electric fields as δ -functions and makes the proportionality between the macroscopic polarization and the response function more straightforward, which makes it easier to interpret results, this is known as the "semi-impulsive limit".

The second assumption is the time-ordering, which is simply the assumption that the pulses interact with the system in a given order, which we have already implicitly included in Equation 2.24 in the limits of integration which we now make explicit.

With these assumptions, we then have the expression: $P^{(n)}(t) \propto R^{(n)}(t)$. Before we consider these higher orders, however, we might stop to see what exactly can be learned with our now well-defined first-order observable.

2.3 Linear spectroscopy

To begin with, since we are working in a perturbative regime with a single pulse, we only consider a two-level system with a ground state and a single excited state, with the system assumed to be completely in the ground state before any interaction. As per previous assumption, our light pulse is resonant with the transition between these two energy levels. We then start from the density matrix and gradually expand outward until we get to a signal that we can see in a laboratory.

To start with, at a time we set to $t = 0$ (we then also assume that at times $t < 0$, the system is completely in the ground state) we have an interaction with the light field, which is what generates an off-diagonal matrix element of the density matrix. We do not care which specific path we take as one element is simply a complex conjugate of the other and is therefore redundant to our calculations. The likelihood that this occurs is proportional to the transition dipole moment between the ground- and excited states μ_{01} . This matrix element then oscillates with the frequency ω_{01} and decays with the dephasing time T_d , as illustrated in

Equation 2.22. Then gathering all these terms into one expression:

$$\rho_{10} \propto i\mu_{01}e^{-i\omega_{01}t}e^{-t/T_d} \quad (2.26)$$

With this expression, we can now go back to the system response, which contains information about our system. The first-order response is, at a given time $t = t_1$ where $t_1 > 0$, as introduced above, proportional to $\langle \mu \rangle = \text{Tr}(\rho\mu)$. This gives the expression:

$$R^{(1)}(t_1) \propto i\mu_{01}^2e^{-i\omega_{01}t_1}e^{-t_1/T_d}. \quad (2.27)$$

Then, in order to get the macroscopic polarization, we need to convolute the system response with the electric field:

$$P^{(1)}(t) \propto \int_0^\infty dt_1 R^{(1)}(t_1) E(t - t_1) e^{-i\omega(t-t_1) + i\vec{k}_1 \cdot \vec{r} + i\phi}. \quad (2.28)$$

Here we have reintroduced the directionality and phase through the following terms: $\vec{k}_1$, which is the wave vector representing the orientation of the field's propagation, $\vec{r}$ represents the spatial coordinate at a given point in space and ϕ represents the field's phase. The field then emitted by the polarization will be at a relative 90° phase shift, by Maxwell's equations^[7]:

$$E_{\text{sig}}^{(1)}(t) \propto iP^{(1)}(t). \quad (2.29)$$

Since we convolute our signal with the electric field, we should ideally use as short a pulse as possible relative to the processes we want to investigate, as otherwise the system response signal will be unresolvable under the signature of the external field. Another important detail, as implied by equations 2.28 and 2.29, is that the emitted electric field, in the linear case, will be emitted in the same direction as the light field/laser pulse (see rule 4 above) which triggered the system response!

Now that we have an emitted electric field, it needs to be measured! In linear spectroscopy, this is typically done with a spectrometer (surprise!). A simple model of a spectrometer consists of two components: a dispersive element which diffracts our electric field in different directions based on their wavelength, and a detector which measures the intensity of the electric field at different points. In so doing, the intensities measured at different points of the detector can be assigned to various wavelengths (after calibration, of course). To apply this model mathematically we then have to take our signal field, which consists of both our laser pulse $E(t)$ and the system response signal $E_{\text{sig}}^{(1)}(t)$, and break them into their component frequencies through use of a Fourier transform (our 'dispersive grating'). We then have to take into account that our detector records

the intensity of the electric field, meaning that we need to take the square modulus of the combined signal field, to get:

$$\begin{aligned}
S(\omega) &\propto \left| \int_0^\infty (E(t) + E_{\text{sig}}^{(1)}(t)) e^{i\omega t} dt \right|^2 \\
&\propto I_0(\omega) + 2\text{Re} \left(\int_0^\infty E(t) e^{i\omega t} \cdot \int_0^\infty E_{\text{sig}}^{(1)}(t) e^{i\omega t} \right) + I_{\text{sig}}^{(1)}(\omega).
\end{aligned} \tag{2.30}$$

Where 'Re' denotes the real component, I_0 and $I_{\text{sig}}^{(1)}$ denote the intensities of the laser field and the response field, respectively. Since the intensity of the signal component field is multiple orders of magnitude lower than the intensity of the laser field, it can usually be assumed to be negligible. This means that the information from the system is functionally encoded in the cross-term of Equation 2.30, which is $\approx 2\text{Re} (E(\omega)E_{\text{sig}}^{(1)}(\omega))$. This effectively gives us:

$$S(\omega) \propto I_0(\omega) + 2\text{Re}(E(\omega)E_{\text{sig}}^{(1)}(\omega)), \tag{2.31}$$

where the two electric field terms will interfere destructively, as the emitted field is perfectly out of phase with the external field, this can be seen by looking at equations 2.25 and 2.29, which each introduce an i to the response relative to the external field. From a more intuitive, physical point of view, this makes sense as it effectively represents our system absorbing light from the external field (the remainder of the energy is then emitted isotropically through spontaneous emission, not modeled here). Then, in order to measure the signal properly, the laser field has to be measured separately at first. Then one can extract the cross-term by weighing the laser signal (which will simply be measured as $I_0(\omega)$ without a system), against the signal described by Equation 2.31. Returning to an earlier assumption that our laser pulse can be assumed to temporally be a δ -function, we can then obtain a relatively simple expression to unpack to obtain information on our system from the two measurements:

$$\begin{aligned}
S'(\omega) &= -\log \frac{S(\omega)}{I_0(\omega)} \approx 2\text{Re} (E(\omega)E_{\text{sig}}^{(1)}(\omega)) \\
&\stackrel{E(t)=\delta(t)}{=} 2\text{Re} \int_0^\infty iR^{(1)}(t) e^{i\omega t} dt \\
&\propto \text{Re} \int_0^\infty \mu_{01}^2 e^{i(\omega-\omega_{01})t_1} e^{-t_1/T_d} dt_1 \\
&\propto \text{Re} \mu_{01}^2 \frac{1}{i(\omega - \omega_{01}) - 1/T_d} \\
&\propto \mu_{01}^2 \frac{1/T_d}{(\omega - \omega_{01})^2 + 1/T_d^2}.
\end{aligned} \tag{2.32}$$

Which is the Lorentzian lineshape, which lets us extract the dephasing time through measuring the full width at half maximum (FWHM), which is given by:

$$\Delta\nu = \frac{\Delta\omega}{2\pi} = \frac{1}{\pi T_d}. \quad (2.33)$$

We are now ready to move on to the more complex nonlinear spectroscopies, keeping what we've derived so far in mind!

2.4 Nonlinear spectroscopy, coherently

In order to move on to nonlinearity by way of a third-order signal, we start in the same way as before, by considering the density matrix in the ground state. However, we now allow our system to have more than two states in general, allowing for additional states above the first excited state, in addition to multiple interactions.

We will start with an example pathway, to then generalize. We then define a time $t = 0$ which is the time of the first interaction, as before. The system is then put into a coherence (an off-diagonal matrix element) as before. However, this time we allow the system to rest for a time t_1 , during which the system dephases and oscillates as in Equation 2.26:

$$\rho_{10} \propto i\mu_{01}e^{-i\omega_{01}t_1}e^{-t_1/T_d}. \quad (2.34)$$

We then also set a second interaction at the same time, giving us:

$$\rho_{11} \propto i\mu_{01}^2e^{-i\omega_{01}t_1}e^{-t_1/T_d}, \quad (2.35)$$

where our system is now in a population state. It then evolves during a time t_2 , during which it does not oscillate, but some population relaxation occurs.

$$\rho_{11} \propto i\mu_{01}^2e^{-i\omega_{01}t_1}e^{-t_1/T_d}e^{-t_2/T_{1R}}, \quad (2.36)$$

where T_{1R} is our first excited-state lifetime (also introduced phenomenologically, as part of the semiclassical model). The system then reverts to the coherence ρ_{10} and oscillates for a time t_3 :

$$\rho_{10} \propto i\mu_{01}^3e^{-i\omega_{01}t_1}e^{-(t_1+t_3)/T_d}e^{-t_2/T_{1R}}e^{-i\omega_{01}t_3}. \quad (2.37)$$

Then, the final emission which returns the system to the ground state gives the third-order response function:

$$R_1^{(3)}(t_1, t_2, t_3) \propto i\mu_{01}^4e^{-i\omega_{01}t_1}e^{-(t_1+t_3)/T_d}e^{-t_2/T_{1R}}e^{-i\omega_{01}t_3}. \quad (2.38)$$

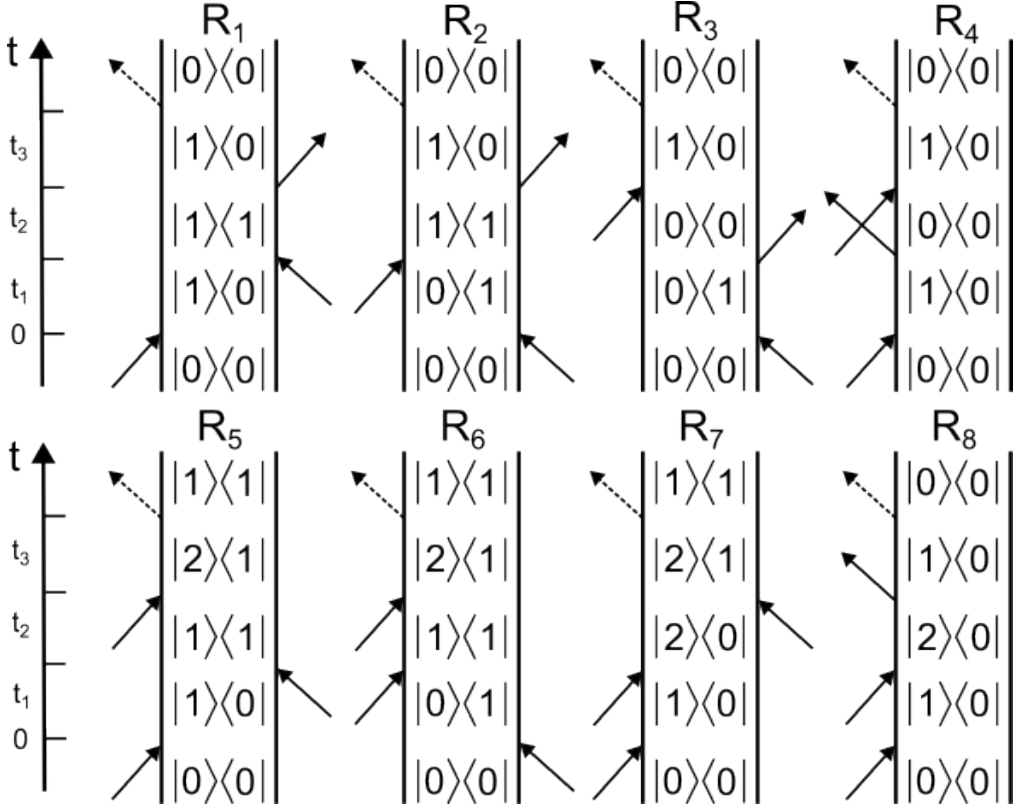


Figure 2.2: All possible third-order Feynman diagrams after applying the time-ordering requirement and the RWA. All complex conjugates are excluded, so that only diagrams with the emission arrow towards the left is shown. The first four diagrams ($R_1 - R_4$) only require the existence of two excited states, whereas the latter four ($R_5 - R_8$) display pathways which require the existence of a second excited state.

This is one example of a pathway for a third-order response out of eight possible ones (again, we do not consider the redundant complex conjugate terms). All eight pathways are illustrated as Feynman diagrams in Figure 2.2. As a comparison $R_2^{(3)}$ is expressed as:

$$R_2^{(3)}(t_1, t_2, t_3) \propto i\mu_{01}^4 e^{+i\omega_{01}t_1} e^{-(t_1+t_3)/T_d} e^{-t_2/T_1} e^{-i\omega_{01}t_3}, \quad (2.39)$$

where it can be seen that the only difference is the sign of the oscillation during the period t_1 . The response functions additionally have the same sign because both pathways have the same amount of interactions from the left and the right.

The pathways shown in Figure 2.2 are generally split into three categories of signal: rephasing (RP), nonrephasing (NRP) and double quantum coherence (DQC). Diagrams R_2 , R_3 and R_6 are examples of pathways which give rise to

an RP signal. The term 'rephasing' here refers to that the oscillations during time intervals t_1 and t_3 have opposite signs to one another and this tends to be by far the strongest signal out of the three. By the same token, 'nonrephasing' signals arise from diagrams R_1 , R_4 and R_5 , i.e. diagrams where the sign of oscillation is the same during intervals t_1 and t_3 . Put briefly, the reason the rephasing signal appears stronger than the non-rephasing has to do with the nature of the statistical mixtures we are using. It can be expected that the coherence frequencies of nearby systems will be similar, but not identical for various reasons, so that they are all slightly out of phase relative to one another at any time after zero. In the RP case, as the oscillation is 'reversing direction' all the systems are allowed to move back again, putting them closer together in phase once more. This leads to a stronger (more coherent, if you will) system response. By comparison, the NRP case where the systems keep getting more and more out of phase with one another leads, in most practical cases, to an extremely weak signal (at least when electronic states are involved).

At this point, one might wonder why diagrams R_7 and R_8 are not included among the RP pathways, and this has to do with the density matrix during the second interval t_2 . This is normally known as the 'population time' as the system is generally in a population state during this interval. In these two diagrams, however, the density matrix is instead in a coherence between the ground state and the second excited state during this time interval. The double-quantum coherence can be used to study many different properties which are generally not accessible with other types of measurements, such as many-body-correlations^[8-11]. However, due to the difficulties involved in obtaining a DQC signal^[8], it is not as commonly measured as the RP signal.

Having introduced these signals, we also run up against another property of the nonlinear response functions; namely the direction of emission. If we assume that each laser pulse in our nonlinear experiment has a different direction, we can separate the signals from the different Feynman diagrams into three different directions^[12], given by the wavevectors: $\vec{k}_{\text{I}} = -\vec{k}_1 + \vec{k}_2 + \vec{k}_3$, $\vec{k}_{\text{II}} = \vec{k}_1 - \vec{k}_2 + \vec{k}_3$ and $\vec{k}_{\text{III}} = \vec{k}_1 + \vec{k}_2 - \vec{k}_3$ (again ignoring complex conjugates). This implies that the directions of $R_1^{(3)}$ and $R_2^{(3)}$ are given by $\vec{k}_{\text{II}}$ and $\vec{k}_{\text{I}}$, respectively. Examining Figure 2.2 and matching the above wavevectors, we find that the RP, NRP and DQC signals match neatly to the $\vec{k}_{\text{I}}$, $\vec{k}_{\text{II}}$ and $\vec{k}_{\text{III}}$ -vectors respectively.

With these distinct directions of emission, it is then possible to measure the emitted electric field of the RP, NRP or DQC signal independently of the exciting laser pulses. If we do this in the manner of the previous section, however, we find that if we attempt to set up the expression for the signal field, as in Equation 2.30 above, we only retain the information from the lifetimes involved, but nothing

about the time-dependence or phase of the emitted field. For this reason, the third-order signal is often heterodyned with a local oscillator, which allows the phase information to be retained, in exchange for having to subtract the local oscillator pulse later^[13–18]. Then, similarly to before, we arrive at the expression for the third-order signal:

$$\begin{aligned} S(t_{\text{LO}}, t_1, t_2) &\propto \int_0^\infty |E_{\text{LO}}(t_3 - t_{\text{LO}}) + E_{\text{sig}}^{(3)}(t_3, t_2, t_1)|^2 dt_3 \\ &\approx I_{\text{LO}} + 2\text{Re} \int_0^\infty E_{\text{LO}}(t_3 - t_{\text{LO}}) \cdot E_{\text{sig}}^{(3)}(t_3, t_2, t_1) dt_3, \end{aligned} \quad (2.40)$$

where we have introduced the electric field and intensity of the linear oscillator, as well as the linear oscillator delay t_{LO} . We then again make use of the semi-impulsive limit approximation for the linear oscillator pulse, i.e. we approximate the envelope to be a delta function, retaining only the phase, carrier frequency and wavevector information. Then, by extension, we get $t_{\text{LO}} = t_3$ and after subtraction of I_{LO} , in the example of an RP signal, we get:

$$S(t_1, t_2, t_3) \propto E_{\text{LO}} \cdot E_{\text{sig}}^{(3)} \propto e^{i(-\phi_1 + \phi_2 + \phi_3 - \phi_{\text{LO}})} \sum_n iR_n(t_1, t_2, t_3), \quad (2.41)$$

where the response functions in question are R_2 , R_3 and R_6 . The above equation then tells us that the the measurement records the response functions directly, in addition to the phase of the signal. Since the phase is defined by the laser pulses, it can be set to zero if one desires. Then, normally one would record the signal in the frequency domain, which is, for third-order, done by passing the signal and local oscillator through a spectrometer and measuring them, and then Fourier transform over the delay t_1 . This gives a frequency map of both the emission and excitation frequencies. This is then described as follows:

$$S(\omega_1, t_2, \omega_3) = \int_0^\infty \int_0^\infty \sum_n iR_n(t_1, t_2, t_3) e^{i\omega_1 t_1} e^{i\omega_3 t_3} dt_1 dt_3. \quad (2.42)$$

For DQC signals, it may instead be desirable to Fourier transform over the 'population time' t_2 , as this is the period during which the double-coherence oscillation takes place.

Then, following similar steps as for the first order, but in two dimensions, we get the following expression for our NRP and RP-terms, showed below by the two-dimensional Fourier transforms of R_1 and R_2 , respectively:

$$R_1^{(3)}(\omega_1, t_2, \omega_3) \propto e^{-t_2/T_{1R}} \frac{1}{i(\omega_1 - \omega_{01}) - 1/T_d} \cdot \frac{1}{i(\omega_3 - \omega_{01}) - 1/T_d} \quad (2.43)$$

$$R_2^{(3)}(\omega_1, t_2, \omega_3) \propto e^{-t_2/T_{1R}} \frac{1}{i(\omega_1 + \omega_{01}) - 1/T_d} \cdot \frac{1}{i(\omega_3 - \omega_{01}) - 1/T_d}. \quad (2.44)$$

We can see that the signal in this case decays with the population relaxation term T_{1R} , allowing us to observe both the lifetime and the lineshape evolving over time.

Generally, when considering the system response, the real and imaginary components are treated as the absorptive and dispersive components of the signal, respectively^[19]. This is for the simple reason that the real component is what modulates the signal amplitude, and the complex component will instead affect the phase component of the signal. In linear spectroscopy these are neatly separated, as only the real component is detected, and one can theoretically select which component is measured through proper phasing between the laser pulses and the signal. In nonlinear spectroscopy, however, we are afforded no such luxury. As seen in equations 2.43 and 2.44, the system responses are products of two complex terms, meaning that even when only detecting the real component, the signal will be composed of both the absorptive and dispersive contributions to the system response. Generally, this can be partially compensated for by adding the RP and NRP signals together (after compensating for the fact that the NRP and RP signals have differently signed oscillations), which yields a 'purely absorptive' signal. Quantum light additionally allows other avenues of control as well^[20].

This method then yields a result which contains the results classically available through linear spectroscopy, though with a view of both excitation and emission frequency axes. This enables us to more quantifiably measure correlations between states^[21;22], or, in the case of e.g. exciton formation, correlations between particles.

With this, we have covered the main principles behind extracting a coherent nonlinear signal in a measurement. There is, however, a nonlinear method which requires no directional wave-vector matching, but instead measures an incoherent signal. This incoherent signal can come in multiple forms, and can be measured as fluorescence^[23], photoelectrons^[24] or photocurrent^[25], to name a few^[26;27]. We will briefly treat this next.

2.5 Nonlinear spectroscopy, incoherently

Incoherent nonlinear spectroscopy, as the name implies, does not rely on a coherent signal being emitted by the system and as such does not require use of a local oscillator. Rather, it makes use of incoherent system emission, such as fluores-

cence, which is generally isotropic and has no dependence on the exciting laser pulse(s) directionality. Since we are relying on an incoherent emission, there are some differences to consider compared to the coherent method. Mainly, since we rely on a 'spontaneous emission' event, we need our system to finish in a population state, as this is what allows for a spontaneous emission or photocurrent to be measured, rather than a coherent polarization response.

So how does this change our previous calculations? Mathematically, this mainly manifests through a change of measurable operator. Whereas we previously used the dipole moment of our system, we now instead rely on a weighted projection operator, which we define as:

$$\hat{N}_{\text{sig}} = \sum_n \Gamma_n |n\rangle\langle n|, \quad (2.45)$$

where Γ_n refers to the quantum efficiency of the radiative spontaneous emission yield of a given state. Another consideration is that in order to end up in a population state, we require four interactions with an external light field. This means that we now require four laser pulses, in turn requiring an additional commutator term in our system response, moving us from third to fourth order. The expression for the fourth-order signal is then:

$$S^{(4)}(t) = \langle \hat{N}_{\text{sig}} \rangle = \text{Tr}(\hat{N}_{\text{sig}} \cdot \rho^{(4)}(t)) = \langle \hat{N}_{\text{sig}} \cdot \rho^{(4)}(t) \rangle, \quad (2.46)$$

where we can see a clear parallel between the expression for our signal and the macroscopic polarization. This gives us the expression for the fourth-order response function for the incoherent signal (see equations 2.24 and 2.25):

$$R^{(4)}(t, \tau_3, \tau_2, \tau_1) = \left(-\frac{i}{\hbar} \right)^4 \langle \hat{N}_{\text{sig}} \cdot [\hat{\mu}_4(\tau_3), [\hat{\mu}_3(\tau_2), [\hat{\mu}_2(\tau_1), [\hat{\mu}_1(0), \rho(-\infty)]]]] \rangle. \quad (2.47)$$

As before, we have defined the time of first interaction to be $t = 0$ and set the density matrix in a ground-state equilibrium before any interaction occurs. The terms $\tau_1, \tau_2, \tau_3, \tau_4$ represent the time of interaction of each laser pulse. Even with our rules as formulated before reducing the total amount, this fourth-order measurement still leaves us with a whopping 16 terms in our results (excluding complex conjugates, of course)! This can be reduced down to 11 terms when removing the terms which place the system in a ground-state population after four interactions. The Feynman diagrams representing these eleven terms are shown in Figure 2.3.

The expression for the signal is then extracted using Equation 2.47 analogously to in the previous section. Since we can no longer use the laser pulse wavevectors

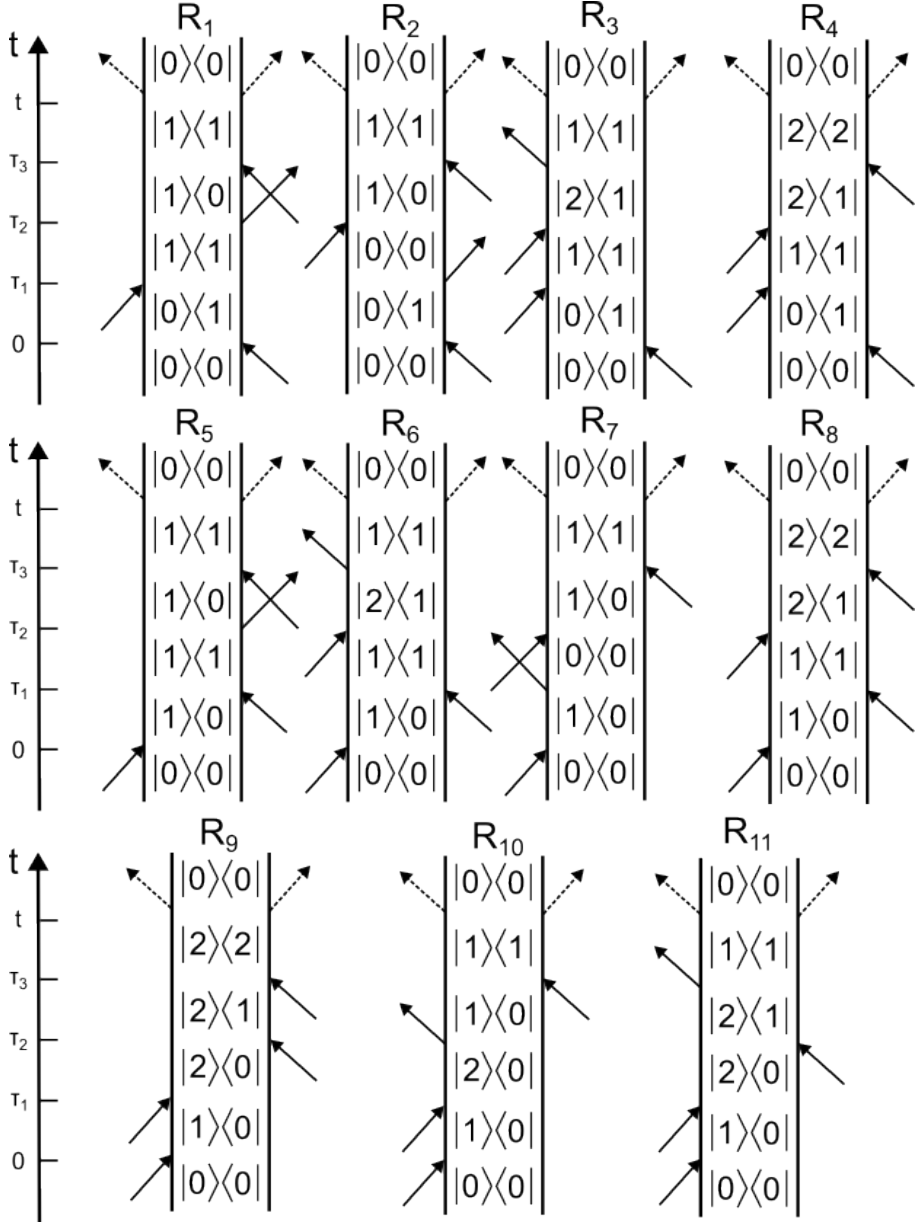


Figure 2.3: All possible fourth-order Feynman diagrams which result in an incoherent emission, with complex conjugates excluded. The first, second and third row of diagrams correspond to the pathways which result in an RP, NRP or DQC-signal, respectively.

to separate our signals from one another, we instead resort to the remaining avenue available to us, namely the phase. In a fashion similar to the previous section, we can then see that the RP, NRP and DQC-signals have the phase-

matching signatures $\phi_{\text{RP}} = -\phi_1 + \phi_2 + \phi_3 - \phi_4$, $\phi_{\text{NRP}} = +\phi_1 - \phi_2 + \phi_3 - \phi_4$ and $\phi_{\text{DQC}} = +\phi_1 + \phi_2 - \phi_3 - \phi_4$, respectively.

Now, a simple fixed phase will not leave a measurable signature in a time-dependent measurement, so one of the methods used to encode a useful signal is to modulate the phase of the laser pulses. This is typically done through some kind of acousto-optic modulation of the pulse train, such that the different signals do not overlap. But how are these signals recorded?

As mentioned before, one method of fourth-order signal collection is the measurement of fluorescence. For a given setting of the inter-pulse delays t_1 , t_2 and t_3 , the fluorescence is recorded at a set sampling frequency (typically aligned with the laser's repetition rate) until a sufficient amount of data points have been recorded. This results in a one-dimensional, real, measurement of fluorescence over time. This data set is then Fourier transformed, and the peaks for the desired signals (RP, NRP and DQC) may be extracted. This procedure is continued for all desired inter-pulse delays until a complete three-dimensional data set is collected. One can then perform a two-dimensional Fourier transform over the desired axes to get a 2D-spectrum dataset in frequency domain!

Satisfied with our successful measurement, we will go on to a short, phenomenological description of 2D spectra and their interpretation. Before we leave this section, however, we shall bring our attention back to Figure 2.3 one more time. Eagle-eyed readers may have noticed that for each of the RP and NRP signals, there are two pathways (represented by R_3 , R_4 for RP and R_6 , R_8 for NRP) which are nearly identical, with the exception of the last interaction acting on the ket or bra. This introduces a bit of a complication, as it means these signals have the opposite sign, but are located in the same position in the 2D spectrum. This is known as incoherent mixing, and its consequences will be addressed briefly in the coming section.

2.6 2D spectra and their interpretation

Now that we have successfully collected our 2D spectra (either through a coherent or incoherent method), we are ready to analyze it! We will start with the more conventional RP and NRP signals, where we plot the excitation frequency ω_1 , against the emission frequency ω_3 for a given population time (or 'waiting time') t_2 . The information given by a given peak in the signal is given by its particular amplitude, position in the spectrum, sign and two-dimensional shape^[28;29].

As an example, a peak located on the diagonal $\omega_1 = \omega_3$ (or $\omega_1 = -\omega_3$ for RP signals). This may imply that the peak in question originates from light being absorbed and emitted by the same state without relaxing to a lower-lying state or similar during the population time. Strictly speaking, however, it means that the signal originates from states with the same energy in during t_1 and t_3 , so two different states with the same energy will also appear in the same position. In the case of a single state, however, analyzing the amplitude of this peak as a function of the population time then gives a regular time-resolved view of the state's lifetime.

To contrast with this, peaks that are off-diagonal, so that $|\omega_1| \neq |\omega_3|$, can instead imply that the excitation has moved around in the system before emission. An example of this is relaxation from an excited state to another state. In this case, the magnitude of the peak instead tells us about the strength of the coupling between the two states that are involved. It can also simply yield information about relaxation to a common ground state. Off-diagonal signals are particularly useful when there are many states within one's accessible bandwidth, so that one can potentially probe many couplings in a single experiment. An important point is that since these peaks are all (ideally) separately resolvable in a two-dimensional frequency space, they can be directly, quantifiably, measured without too much convolution with other signals. In reality, however, there is often still a significant overlap between peaks that must be analyzed carefully. It is still noteworthy that the degree of convolution will in general be lessened compared to linear spectroscopy, which flattens all responses along one axis, easing 2D interpretation, relatively speaking.

In general, the sign convention of 2D electronic spectroscopy (2DES) is such that a positive signal indicates that that specific peak indicates a decrease in absorbance, i.e. the system is less absorptive in a given region after the exciting interaction, and vice versa for a negative peak. We will explain this by introducing some of the relevant terms used to interpret the peaks and Feynman diagrams. The different pathways shown by the Feynman diagrams are assigned names based on the interpretation of the processes involved, and the sign of the diagram aligns with the sign of their respective peaks in the 2D map. An example of one of these processes is known as 'ground state bleach' (GSB). This refers to the fact that after excitation, part of the previous ground state population will instead be in an excited state and therefore a subsequent, but otherwise identical, pulse will necessarily not be able to produce as many excited states, leading to a 'bleaching' effect. GSB is therefore an effect that produces a positive signal, as it leads to a reduction in sample absorbance.

The next major pathway is known as 'stimulated emission' (SE), also known as

the phenomenon that allowed the creation of lasers (and masers)^[30]! Simply put, an excited state which comes into contact with light resonant to a transition to a lower state may 'stimulate' the relaxation of the state and lead to an emission of light which will be coherent with, and travel in the same direction as, the stimulating light in question. Similarly to GSB, this results in a positive signal, as the SE process does not result in photons being absorbed (rather, it causes the sample to emit!).

The third and final of the main pathways is known as 'excited state absorption' (ESA). It can occur when the exciting pulse(s) leave the system in an excited state population, when a second excited state is accessible with the following pulses (i.e. $|\omega| = |\omega_{01}| \approx |\omega_{12}|$). The ESA signal is then given by the portion of the light which is absorbed to take the system into a second excited state, from the first one, hence the name. As ESA is a pathway that contributes to an increase in absorption, it results in a negative signal. There is, however, an exception to this which we mentioned in passing before: namely incoherent mixing in fourth-order measurements, we will discuss this along with some other possible measurement artifacts later in this section.

At a given population time one may have several peaks in one's spectrum. As mentioned, these peaks will also have some typical time-dependence (an excited population state will naturally relax over time, etc.) which may yield some lifetime information of a given state, but peaks may also oscillate with time. This can indicate a population-time coherence, such as the one discussed in Paper II. Depending on the signature and frequency of these oscillations, one may identify these as electronic or vibrational coherences, and their dephasing times.

The shape of a peak may also reveal information about the states involved. In general, for an absorptive spectrum, the antidiagonal width of a peak records the homogeneous linewidth of the transition. This is particularly useful in cases where strong inhomogeneous line-broadening is expected due to system interactions with the environment, e.g. molecules in a solution. On the contrary, as the diagonal width behaves similar to standard linear spectroscopy, it provides information on inhomogeneous line-broadening, allowing 2D spectroscopy to collect information on both homogeneous and inhomogeneous line-broadening simultaneously. It is useful to note that peaks will tend to become symmetric with increasing population time, even when there is strong inhomogeneous line-broadening, as the states decohere over time^[31]. Therefore, one must look at early delay times to separate the two components.

2.6.1 Artifacts in 2D spectra

We have now covered most of the regular features of a 2D spectrum, and will now discuss some common pitfalls and artifacts^[32] which may complicate an accurate interpretation of the spectrum.

To start with, we will return to a topic mentioned before: incoherent mixing. Incoherent mixing is a type of artifact that arises specifically from incoherent detection schemes^[33] (as the name implies), where two mostly identical ESA pathways have opposite signs. An example of this is illustrated by R_3 and R_4 in Figure 2.3. Since the pathways are near-identical, but carry opposite signs, they may partially or completely cancel one another out in an actual measurement. The exact degree to which they cancel one another out is proportional to the ratio of the radiative (in case of fluorescence) quantum yield of the doubly excited state versus the singly excited state. Complete cancellation occurs when these quantum yields are identical, but partial cancellation must still be taken into account. A typical sign of complete cancellation is the appearance of off-diagonal peaks at zero time-delay, which should not normally be possible^[34], as there is no time for state transitions to occur. Incoherent mixing can then easily lead to misinterpretation of fourth-order spectra unless carefully taken into account and modeled.

Another source of errors is pulse overlap artifacts, also discussed in Paper I. Typical of early time-scales with small delays relative to laser pulse widths, these artifacts arise when the assumption that interactions are time-ordered breaks down, such as when laser pulses in the pulse train are overlapped with one another. This can occur in both third-order and fourth-order spectroscopies, unlike incoherent mixing. Since there is no guarantee of time-ordering, many kinds of peaks which do not carry any physical meaning can be observed. This is particularly troublesome when the effect one wishes to observe is short-lived enough that it does not last significantly longer than the pulse overlap, such as DQC effects. One therefore must take great care when interpreting results obtained when significant, or even partial pulse overlap is expected.

Figure 2.4 shows a simulated fourth-order signal from an isolated system with a single excited state, with a modulation frequency signature of a single coherence of 500 kHz. As can be seen in the figure, however, a frequency-doubled peak (normally interpreted as a DQC signature) can be found as well, with a third peak being slightly visible at 1500 kHz. Thus, even in simulated measurements the pulse overlap artifact is fundamental and is mathematically unavoidable, even when one has full control of the system and measurement, provided there is pulse overlap. As a true DQC signal in a system, where one would not normally

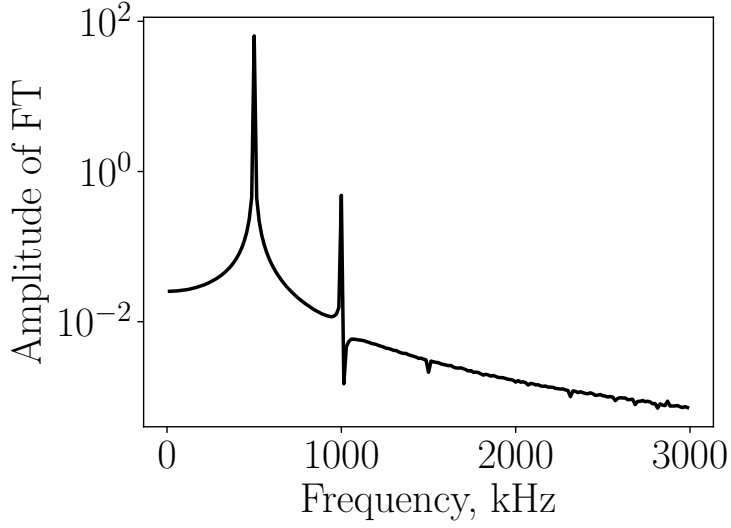


Figure 2.4: The Fourier transform of a simulated fourth-order signal measurement containing pulse overlap artifacts which may be incorrectly interpreted as DQC (and higher) components. The peak at 0 has been subtracted for visibility. The simulation was run with a modulation frequency of 500 kHz, yielding the shown modulation peaks in the population lifetime of the system. Figure generated by Andreas Wacker, used with permission.

expect to see a doubly excited state, can be used as evidence of exciton formation or communication between systems^[35–39], failing to take it into account properly may lead to some very incorrect conclusions about one’s measurement. This is discussed more in Paper I.

3 Quantum optics and Entanglement

Up until now, we have kept our descriptions of light-matter interactions to a semiclassical model. We will now move to a quantum treatment of light, which will allow us to incorporate quantum interference effects into our formalism as well. Since the aim here is to work our way to interferometry, we will start with a brief definition of the electric field and partial reflections below.

3.1 The quantized electric field, interference and detection

We begin with the expression for the electric field, expressed as a sum of normal modes, which is derived through use of Maxwell's equations and canonical commutator relations^[40]:

$$\vec{E}(\vec{r}, t) = \sum_l \vec{\epsilon}_l \epsilon_l^{(1)} \left(i\alpha_l(t) e^{i\vec{k}_l \cdot \vec{r}} - i\alpha_l^*(t) e^{-i\vec{k}_l \cdot \vec{r}} \right), \quad (3.1)$$

where $\alpha_l(t) = |\alpha_l| e^{i\phi_l} e^{-i\omega_l t}$ represents a monochromatic oscillation in time, $\vec{\epsilon}_l$ represents the polarization, and $\epsilon_l^{(1)}$ is a constant. In total, this gives us the expression of the electric field as a sum of traveling, polarized monochromatic waves. The electric field is then often split into two components with opposite complex frequency:

$$\vec{E}(\vec{r}, t) = \vec{E}^{(+)}(\vec{r}, t) + \vec{E}^{(-)}(\vec{r}, t). \quad (3.2)$$

Where we define the 'positive' component (also known as the analytic signal) as:

$$\vec{E}^{(+)}(\vec{r}, t) = i \sum_l \vec{\epsilon}_l \epsilon_l^{(1)} \alpha_l(t) e^{i\vec{k}_l \cdot \vec{r}}, \quad (3.3)$$

with $\vec{E}^{(-)}(\vec{r}, t)$ being its Hermitian conjugate.

Now that we have a new (though familiar) expression for the electric field, we go on to describe interference. To start, we begin by describing two identical electric fields passing through a Mach-Zehnder interferometer (MZI)^[41], illustrated in Figure 3.1. The MZI will form the basis of our interferometric descriptions from here on as well. Here, we assume the beamsplitters are all lossless and have a 50:50 ratio of transmission to reflection. If we consider the interface where the input modes 1 and 2 go into the interferometer modes 1' and 2', we get, for the interferometer mode electric fields in terms of the input fields at BS₁:

$$\hat{E}_{1'}^{(+)} = \frac{1}{\sqrt{2}} (\hat{E}_1^{(+)} - \hat{E}_2^{(+)}), \quad (3.4)$$

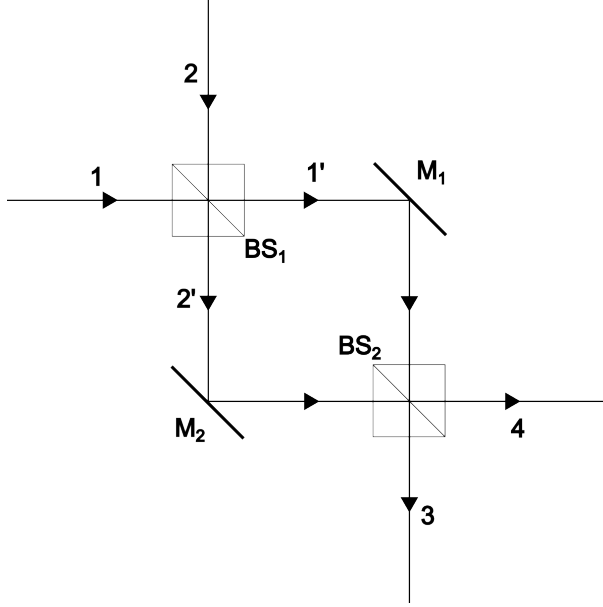


Figure 3.1: An illustration of an MZI, with input modes 1 and 2, and output modes 3 and 4. Modes are coupled in and out through beamsplitters BS_1 and BS_2 , respectively. Interferometer modes $1'$ and $2'$ are reflected on mirrors M_1 and M_2 , respectively, which are controlled to alter the path lengths of the interferometer modes.

$$\hat{E}_{2'}^{(+)} = \frac{1}{\sqrt{2}}(\hat{E}_1^{(+)} + \hat{E}_2^{(+)}). \quad (3.5)$$

Where we have defined the surface coupling mode 2 into $1'$ as the one with cement, and therefore internal reflection occurs, leading to the minus sign in Equation 3.4. We have also put the analytic field operators in place of the classical field expression¹, which allows us to take the expectation value of the field operators directly^[40]. We additionally ignore the direction of propagation in the wavevectors and assume a polarization orthogonal to the plane of the figure.

To then take the next step toward the complete treatment of the MZI, we have to include the path length between beamsplitters for each interferometer mode, which we call $L_{1'}$ and $L_{2'}$ for the modes $1'$ and $2'$ respectively. Moving then, to BS_2 , we propagate the interferometer modes to get:

$$\hat{E}_3^{(+)} = \frac{1}{\sqrt{2}}(\hat{E}_{1'}^{(+)} e^{ikL_{1'}} - \hat{E}_{2'}^{(+)} e^{ikL_{2'}}), \quad (3.6)$$

¹It seems extremely complicated to do this association rigorously and the way it is treated in most textbooks I've read seems a little dubious, but please bear with me for now.

$$\hat{E}_4^{(+)} = \frac{1}{\sqrt{2}}(\hat{E}_1^{(+)}e^{ikL_{1'}} + \hat{E}_2^{(+)}e^{ikL_{2'}}), \quad (3.7)$$

where we have defined the side of internal reflection in BS₂ to be the side reflecting mode 2' to output mode 3. Then, using the expressions in equations 3.4 and 3.5 we get, at BS₂:

$$\hat{E}_3^{(+)} = -e^{ik\bar{L}'}(i \sin\left(k\frac{\delta L'}{2}\right)\hat{E}_1^{(+)} + \cos\left(k\frac{\delta L'}{2}\right)\hat{E}_2^{(+)}), \quad (3.8)$$

$$\hat{E}_4^{(+)} = e^{ik\bar{L}'}(\cos\left(k\frac{\delta L'}{2}\right)\hat{E}_1^{(+)} + i \sin\left(k\frac{\delta L'}{2}\right)\hat{E}_2^{(+)}). \quad (3.9)$$

Here, we have introduced the average interferometer path length $\bar{L}' = (L_{1'} + L_{2'})/2$ and the path length difference $\delta L' = L_{2'} - L_{1'}$. Interestingly, these expressions reduce to $\hat{E}_3^{(+)} = -e^{ik\bar{L}'} \cdot \hat{E}_2^{(+)}$ and $\hat{E}_4^{(+)} = e^{ik\bar{L}'} \cdot \hat{E}_1^{(+)}$ at $\delta L' = 0$, which means that at zero path length difference, the two input fields (with a difference in phase, of course) exit completely separate of one another in this case! We will return to this later...

We then move on to one of the most important interactions of quantized radiation: measurement by a detector! Since detectors in reality do not have infinitesimal time-resolution, we instead use an expression for an average rate of detections per unit time, given by:

$$w(\vec{r}, t) = s \langle \Psi(t) | \hat{\vec{E}}^{(-)}(\vec{r}) \cdot \hat{\vec{E}}^{(+)}(\vec{r}) | \Psi(t) \rangle = s || \hat{\vec{E}}^{(+)}(\vec{r}) | \Psi(t) ||^2. \quad (3.10)$$

Here, s refers to the sensitivity of the detector, $|\Psi(t)\rangle$ is the state of the light, to which we have now moved the time-dependence, and $\hat{\vec{E}}^{(+)}(\vec{r})$ is the positive-frequency component of the electric field, now reintroducing the relevant vectors into the description. A similarly important expression is the rate of coincidence detection, i.e. detection at two separate points in space within a given time interval, given by:

$$w^{(2)}(\vec{r}_1, \vec{r}_2, t) = s^2 \sum_{i,j=x,y,z} \langle \Psi(t) | \hat{\vec{E}}_i^{(-)}(\vec{r}_1) \cdot \hat{\vec{E}}_j^{(-)}(\vec{r}_2) \cdot \hat{\vec{E}}_j^{(+)}(\vec{r}_2) \cdot \hat{\vec{E}}_i^{(+)}(\vec{r}_1) | \Psi(t) \rangle. \quad (3.11)$$

With these basic interference terms out of the way, we will move on to three-wave mixing processes. These will allow us to generate interesting states that are useful for interferometry!

3.2 Three-wave mixing and quantum interference

Three-wave mixing is a collective term for many nonlinear optical processes. Nonlinear in this case refers to that the polarization of a transparent material

is no longer linearly proportional to our electric field. Generally speaking, in an isotropic medium which is transparent to an external electric field (and neglecting dispersion), the polarization can be described in a semiclassical way as:

$$\vec{P}(\vec{r}, t) = \epsilon_0 \chi^{(1)} \vec{E}(\vec{r}, t), \quad (3.12)$$

where ϵ_0 is the vacuum permittivity and $\chi^{(1)}$ is the linear susceptibility, which is completely real for a transparent medium. For stronger electric fields, this expression breaks down, and higher orders of susceptibility come into play^[42]. Here, the order of nonlinearity is determined by the proportionality to the electric field. That is to say, a first-order polarization is proportional to the electric field, whereas the second order is proportional to the square of the electric field $P^{(2)} \propto E^2$, and so on.

In general, even for powerful lasers, one can often neglect anything over second order, or third order in a centrosymmetric medium where the second order susceptibility turns out to be zero in general. One generally also needs to consider the relative orientations of polarization and susceptibility, but we will avoid treating this explicitly here, unless absolutely necessary. We will briefly stay in the semiclassical picture of nonlinear polarization to display some of the possible second-order nonlinearities before moving on. To begin with, we give the more general expression for the (nonlinear) polarization of a transparent material (ignoring dispersion, time-dependence and spatial position/orientation):

$$P = \epsilon_0 (\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots). \quad (3.13)$$

Then, to examine the second-order term, we use two monochromatic, overlapped electric fields, so that we have:

$$E_1(t) = E'_1(e^{-i\omega_1 t} + e^{+i\omega_1 t}), \quad (3.14)$$

$$E_2(t) = E'_2(e^{-i\omega_2 t} + e^{+i\omega_2 t}). \quad (3.15)$$

With a total field $E(t) = E_1(t) + E_2(t)$. Then the second-order polarization term will be:

$$\begin{aligned} P^{(2)}(t) &= \epsilon_0 \chi^{(2)} E(t)^2 \\ &= \epsilon_0 (E_1'^2 e^{-2i\omega_1 t} + E_2'^2 e^{-2i\omega_2 t} + 2|E_1'|^2 + 2|E_2'|^2 \\ &\quad + 2E_1' E_2' e^{-i(\omega_1 + \omega_2)t} + 2E_1' E_2'^* e^{-i(\omega_1 - \omega_2)t} + \dots), \end{aligned} \quad (3.16)$$

where we have excluded the complex conjugates of the complex terms. As we can see, there are multiple terms which we can now associate with different phenomena, such as frequency doubling (also known as second harmonic generation, given by e.g. $E_1'^2 e^{-2i\omega_1 t} + \text{c.c.}$), sum-frequency generation ($2E_1' E_2' e^{-i(\omega_1 + \omega_2)t} +$

c.c.) and difference-frequency generation ($2E_1'E_2'^*e^{-i(\omega_1-\omega_2)t} + \text{c.c.}$). For this to occur, there are also phase-matching conditions that must be fulfilled, the specifics of which are determined by the process in question. These processes are all harnessed in laser laboratories all over the world for different purposes.

A specific example of this is difference-frequency generation as applied in optical parametric amplification (OPA). In OPA, a strong beam, referred to as the 'pump', amplifies a weaker beam, known as the 'signal'. We assign these frequencies ω_1 and ω_2 , respectively. As a consequence of this, a third beam (with frequency given by the relation $\omega_3 = \omega_1 - \omega_2$) emerges, provided the phase matching conditions for this process occurring are met. The third, emergent beam is known as the 'idler'. This process therefore amplifies the signal beam with as many photons as are generated in the idler beam and can be tuned, depending on adjustments of the phase-matching conditions. Something interesting occurs, however, when the power of the signal beam is reduced to zero. Even with all other experimental conditions being the same, without an E_2 -term in our total electric field, all the cross-terms in Equation 3.16 disappear, including the one governing difference-frequency generation. In an actual experiment, however, one may find that signal and idler beams are still generated! This is due to a process called spontaneous parametric downconversion (SPDC) and which cannot be accounted for semiclassically. This is still, of course, subject to the phase-matching and frequency-relations:

$$\vec{k}_1 = \vec{k}_2 + \vec{k}_3, \quad (3.17)$$

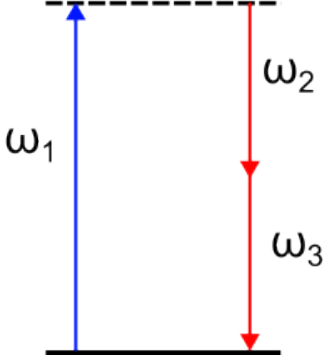
$$\omega_1 = \omega_2 + \omega_3. \quad (3.18)$$

These relations correspond to the conservation of momentum and conservation of energy, respectively, and are illustrated in Figure 3.2. Since semiclassical physics are not enough to describe SPDC, we shall simply have to use a quantum mechanical description instead. Then, considering electric field modes which fulfill the above requirements and keeping in mind that we are in a non-absorbing material (by assumption), we can make a Hamiltonian which describes the SPDC interaction. For this Hamiltonian, we include the typical term for the photon energy in addition to the coupling terms which we set to describe the entire process:

$$\hat{H} = \sum_{i=1}^3 \hbar\omega_i(\hat{a}_i^\dagger\hat{a}_i\frac{1}{2}) + \hbar g(\hat{a}_1\hat{a}_2^\dagger\hat{a}_3^\dagger + \hat{a}_1^\dagger\hat{a}_2\hat{a}_3), \quad (3.19)$$

where $\hat{a}_i$ and $\hat{a}_i^\dagger$ are the annihilation and creation operators of a given mode $i = 1, 2, 3$ respectively, and g is a coupling constant. The first coupling term

Frequency-matching



Wavevector-matching

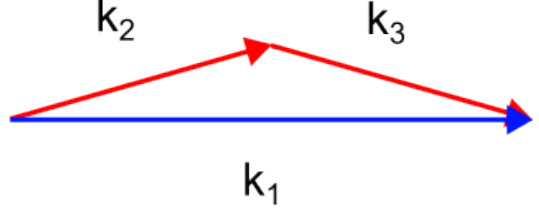


Figure 3.2: A diagram illustrating the two matching conditions for the SPDC process. The frequency-matching condition is directly analogous to the conservation of energy, and the wavevector-matching condition is the direct analogue of the conservation of momentum.

describes the process where a signal and idler photon are created at the expense of a pump photon, and vice versa for the second term. We then consider the case where we do indeed only have the pump beam present to begin with, giving us the initial state:

$$|\Psi(t=0)\rangle = |N_1, 0, 0\rangle, \quad (3.20)$$

where $N_i = \hat{a}_i^\dagger \hat{a}_i$ is the photon number operator for a given mode $i = 1, 2, 3$. Then, by treating the coupling term perturbatively relative to the freely evolving term, similarly to what we did in the previous chapter with the interaction component, we get for small times t :

$$|\Psi(t)\rangle = e^{-i\omega_1(N_1 + \frac{1}{2})t}(|N_1, 0, 0\rangle - i g t \sqrt{N_1} |N_1 - 1, 1, 1\rangle). \quad (3.21)$$

Then recalling that the time t here, as far as the coupling term is concerned, will refer to the time which the photons spend inside the material, we can replace t with L/c . Here L is then the length of the material in question. The freely evolving term will remain relatively unchanged as long as we stay within the perturbative regime as well. Considering that there are multiple ways to fulfill the requirements in equations 3.17 and 3.18, we can collect the modes which satisfy this condition and then get the final state (ignoring the phase):

$$|\Psi(L/c)\rangle = |N_1, 0, 0\rangle + \sum_{i,j} C_{ij} |N_1 - 1, 1_i, 1_j\rangle, \quad (3.22)$$

where C_{ij} is simply a constant, gathered for each valid mode combination defined as $|C| = gL\sqrt{N_1}/c$. Since we are in the perturbative regime, we definitionally require $|C| \ll 1$ as well.

We can simplify our expression for the many modes by introducing a frequency detuning term δ :

$$\omega_2 = \omega_2^{(0)} + \delta, \quad (3.23)$$

$$\omega_3 = \omega_3^{(0)} - \delta, \quad (3.24)$$

where $\omega_2^{(0)} = \omega_3^{(0)} = \omega_1/2$, so that the condition in Equation 3.18 is fulfilled. We also define separate directions for the signal and idler with unit vectors $\vec{u}_2$ and $\vec{u}_3$ so that:

$$\vec{k}_2 = \vec{u}_2 \frac{\omega_2}{c}, \quad (3.25)$$

$$\vec{k}_3 = \vec{u}_3 \frac{\omega_3}{c}. \quad (3.26)$$

We have here assumed that the wavevector-matching condition will lead to the signal and idler being emitted in different directions, which is plausible for SPDC processes, but we focus on modes emitted in a direction which is convenient in an assumed experiment (since in general there will be many pairs of vectors $\vec{k}_2, \vec{k}_3$ that satisfy our conditions). We can define a new state which only includes the signal and idler at the output of the crystal (where we restrict ourselves to modes traveling in our defined directions) in terms of our new parameters, so that:

$$|\Psi_{\text{si}}(L/c)\rangle = \sum_{\delta} C(\delta) |1_{\vec{u}_2, +\delta}, 1_{\vec{u}_3, -\delta}\rangle. \quad (3.27)$$

We are also here assuming that $|C(\delta)|$ has its maximum at, and is symmetric around, $\delta = 0$. We normally assume a Gaussian distribution around this center of a reasonable width, but in reality this is determined by the tolerance of the wavevector-matching Δk , which depends on crystal length and other parameters. Having defined this state at a specific point in time, we then take the opportunity to move the time-dependence from the state vector to the operators and go into the Heisenberg picture. This does not change the physics of our system, but it does make our calculations more convenient, as we shall see.

Now we move on to consider what comes after our wonderful downconversion crystal and set up what is known as a Hong-Ou-Mandel^[43] (HOM) interference experiment, illustrated by Figure 3.3. We then set up our electric field operators just after exiting the crystal, assigning 1 and 2 to the signal and idler, respectively.

$$\hat{E}_1^{(+)}(\vec{r}_s, t) = i \sum_{\delta} \varepsilon_{\delta}^{(1)} e^{i\omega_2(\tau_1 - t)} \hat{a}_{\delta}, \quad (3.28)$$

$$\hat{E}_2^{(+)}(\vec{r}_s, t) = i \sum_{\delta} \varepsilon_{(-\delta)}^{(1)} e^{i\omega_3(\tau_2 - t)} \hat{a}_{(-\delta)}. \quad (3.29)$$

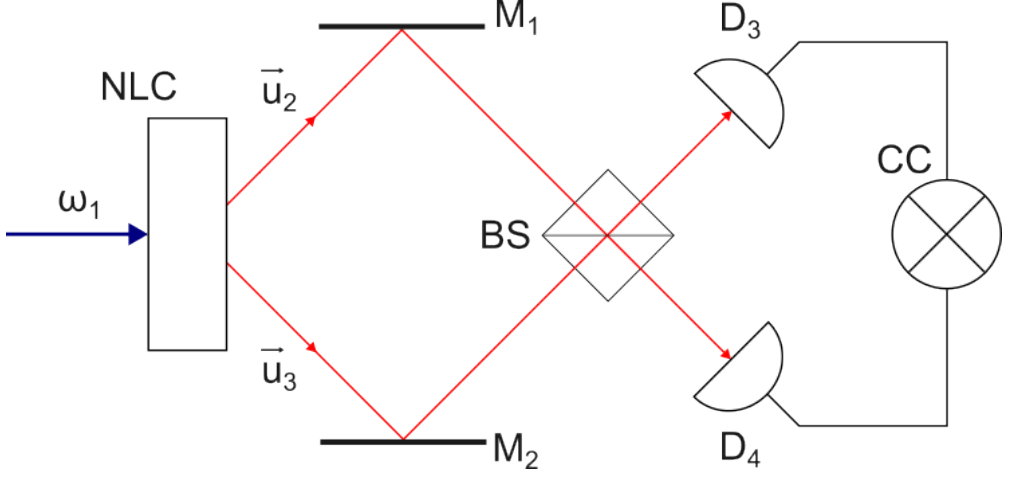


Figure 3.3: An illustration of a HOM interference experiment. NLC refers to the nonlinear crystal where SPDC occurs, ω_1 refers to the pump laser frequency which is the only part of it we consider in our calculations. $\vec{u}_2, \vec{u}_3$ refer to the unit vectors of the modes we consider for the signal and idler modes, respectively. Mirrors M_1, M_2 can be altered to adjust the relative delay of the photon channels going onto the beamsplitter BS. Detectors D_3 and D_4 detect the electric fields after the beamsplitter outputs and are coupled to a coincidence detection circuit CC which allows correlation measurements of the incoming photons.

Here τ_1, τ_2 refer to the photon arrival times at the beamsplitter, affected by mirrors M_1 and M_2 respectively. Normally, for a full description of the mode, we should include the unit vectors in the summation as well, but here we restrict ourselves to a single direction (i.e. a single $\vec{u}_2$ and $\vec{u}_3$) we do not include them explicitly here. Then, to describe the electric field at the detectors, we do the same operation as before to get our two modes out:

$$\hat{E}_3^{(+)}(\vec{r}_s, t) = \frac{1}{\sqrt{2}}(\hat{E}_1^{(+)}(\vec{r}_s, t) + \hat{E}_2^{(+)}(\vec{r}_s, t)), \quad (3.30)$$

$$\hat{E}_4^{(+)}(\vec{r}_s, t) = \frac{1}{\sqrt{2}}(\hat{E}_1^{(+)}(\vec{r}_s, t) - \hat{E}_2^{(+)}(\vec{r}_s, t)). \quad (3.31)$$

Here, we have again assumed losslessness and a perfect 50:50 ratio of transmission and reflection in the beamsplitter. Now that we have our output electric fields, we can calculate the detection probability using Equation 3.10 at detector D_3 :

$$w(D_3, t) = s ||\hat{E}_3^{(+)}(\vec{r}_s, t)|\Psi_{\text{si}}\rangle||^2, \quad (3.32)$$

where we have, from Equation 3.27:

$$\begin{aligned} \hat{E}_3^{(+)}(\vec{r}_s, t)|\Psi_{\text{si}}\rangle &= \frac{i}{\sqrt{2}} \sum_{\delta} C(\delta) \varepsilon_{\delta}^{(1)} e^{i\omega_2(\tau_1-t)} |0_{\vec{u}_2, +\delta}, 1_{\vec{u}_3, -\delta}\rangle \\ &+ \frac{i}{\sqrt{2}} \sum_{\delta} C(\delta) \varepsilon_{(-\delta)}^{(1)} e^{i\omega_3(\tau_2-t)} |1_{\vec{u}_2, +\delta}, 0_{\vec{u}_3, -\delta}\rangle. \end{aligned} \quad (3.33)$$

Since these vectors are orthogonal, we ultimately end up with:

$$w(D_3, t) = \frac{s}{2} \sum_{\delta} |C(\delta)|^2 \left((\varepsilon_{\delta}^{(1)})^2 + (\varepsilon_{(-\delta)}^{(1)})^2 \right). \quad (3.34)$$

A consequence of this we can immediately see is that the single-photon detection at the detectors is completely time-independent and should therefore not change regardless of the length in the two photon paths before the beamsplitter. The calculation is much the same for detection at detector D_4 , so instead of treating that, we hurry onward to use Equation 3.11 to deal with coincidence detection between D_3 and D_4 :

$$w^{(2)}(D_3, t; D_4, t') = s^2 ||\hat{E}_3^{(+)}(\vec{r}_s, t) \cdot \hat{E}_4^{(+)}(\vec{r}_s, t') |\Psi_{\text{si}}\rangle||^2. \quad (3.35)$$

Then, in a similar fashion to before we find:

$$\begin{aligned} \hat{E}_3^{(+)}(\vec{r}_s, t) \hat{E}_4^{(+)}(\vec{r}_s, t') |\Psi_{\text{si}}\rangle = & -\frac{1}{2} \sum_{\delta} C(\delta) \varepsilon_{\delta}^{(1)} \varepsilon_{-\delta}^{(1)} (e^{i\omega_2(\tau_1-t')} e^{i\omega_3(\tau_2-t)} \\ & - e^{i\omega_2(\tau_1-t)} e^{i\omega_3(\tau_2-t')}) |0_{\vec{u}_2, +\delta}, 0_{\vec{u}_3, -\delta}\rangle. \end{aligned} \quad (3.36)$$

To move forward from this, we remember the definition of the detuning term and that $\omega_2^{(0)} = \omega_3^{(0)} = \omega_1/2$, then we get:

$$\begin{aligned} \hat{E}_3^{(+)}(\vec{r}_s, t) \hat{E}_4^{(+)}(\vec{r}_s, t') |\Psi_{\text{si}}\rangle = & -\frac{e^{i\omega_1(\tau_1+\tau_2-t-t')/2}}{2} \sum_{\delta} C(\delta) \varepsilon_{\delta}^{(1)} \varepsilon_{-\delta}^{(1)} \\ & \cdot (e^{i\delta(\tau_1-t'-\tau_2+t)} - e^{i\delta(\tau_1-t-\tau_2+t')}) |0_{\vec{u}_2, +\delta}, 0_{\vec{u}_3, -\delta}\rangle. \end{aligned} \quad (3.37)$$

Now, in order to solve this completely, it becomes expedient to explicitly define $C(\delta)$ and to put our turn our sum into an integral. This is reasonable, as we expect our modes to be gathered, in frequency space, in a continuum with a Gaussian envelope. With this in mind, we define a bandwidth of our downconversion process Δ , so that:

$$C(\delta) = \frac{C_0}{\sqrt{2\pi}\Delta} e^{-\frac{\delta^2}{2\Delta^2}} \quad (3.38)$$

we then take the first term from Equation 3.37 and carry out the integral of the amplitude:

$$\begin{aligned} A_{t-t'} = & -\frac{e^{i\omega_1(\tau_1+\tau_2-t-t')/2}}{2} \varepsilon_0^{(1)2} \int d\delta C(\delta) e^{i\delta(\tau_1-t'-\tau_2+t)} \\ = & -\frac{e^{i\omega_1(\tau_1+\tau_2-t-t')/2}}{2} \varepsilon_0^{(1)2} \cdot C_0 e^{-\Delta^2(\tau_1-\tau_2+t-t')^2/2}, \end{aligned} \quad (3.39)$$

where we have moved the $\varepsilon^{(1)}$ -terms outside the integral and set them to their central value, as they will not change much inside the bandwidth of the down-converted photons. The second term, $A_{t'-t}$ is identical, except the signs of t and t' in the integral are reversed. Then, returning to the coincidence detection rate, we get:

$$w^{(2)}(D_3, t; D_4, t') = s^2 |A_{t-t'}(t - t') - A_{t'-t}(t - t')|^2. \quad (3.40)$$

Normally, the temporal width of the photons are far too small to be resolved by detectors (perhaps on the order of 10-100 fs), so we therefore will generally detect coincidences for many possible detector-times centered around $t - t' = 0$ with a width determined by the detector time-resolution. Then, to determine the total coincidence rate, provided that we assume the path length difference for into the beamsplitter is small enough that $|\tau_1 - \tau_2|$ is smaller than our detection window, we integrate over all intervals $\theta = t - t'$ to get:

$$\begin{aligned} w_{\text{ctot}}^{(2)}(D_3, D_4) &= s^2 \int d\theta |A_{t-t'}(\theta) - A_{t'-t}(\theta)|^2 \\ &= \frac{s^2}{2} (\varepsilon_0^{(1)})^4 C_0^2 \sqrt{\pi} \Delta^{-1} (1 - e^{-\Delta^2(\tau_1 - \tau_2)^2}). \end{aligned} \quad (3.41)$$

Then we can see that outside the limit where $|\tau_1 - \tau_2|$ is very close to zero, the coincidence count rate is effectively constant, due to the narrowness of Δ . We can also see that at exactly $|\tau_1 - \tau_2| = 0$, we can go as low as zero coincidences! We then have the situation that while single photon counts in each detector remain constant, around $|\tau_1 - \tau_2| = 0$ we lose all or nearly all coincidence counts. This is then what is known as Hon-Ou-Mandel interference (which we will also simply refer to as HOM).

An interesting thing to note is that this 'dip' or loss in coincidence counting can be seen far beyond detector resolution, as it is dependent on Δ and $|\tau_1 - \tau_2|$ and is a local interference effect. The implications regarding the photon paths are also interesting, namely that since coincidences are zero for equal delays, this implies that if the two photons meet at the beamsplitter at the same time, they will always exit through the same beamsplitter port! The beamsplitter output port is still chosen randomly with equal probability, but the photons remain in their pairs! This is a consequence of a fully quantum mechanical description, as a classical optical calculation would indeed find a dip (50 %) in coincidences, but would not be able to account for the complete absence of them in the center. An experimental measurement of HOM interference is shown in Fig. 3.4, where a sharp decrease in measured coincidences can be noticed, with only a small reduction in single-photon counts due to the inability of the detectors to measure more than a single photon at a time.

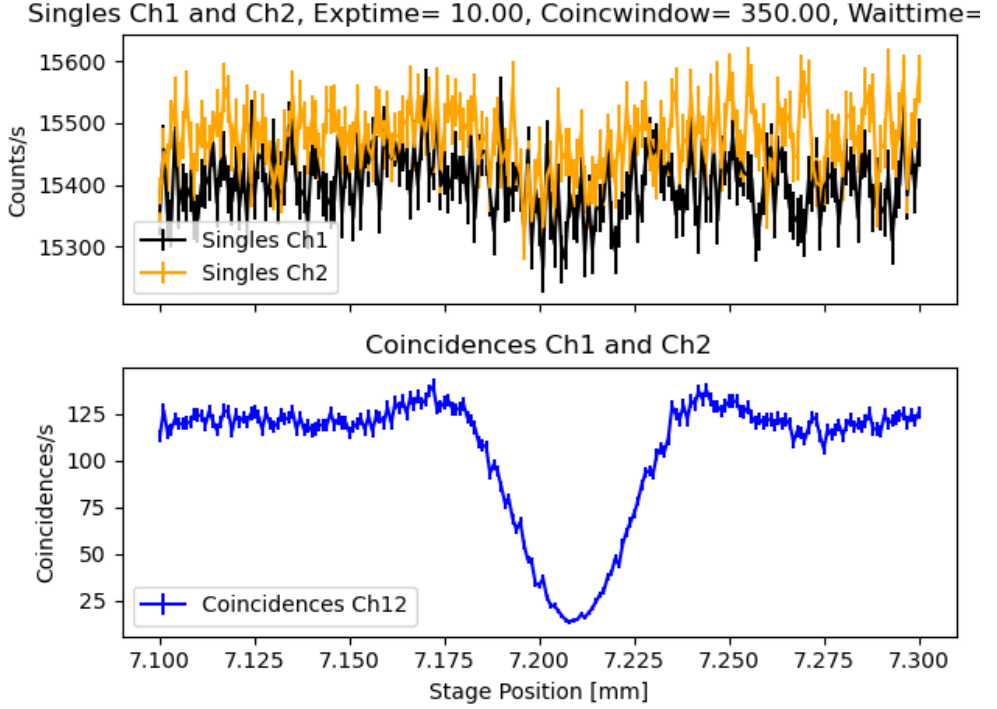


Figure 3.4: A laboratory measurement of Hong-Ou-Mandel interference, imperfect conditions lead to the dip measured not going all the way to zero coincidences, but is still beyond what is predicted by classical electromagnetics (as it turns out, getting an experiment to fit the theory perfectly is quite difficult!). The width of the dip reveals the temporal width of the photons (and by Fourier relation, their bandwidth).

Since this dip as predicted by quantum mechanics isn't due to electromagnetic interference, but rather probability amplitude interference exclusive to quantum theory, we refer to it as quantum interference instead. While in the case of SPDC (and several other three-wave mixing processes) the signal and idler photons are entangled, we do not use this 'entanglement' property in HOM, as it only requires that the two photons incident on the beamsplitter are indistinguishable. Furthermore, as HOM is a local phenomenon (the photons must 'meet' at the beamsplitter) it is not a consequence of entanglement, which is a non-local phenomenon. If you are interested in seeing how the HOM interference was measured in our setup, please refer to Appendix A.

"But wait!?! What is this about entanglement?" I hear you say. Worry not, dear reader! This is exactly the phenomenon we will treat in the coming section, and its further usefulness to us will be discussed as we then introduce the Franson interferometer^[44].

3.3 Entanglement and Bell's inequality

Entanglement is an important phenomenon within quantum physics and is often used as an example of quantum mechanics' inherent strangeness (not the quark-antiquark measurement, regular weirdness, mind you!). Famously, Einstein, Rosen and Podolsky used it as an example of quantum mechanics being 'incomplete' and requiring the introduction of some 'hidden variables' to complete the quantum mechanical description of physics^[45]. Bohr, however, argued against this^[46], but it wasn't until the sixties that there seemed to be any way to definitively exclude either possibility. This change came with the publication of Bell's 1964 article^[47] where he predicted that a local hidden variable theory would be unable to fully reproduce all of the results predicted by quantum mechanics. This prediction was made in the form of an inequality relation (Bell's inequality!) which held true for any hidden-variable theory but could be violated by quantum-mechanical predictions. The expression of this inequality was later refined by Clauser, Horne, Shimony and Holt into a proposed experiment^[48] which was finally tested by Aspect, Dalibard and Gérard in 1982^[1] with use of time-varying analyzers. There were, however, several loopholes which remained, most of which were finally closed in an experiment performed in 2015^[49]. Anyway, that's a whole lot of interesting history to look into for a curious reader (especially if you want to get into all the possible measurement loopholes!), but we still haven't answered what entanglement actually is.

Put in the most concise possible way, entanglement is a consequence of having a multi-particle non-factorizable state. As an entangled system then cannot be factorized in terms of the bases of its composite parts, measurements on the subsystems can show correlations which cannot be explained by some kind of local-hidden variable model. To be clear, this does not mean that one particle sends some sort of signal to the other (as that would be limited by the speed of light) but it rather seems to imply that a true instantaneous action at a distance has occurred. As long as the quantum state remains intact, this remains true no matter the spatial separation, etc. of the particles. This does not, however, mean that it is possible to transmit information at faster-than-light speeds using entanglement. One would still need to communicate one's own measurement to any observer one wanted to communicate with in order to actually convey any useful information about the quantum state (the interested reader is recommended to look into the 'no-communication theorem'^[50;51]). That is a lot to consider, so how do we go about formulating it in a simple way, i.e. mathematically?

Taking the example of polarization, we consider one of the simplest possible

cases: Two electric field single-photon modes which are identical in every way, except for the orientation of their polarizations, which are orthogonal to one another. We call these modes x and y , for convenience. These two modes then span a basis $\{|x\rangle; |y\rangle\}$ for all polarization states for photons with their same wavevector. The polarization can then be measured with a polarizer, which separates the photons according to the orientation of their polarization, whose outputs we can assign as channels $+1$ and -1 . When the polarizer is aligned with the x -orientation, $|x\rangle$ -photons are channeled into output $+1$ and $|y\rangle$ -photons into output -1 . We can then define an observable $\hat{O}$ with $|x\rangle$ and $|y\rangle$ as its basis vectors which has the above polarizer outputs as its eigenvalues. To generalize this, we also allow for rotation about the optical axis (which we can call the z -axis) with an angle θ relative to the x -axis. This gives the matrix expression for the operator:

$$\hat{O}(\theta) = \begin{pmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{pmatrix}, \quad (3.42)$$

where we have 2θ in our expressions because an angle of π relative to the x -axis produces the same result as an angle of zero. The eigenvectors of this observable are then:

$$|+\theta\rangle = \cos\theta|x\rangle + \sin\theta|y\rangle, \quad (3.43)$$

$$|-\theta\rangle = -\sin\theta|x\rangle + \cos\theta|y\rangle, \quad (3.44)$$

where $\hat{O}|\pm\theta\rangle = \pm|\pm\theta\rangle$. Now having defined our vectors in this way, we can express the state of a photon with an arbitrary linear polarization with relative angle Θ to x and the same wavevector as our basis modes as:

$$|\Psi(\Theta)\rangle = \cos\Theta|x\rangle + \sin\Theta|y\rangle. \quad (3.45)$$

A measurement with our polarizer will then yield a $+1$ -result with the probability:

$$P_+(\theta, \Theta) = |\langle +\theta|\Psi(\Theta)\rangle|^2 = \cos^2(\theta - \Theta), \quad (3.46)$$

and vice versa for the probability of measuring -1 . If we then move on to consider an entangled state, we have a pair of photons with correlated polarizations, such that:

$$|\Psi_{\text{Ent}}\rangle = \frac{1}{\sqrt{2}}(|x, x\rangle + |y, y\rangle), \quad (3.47)$$

where $|x, x\rangle = |x_1\rangle \otimes |x_2\rangle$, where x_1 refers x for one photon and x_2 the other and the same for y as well. The state is non-factorizable, which makes it impossible to determine the polarization of one photon without simultaneously determining the other. If we then allow these photons to travel in opposite directions (but

otherwise still the same) we can carry out correlation measurements with one polarizer per photon. Then, allowing each photon to be measured separately, we find the probability of measuring them both with a +1 to be:

$$\begin{aligned}
P_{++}(\vec{a}, \vec{b}) &= |\langle +_{\vec{a}}, +_{\vec{b}} | \Psi_{\text{Ent}} \rangle|^2 = \frac{1}{2} |(\langle x, x | \cos(\theta_{\vec{a}}) \cos(\theta_{\vec{b}}) \\
&\quad + \langle y, y | \sin(\theta_{\vec{a}}) \sin(\theta_{\vec{b}})) \cdot (|x, x\rangle + |y, y\rangle)|^2 \\
&= \frac{1}{2} \cos^2(\theta_{\vec{a}} - \theta_{\vec{b}}),
\end{aligned} \tag{3.48}$$

where $\vec{a}, \vec{b}$ are the orientations of the polarizers with angles, relative to x , $\theta_{\vec{a}}$ and $\theta_{\vec{b}}$, respectively. We have chosen to exclude cross-terms (and will continue to do so) as they all disappear. An interesting outcome here is that it is the relative angle $(\theta_{\vec{a}} - \theta_{\vec{b}})$ that determines the outcome of the measurement, rather than the individual orientations of the polarizers themselves. We find that checking $P_{--}(\vec{a}, \vec{b})$ yields the same result as above and:

$$\begin{aligned}
P_{--}(\vec{a}, \vec{b}) &= |\langle -_{\vec{a}}, -_{\vec{b}} | \Psi_{\text{Ent}} \rangle|^2 = \frac{1}{2} |(-\langle x, x | \sin(\theta_{\vec{a}}) \cos(\theta_{\vec{b}}) \\
&\quad + \langle y, y | \cos(\theta_{\vec{a}}) \sin(\theta_{\vec{b}})) \cdot (|x, x\rangle + |y, y\rangle)|^2 \\
&= \frac{1}{2} \sin^2(\theta_{\vec{a}} - \theta_{\vec{b}}),
\end{aligned} \tag{3.49}$$

where we again do not include cross-terms in the expression. We find the same outcome for $P_{+-}((\vec{a}, \vec{b}))$, and are now ready to move on.

Measuring a single photon yields a 1/2 probability of finding either result regardless of the angle of the polarizer. This can be seen by considering that the probability of the second photon yielding a positive result $P_{2+} = P_{++}(\vec{a}, \vec{b}) + P_{-+}(\vec{a}, \vec{b}) = 1/2$. One can easily check that this is true for all permutations of single-photon measurements. From this, we can say that the individual polarization of either photon is a truly statistically random variable, while they remain correlated. To show that they are indeed correlated, we introduce the measurement outcome variables $\alpha(\vec{a})$ and $\beta(\vec{b})$ for photons 1 and 2, respectively. These have the possible values +1 or -1 with equal probability, and so their average value is zero, in accordance with the above findings. We then take a look at the correlation coefficient between these two variables:

$$E(\vec{a}, \vec{b}) = \frac{\overline{\alpha(\vec{a}) \cdot \beta(\vec{b})} - \overline{\alpha(\vec{a})} \cdot \overline{\beta(\vec{b})}}{\sqrt{|\overline{\alpha(\vec{a})}|^2} \cdot \sqrt{|\overline{\beta(\vec{b})}|^2}}. \tag{3.50}$$

We can then easily see that the second term in the numerator is zero, and that the denominator is one from our previous assertions. The first term in the numerator, however, is a bit more complicated. If we take a step back and think about what it means, it is the average over the possible double-measurement outcomes. Now, since we are considering the measurement outcome, and not just the probability, we also have to multiply our probabilities with the result so that we have:

$$\begin{aligned}\overline{\alpha(\vec{a}) \cdot \beta(\vec{b})} &= P_{++} + P_{--} - P_{+-} - P_{-+} \\ &= \cos^2(\theta_{\vec{a}} - \theta_{\vec{b}}) - \sin^2(\theta_{\vec{a}} - \theta_{\vec{b}}) \\ &= \cos(2(\theta_{\vec{a}} - \theta_{\vec{b}})).\end{aligned}\tag{3.51}$$

This tells us that our correlation coefficient is:

$$E(\vec{a}, \vec{b}) = \cos(2(\theta_{\vec{a}} - \theta_{\vec{b}})),\tag{3.52}$$

which again depends only on the relative angle $(\theta_{\vec{a}} - \theta_{\vec{b}})$. Interestingly, this means that as long as our polarizers are oriented the same way, the measurements of photon 1 and 2 will always be identical, regardless of orientation relative to x or y ^[52]. What this tells us, indirectly, is that the measurement of one photon tells us outcome of the other's measurement through their correlation! This idea proved philosophically difficult to accept^[45] and led directly to the formulation of a local hidden variable theory. This is the theory that the outcome is determined by some unknown shared parameter λ which is shared by the particles since their generation, rather than at random at the time of measurement.

We will now proceed to derive a way to measure the validity of this theory vis-à-vis the regular quantum formalism by formulating the version of the Bell inequality^[47] proposed by Clauser, Horne, Shimony and Holt^[48] which we will call the CHSH inequality. To do this, we need to set some general properties for our shared hidden variable λ which will determine the outcome of our polarization correlation measurements. To start with, we allow λ to have a completely random value, but with a positive definite probability density $\rho(\lambda)$, so that:

$$\rho(\lambda) \geq 0,\tag{3.53}$$

$$\int d\lambda \rho(\lambda) = 1.\tag{3.54}$$

We then also need to constrain the randomness of λ in such a way that our measurement outcomes $\alpha(\lambda, \vec{a})$ and $\beta(\lambda, \vec{b})$ are always either $+1$ or -1 . These measurements should also have an equal probability of occurring. This can be formulated as:

$$\int d\lambda \rho(\lambda) \alpha(\lambda, \vec{a}) = \int d\lambda \rho(\lambda) \beta(\lambda, \vec{b}) = 0,\tag{3.55}$$

which is the hidden-variable equivalent of our previous expressions for α and β . Then, our new formulation of the correlation is defined in the same way as Equation 3.50, giving us:

$$E_{\text{LHV}}(\vec{a}, \vec{b}) = \overline{\alpha(\lambda, \vec{a}) \cdot \beta(\lambda, \vec{b})} = \int \rho(\lambda) \alpha(\lambda, \vec{a}) \beta(\lambda, \vec{b}). \quad (3.56)$$

As long as the above constraints and relations are fulfilled, we can use our hidden variable to create our Bell inequality. We then have to take a bit of a leap of faith and make up a quantity with the following definition:

$$\begin{aligned} s(\lambda, \vec{a}, \vec{a}', \vec{b}, \vec{b}') &\equiv \alpha(\lambda, \vec{a}) \cdot \beta(\lambda, \vec{b}) - \alpha(\lambda, \vec{a}) \cdot \beta(\lambda, \vec{b}') \\ &\quad + \alpha(\lambda, \vec{a}') \cdot \beta(\lambda, \vec{b}) + \alpha(\lambda, \vec{a}') \cdot \beta(\lambda, \vec{b}') \\ &= \pm 2, \end{aligned} \quad (3.57)$$

where the only new thing we have introduced is two new possible orientations $\vec{a}'$ and $\vec{b}'$ for our polarizers. This holds for any value of λ (you can try it yourself if you'd like to double-check!). When we then average this quantity over all values of λ , we must then naturally get:

$$-2 \leq \int d\lambda \rho(\lambda) s(\lambda, \vec{a}, \vec{a}', \vec{b}, \vec{b}') \leq 2. \quad (3.58)$$

For convenience, we abbreviate the above expression as $S(\vec{a}, \vec{a}', \vec{b}, \vec{b}')$. Again taking a step back to examine this expression and looking over at Equation 3.56 we can then see:

$$S(\vec{a}, \vec{a}', \vec{b}, \vec{b}') = E_{\text{LHV}}(\vec{a}, \vec{b}) - E_{\text{LHV}}(\vec{a}, \vec{b}') + E_{\text{LHV}}(\vec{a}', \vec{b}) + E_{\text{LHV}}(\vec{a}', \vec{b}'). \quad (3.59)$$

We now have a measurable quantity which we can use to compare with results from the quantum theory! Then, all we need to do is measure a result which violates this inequality beyond whatever statistical uncertainties are present in our experiment to see whether or not the local hidden variable theory holds. Is this possible to do, even in theory though?

I won't keep you in suspense, it is eminently possible! A way we can see this simply by choosing some orientations for $\vec{a}, \vec{a}', \vec{b}, \vec{b}'$ that maximize S , we then pick so that:

$$(\theta_{\vec{a}} - \theta_{\vec{b}}) = (\theta_{\vec{b}} - \theta_{\vec{a}'}) = (\theta_{\vec{a}'} - \theta_{\vec{b}'}) = \pi/8 \implies \quad (3.60)$$

$$\implies (\theta_{\vec{a}} - \theta_{\vec{b}'}) = 3\pi/8. \quad (3.61)$$

Using the above values in S , using Equation 3.52, we get:

$$S_{\text{QM}}(\vec{a}, \vec{a}', \vec{b}, \vec{b}') = 2\sqrt{2}, \quad (3.62)$$

which is clearly greater than two! Then, successfully measuring this in a statistically significant, loophole-free way would show that a local hidden-variable model is unable to fully describe all physical results and thus be incomplete. A statistically significant measurement of a Bell-inequality violation was demonstrated in 1982 by Alain Aspect and co-workers^[1] which won him a part of the 2022 Nobel prize in Physics along with Anton Zeilinger and John Clauser! Their experiment is not considered to be completely loophole-free, but it was nevertheless a landmark experiment with regards to Bell-inequality measurements.

We have, however, made our job easy² here by picking polarization as our entangled parameter. This has allowed us to set up our Bell inequality with relative ease as our measurement outcome is completely binary (either $+1$ or -1)! Are we willing to be satisfied with this? No, why would we want to take the easy way? Also, there is still no direct coupling to spectroscopy here (polarization control actually plays a large role in many nonlinear spectroscopy measurements, but ignore that for now) even though that is our ultimate goal! We must then move on to a different kind of entanglement, as discussed by James Franson^[44]...

3.4 Franson interference

If our entanglement parameter is no longer polarization, then what could it be? Another possible common parameter which could be our next step would be position/time. These two quantities are generally not interchangeable, but for photons with a well-determined direction of emission, they functionally can be. We then consider how such a temporal entanglement might be arranged? Well, we already have a good example! The SPDC process that was described earlier provides photons that are generated and emitted from the nonlinear crystal within a time interval τ_p , which pump photon coherence time. This governs the interval in time within which a single photon pair can be generated/emitted. The signal and idler photons have a spectral width, as allowed by the phase-matching tolerance, which additionally defines their coherence time σ_t .

So, the photons are emitted within a certain (microscopic) temporal interval of one another, and their exact time of emission is uncertain. Then, even if we only detect one of the pair (assumed to be emitted in different directions due to phase-matching, as before) we instantaneously know the position of the other photon

²Decades passed between the initial formulation of the EPR paper and the publication of Bell's theorem. The first statistically significant measurement of the inequality violation was made more than a decade after Bell's paper came out. Closing most major loopholes took another 30 years after that. It seems like an easy process to step through here in hindsight, but it has historically been very difficult!

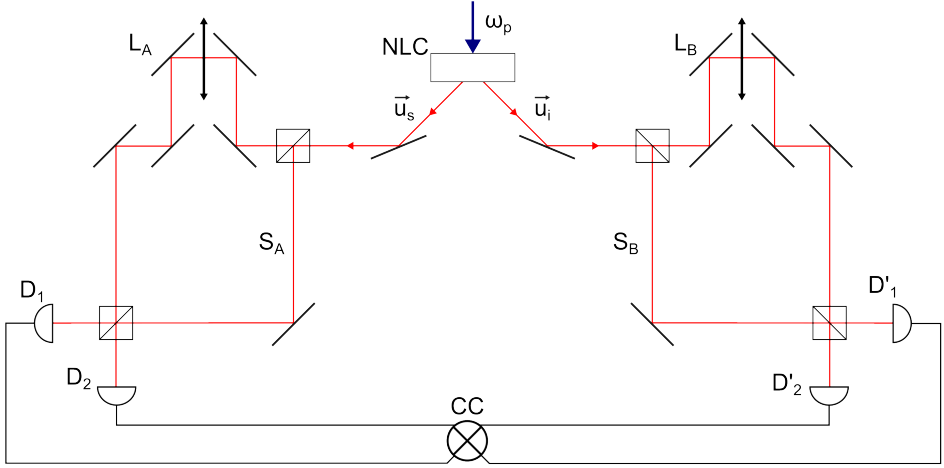


Figure 3.5: A diagram of a Franson interferometer. The subscripts p,s and i refer to the pump, signal and idler beams respectively. L and S refer to the long and short paths of the unbalanced MZI's and the subscripts A and B refer to the MZI's (also here referred to as the interferometer's 'arms') traversed by the signal and idler, respectively. The path lengths of the long arms can be adjusted with motorized retroreflectors. In general, the coincidence counting circuit CC is only used to compare one detector from each arm at a time.

and their mutual time of generation/emission (to within the detector's time resolution). These are still, however, parameters which may very well simply be correlated in a classical way, so in order to test whether there is any so-called 'time-entanglement' we need to devise another Bell inequality to check! To do this, we make use of a Franson interferometer, see Figure 3.5, where we direct the signal and idler photons into separate, unbalanced MZI's (for comparison, see Figure 3.1). Unbalanced here means that there is a path in each MZI which is always longer than the other, short, path. We then set up our experiment so that the path length difference between the short and long paths in each arm is roughly equal, i.e. $\Delta_A \approx \Delta_B$, where Δ_A is the path-length difference between L_A and S_A , Δ_B is defined similarly. We also define the relative delay $\Delta_{AB} \equiv \Delta_A - \Delta_B$, or converted into temporal domain, $\Delta_{AB}/c = \Delta T$, $\Delta_A/c = T_A$ and $\Delta_B/c = T_B$ which will be useful later.

We then would like the long-short path length difference to be both significantly longer than the coherence length of our signal and idler photons, and shorter than our emission-time ambiguity (effectively our pump coherence time) τ_p so that we have $\sigma_t \ll T_{A,B} \ll \tau_p$. The first condition allows us to discount the possibility of any single-photon interference inside the interferometer. Meanwhile, the second condition makes early long-path emissions indistinguishable from late short-path emissions, as both cases can occur with roughly equal probabilities, which is crucial to our interference conditions as we shall see. Similar to HOM interference, the Franson interferometer only leaves traces in coincidence detec-

tion, when comparing between two detectors at the ends of different arms (i.e. comparing D_1, D_2 against D'_1, D'_2 , see Figure 3.5), while single-photon count rates remain constant in all detectors. We then go on to set up the expressions for the coincidence counts between detectors D_1 and D'_1 , using the SPDC state from Equation 3.27 as our state:

$$w^{(2)}(D_1, t + \tau; D'_1, t) = s^2 ||\hat{E}_{1'}(t)\hat{E}_1(t + \tau)|\Psi_{\text{si}}\rangle||^2, \quad (3.63)$$

here, τ refers to the difference in time between a detection at D_1 and D'_1 . The electric fields at the detector positions are given by:

$$\hat{E}_1 = \frac{1}{\sqrt{2}} \left(\hat{E}_s(t) + \hat{E}_s(t - T_A) \right), \quad (3.64)$$

$$\hat{E}_{1'} = \frac{1}{\sqrt{2}} \left(\hat{E}_i(t) + \hat{E}_i(t - T_B) \right). \quad (3.65)$$

Here, we use the SPDC fields (now defined in integral form):

$$\hat{E}_N(t) = i \int d\delta \varepsilon_N^{(1)} e^{-i\omega_N t} \hat{a}_N, \quad (3.66)$$

where $N = \text{s,i}$. We now introduce a cross-correlation function^[53], (analogously to what we did in Equation 3.37):

$$g(t_s, t_i) \propto e^{-i\omega_p(t_s+t_i)/2} \int d\delta \psi(\omega_p/2 + \delta) e^{-i\delta(t_s-t_i)}, \quad (3.67)$$

where we use the assumption that our pump laser has an extremely narrow bandwidth abbreviate our expression and reduce it to terms of pump frequency and detuning^[54]. $\psi(\omega_p/2 + \delta)$ is the phase-matching function which determines the spectrum of our downconverted photons. We can then see that the integral in Equation 3.67 is the Fourier transform over the downconverted spectrum (which by previous assumption is symmetric and Gaussian) with a time variable $(t_s - t_i)$, so that we have:

$$f(t_s - t_i) = \int d\delta \psi(\omega_p/2 + \delta) e^{-i\delta(t_s-t_i)} \quad (3.68)$$

We can then rewrite Equation 3.63 as:

$$\begin{aligned} w^{(2)}(D_1, t + \tau; D'_1, t) = & |g(t + \tau, t)|^2 + |g(t + \tau - T_A, t - T_B)|^2 \\ & + 2\text{Re} [g^*(t + \tau, t)g(t + \tau - T_A, t - T_B)] \\ & + |g(t + \tau - T_A, t)|^2 + |g(t + \tau, t - T_B)|^2. \end{aligned} \quad (3.69)$$

All but one cross-term disappear due to our time-scale restrictions, which prevent single-photon interference, but leaves a possibility for late long-path photons to arrive at the same time as early short-path photons (hence our one cross-term can survive). We can then rid ourselves of the pesky time variable t by inserting Equation 3.68, so that we have:

$$\begin{aligned}
w^{(2)}(D_1; D'_1; \tau) \propto & |f(\tau)|^2 + |f(\tau + \Delta T)|^2 \\
& + 2\text{Re}[f^*(\tau)f(\tau + \Delta T)] \cos(\omega_p(T_A + T_B)/2 + \phi_0) \\
& + |f(\tau - T_A)|^2 + |f(\tau + T_B)|^2.
\end{aligned} \tag{3.70}$$

ϕ_0 is a phase difference between arms A and B. Then, to get our coincidence count rate, we must integrate our expression over our entire coincidence interval τ_{coinc} . Similar to before, since our coincidence window in reality will be much larger than the width of our function $f(\tau)$, we can integrate over all possible values (i.e. $-\infty$ to ∞). We also have an important threshold value for τ_{coinc} , namely $T_{A,B}$. If τ_{coinc} is smaller than these delays, then coincidences are only registered when the signal and idler photons both travel the long paths or the short paths (conversely, that no coincidences are registered if either photon takes a different path relative to the other). The consequence this has in our coincidence integral is then that the last two terms disappear, so we can reformulate it as:

$$\begin{aligned}
w_{\text{ctot}}^{(2)}(D_1, D'_1) \propto & 1 + \frac{\int_{-\infty}^{\infty} d\tau \text{Re}[f^*(\tau)f(\tau + \Delta T)]}{\int_{-\infty}^{\infty} d\tau |f(\tau)|^2} \cos(\omega_p(T_A + T_B)/2 + \phi_0) \\
= & 1 + e^{-\frac{(\Delta/2)^2 \Delta T^2}{2}} \cos(\omega_p(T_A + T_B)/2 + \phi_0) \geq 0,
\end{aligned} \tag{3.71}$$

where we have again used the assumption of a Gaussian spectrum with a bandwidth Δ . This expression tells us that our coincidence counts could potentially reach zero if the delays are perfectly balanced so that $\Delta T = 0$! It also tells us that our interference fringes oscillate with the central downconversion frequency $\omega_p/2$. Additionally, as the 'envelope factor' in the second term ($\exp(-(\Delta/2)^2 \Delta T^2/2)$) is derived from the SPDC-photon Fourier transforms, the spectrum of our downconverted photons play a major role in the shaping of the envelope! As an example, in Paper IV, we see that when we filter our downconverted photons through a 'notch' or 'step'-filter we find that our Franson interference has a sinc-like envelope³!

We can find a similar result when using different detector pairs (as long as both detectors are still in different arms) with the main difference being the sign in

³The Fourier transform of a step function is a sinc function, in case you didn't know. Also, if you've read this far and don't know what a Fourier transform is, I am so sorry.

front of the second term, so that:

$$w_{\text{ctot}}^{(2)}(D_i, D'_j) \propto 1 + (-1)^{(i+j)} e^{-\frac{(\Delta/2)^2 \Delta T^2}{2}} \cos(\omega_p(T_A + T_B)/2 + \phi_0), \quad (3.72)$$

where $i, j = 1$ or 2 , depending on which compatible detector pair we use. This sign difference arises due to the difference in phase when using detectors $i \neq j$ as there is a different amount of reflections/transmissions inside the paths. To clarify, when a photon is detected in D_1 or D'_1 , regardless of which path the photon took through the interferometer, it has been reflected in one beamsplitter and transmitted through the other. If the photon is detected in D_2 or D'_2 instead, it has either been transmitted or reflected twice (long path and short path, respectively) which leads to a phase difference of one reflection (π) between the paths, hence giving us a different sign when detector pairs $i \neq j$ are compared. This also makes sense intuitively, as if we consider D_1, D'_1 -coincidences at a given interval ΔT puts us down to zero coincidences, since there are no photons lost and single photon counts are constant, there must then instead be a coincidence peak between detectors D_1, D'_2 (and between D_2, D'_1 as well).

In the case where our detection window is too large to fulfill the $\tau_{\text{coinc}} < T_{A,B}$ condition, no terms cancel which gives us a constant background from short-long path coincidences (as there can be no interference in these cases) so that we effectively get:

$$w_{\text{ctot}}^{(2)}(D_1, D'_1) \propto 1 + \frac{1}{2} e^{-\frac{(\Delta/2)^2 \Delta T^2}{2}} \cos(\omega_p(T_A + T_B)/2 + \phi_0), \quad (3.73)$$

This puts the practical requirement on us that our detectors must be able to resolve time intervals shorter than $T_{A,B}$ for optimal fringe visibility, which is defined here in terms of our coincidence rate as:

$$V = \frac{R_{c\text{Max}} - R_{c\text{Min}}}{R_{c\text{Max}} + R_{c\text{Min}}} \quad (3.74)$$

We have now made our quantum mechanical prediction for our coincidence interference pattern^[55], but we have nothing yet to test it against. One might think that we ought to set up a CHSH-inequality as before, but in fact a local hidden variable theory can indeed account for the above results as well. Truly the worst possible news for someone wanting to show a violation of a Bell inequality for time! This originates in the fact that when we can distinguish (and remove) long-short path coincidences, the post-selection process makes it possible for a local hidden-variable model to account for the full fringe visibility^[56]. In the polarization-case, we can avoid this because we measure and account for all photons with no post-selection. All is not lost however, as it is still possible to prove a violation of a Bell inequality through use of the Franson geometry.

To do this, we need to both impose a fast-switching condition on the phase/delays in the interferometer and to extend our CHSH Bell inequality. The fast-switching condition requires that the delay/phase settings in the interferometer arms are switched randomly and rapidly enough that this switching takes only a short time Δ_{switch} , so that $\Delta_{\text{switch}} < T_{\text{A,B}}$. We will lay the groundwork for understanding this requirement here. To start with, in the local hidden-variable case an early-emission photon arrives at a detector at some time t_e after emission, whereas a late-emission photon taking the same path arrives at some time $t_e + T_{\text{A,B}}$ (from our indistinguishability requirement). Then we define a constant $t_{\varphi\text{D}}$, which represents the time it takes for a photon in the long path to travel to the detector from the delay stage in the long arm. We can additionally state that the 'decision' whether or not a photon emission will be early or late must occur at the latest at t_e , or the path indistinguishability would be lost. This means that for an early emission, a delay-stage switching after the time $t_e - t_{\varphi\text{D}}$ cannot causally affect whether an early or late emission even will occur, as given by our hidden variable(s). Whether the photons will end up in detectors 1 or 2 on either side can be causally determined up to the arrival time at the beamsplitter t_d which for early emissions is t_e and for late emissions is $t_e + T_{\text{A,B}}$. Then, if delay-switching occurs fast enough that $\Delta_{\text{switch}} < T_{\text{A,B}}$, the outcome may be determined based on a different delay setting, in a causal way, for late emissions. This opens the way to set up a Bell inequality for the late emissions^[56].

Now, there is a slight problem with this: we cannot in any way tell which detection event originates from an early or late emission. What we can tell, however, is whether or not we have different phase settings at times $t_d - T_{\text{A,B}} - t_{\varphi\text{D}}$ and $t_d - t_{\varphi\text{D}}$ for a given detection. From the discussion above, we also know that if the detection was from a late emission, the phase setting at time $t_d - t_{\varphi\text{D}}$ cannot have affected the early-late emission 'decision'. In such a way, by post-selecting detections for a specific setting of the delay/phase at $t_d - T_{\text{A,B}} - t_{\varphi\text{D}}$, we can ensure that the late emissions will always occur with the same delay conditions, even if we're switching rapidly and randomly, while early emissions will have random conditions. Notably, this random fast switching must be carried out in both arms, and we must choose specific pairs of delays $T_{\text{A,B}}$ to select for. In this way, we attempt dig ourselves out of the post-selection hole by performing even more post-selection!

Then, we define a correlation coefficient^[57]:

$$E(\Phi_{\text{A}}, \Phi_{\text{B}}) = \frac{w_{\text{ctot}}^{(2)}(D_1, D'_1) - w_{\text{ctot}}^{(2)}(D_1, D'_2) - w_{\text{ctot}}^{(2)}(D_2, D'_1) + w_{\text{ctot}}^{(2)}(D_2, D'_2)}{w_{\text{ctot}}^{(2)}(D_1, D'_1) + w_{\text{ctot}}^{(2)}(D_1, D'_2) + w_{\text{ctot}}^{(2)}(D_2, D'_1) + w_{\text{ctot}}^{(2)}(D_2, D'_2)}, \quad (3.75)$$

where we are letting the $T_{A,B}$ -dependence in $w_{\text{ctot}}^{(2)}$ remain implicit. We also define $\Phi_{A,B} = \omega_p T_{A,B}/2$. If we look at Equation 3.72, we can then shorten this to:

$$E(\Phi_A, \Phi_B) \propto e^{-\frac{(\Delta/2)^2 \Delta T^2}{2}} \cos(\Phi_A + \Phi_B), \quad (3.76)$$

where we have again assumed sufficient time resolution to fulfill the $\tau_{\text{coinc}} < T_{A,B}$ requirement. Otherwise, we would effectively reduce the amplitude of $E(\Phi_A, \Phi_B)$. We have also removed the phase term for brevity.

Then, as before, we set up the CHSH Bell inequality^[58]:

$$S = |E(\Phi_A, \Phi_B) + E(\Phi_A, \Phi'_B)| + |E(\Phi'_A, \Phi_B) - E(\Phi'_A, \Phi'_B)| \leq 2, \quad (3.77)$$

which only holds for our late-emission coincidences, importantly⁴. The only thing we can say about the correlation function for the early emissions is:

$$|E_e(\Phi_A, \Phi_B)| \leq 1. \quad (3.78)$$

Then, since half of our recorded coincidences will still be early-emission coincidences we cannot apply the typical CHSH Bell inequality due to the constant background from early emissions. If we take the above into account, we find that inequality takes the value:

$$S_{e+l} \leq 3, \quad (3.79)$$

which we cannot reach with the quantum mechanical model, as our maximum for S then is $2\sqrt{2}$. Another, extended Bell inequality can be defined^[56] which gives:

$$\begin{aligned} S_{\text{LHVTtext}} &= |E_{e+l}(\Phi_A, \Phi_B) + E_{e+l}(\Phi'_A, \Phi_B)| + |E_{e+l}(\Phi'_A, \Phi'_B) + E_{e+l}(\Phi''_A, \Phi'_B)| \\ &\quad + |E_{e+l}(\Phi''_A, \Phi''_B) - E_{e+l}(\Phi_A, \Phi''_B)| \\ &\leq \frac{1}{2}(4 + 6) = 5. \end{aligned} \quad (3.80)$$

The 4 and 6 are the contributions from the late- and early emission coincidences, respectively. Crucially, we find that with maximally-valued quantum predictions, given by $\Phi_A = 0$, $\Phi'_A = -\pi/3$, $\Phi''_A = -2\pi/3$, $\Phi_B = \pi/6$, $\Phi'_B = \pi/2$ and $\Phi''_B = 5\pi/6$, we get:

$$S_{\text{QM}} = 6 \cos\left(\frac{\pi}{6}\right) > 5. \quad (3.81)$$

⁴We do in fact fulfill the requirements on the hidden variable λ from equations 3.53 and 3.54 for late emissions here. Our conditions on measurement outcomes also hold if we consider a detection in D_1 or D'_1 as +1 and a detection in D_2 or D'_2 as -1, as the photons are equally likely to reach either detector!

To be able to measure this result, the visibility of our Franson fringes needs to be an incredible 96%! If one is able to measure such a result, however, one is able to say that the photons are indeed time and, by Fourier relation, frequency entangled⁵! This is also referred to simply as time-frequency entanglement, and the strong correlation between the photon frequencies does indeed have potential for applications within spectroscopy!

In practice, we of course do not properly measure our photons in the setup to confirm their entanglement completely, but rather accept based on past results^[1;49;59] that there are no local hidden variables here. Either way, a large visibility in the Franson fringes does indicate a strong frequency anticorrelation between the photons, as can be seen when one has to treat our derivation of Franson interference without the luxury of a narrow-band pump laser^{[54]6}. The large visibilities yielded in some of our experiments, as seen in Paper IV, combined with the assumptions involved in the use of our SPDC source, at the very least provide evidence for strong time-frequency correlations usable in spectroscopic experiments.

⁵If you are interested in the full treatment of the Franson Bell inequality, I can heartily recommend reading ref.^[56] as it covers every detail of the process. Without it, I would still be laboring under the misapprehension that a visibility of 71% in the Franson fringes is enough to prove entanglement!

⁶You wouldn't believe the things I have seen in my Franson measurements when our pump laser fails to emit in single-mode, all hell broken loose, truly! To keep this brief I will simply refer you to chapter 55 of *Moby Dick* to convey my opinion on these interference measurements for you, it is similar to Melville's opinion on contemporaneous artistic depictions of whales^[60]. If you are for some reason interested in some examples of these figures, see the supplementary material for Paper IV

4 Quantum dots: Size dependence, vibrational couplings

We have now spent a significant amount of time discussing light, both on its own and its interaction with a material. We have not, however, touched upon the nature of the material in much depth at all, other than the vague quantum mechanical treatment where we simply assign energy levels and an electric dipole. Since quantum dots are the topic of investigation in both Paper II and Paper III, we shall aim to amend this simplified picture of our materials and what has been investigated here.

4.1 Quantum dots and confinement

Put briefly, quantum dots (QDs) are nanocrystals, mostly sized between 1 and 100 nm. These small sizes are required to cause confinement inside the crystals, the implications of which we will discuss a bit later. The QDs we will discuss are colloidal, meaning that they are suspended in solution and as such are not attached to any surfaces. QDs are often composed of at least two types of semiconductors. They are classified as nanomaterials, as they have to be on the scale of nanometers for their distinct characteristics to appear^[61–63]. They were first synthesized and characterized in the early eighties^[64–66]. The main difference between QDs and their otherwise-identical bulk counterparts arises from the confinement of their electronic wave functions due to their small size. This is similar what happens in a 'particle in a box' model^[67], where the states are defined by the allowed modes of the wavefunction which in turn arise dependent on the width of the given potential well. This effectively makes QDs a sort of hybrid between a bulk material and an atom. The state manifolds which make up their bands becoming more defined and structured as less material is present, becoming similar to the energy levels in an atom as the dot's size decreases. On the other hand a QD still vibrates, like a bulk material or molecule, making it possible to find both acoustic and optic phonon modes, with optic modes coupling to the electronic structure of CdSe QDs^[68;69] featuring in Paper II.

As you may have come to realize, size is very important for the unique properties of QDs. They can be used as light-emitters^[70–72] or sensors^[73;74] with tunable band-gaps, with the tuning parameter in question being their size. What determines the properties of a QD is not only its size in absolute, but also its size in relation to its excitons. As the name implies, an exciton is created upon excitation of a material and refers to the state that may be formed by the negatively

charged excited-state electron and the positive (in relation to the ground state electrons surrounding it) hole that it has left behind in the ground state^[75]. Since the electron will in general be attracted through Coulomb forces to the relatively positive hole, it can form a type of bound state not entirely dissimilar to a hydrogen atom. This quasi-particle is what we call an exciton. The exact properties of an exciton in turn depend on the material in which it is formed. In materials with higher relative permittivities, and therefore more freely flowing electrons, the electron-hole interaction is screened, thus weakening it and causing the bound state to delocalize, giving a larger effective exciton radius. Conversely, a material with low permittivity allows the exciton to be confined to a smaller space because the electron-hole pair Coulomb attraction is effectively stronger in the absence of strong screening. These two 'extreme' cases are called Wannier-Mott excitons and Frenkel excitons, respectively^[76]. Through analogy with hydrogen, the expression of the exciton radius⁷ in a bulk material is given by:

$$r_{\text{exc}} = \frac{\epsilon \cdot m_e \cdot a_0}{\mu}, \quad (4.1)$$

where ϵ is the material's relative permittivity, m_e is the electron mass, a_0 is the Bohr radius and μ is the reduced electron-hole mass. A QD then has to have a radius comparable to the exciton radius, so that the exciton is confined to the QD. This confinement increases for smaller and smaller QD radii, leading to a discretization of the energy levels. As the size of the QD changes, the Coulomb attraction between electron and hole also changes, with smaller sizes bringing them closer together, increasing their attraction. In general, three regimes of QD radius are discussed: Firstly, the weak confinement regime, where the QD radius is larger than r_{exc} , where confinement effects are weak. Secondly, there is the strong confinement regime, where the QD radius is significantly smaller than r_{exc} and the exciton, hole and electron are all tightly confined. Lastly, there is also an intermediate confinement regime between these two, where the confinement potential is comparable to the exciton radius. In general, small differences in the balance of confinement, band gap energies and Coulomb forces for strongly confined QD's give rise to the differences in e.g. emission wavelengths^[77] that can be observed in QDs of different sizes, this is illustrated in Figure 4.1. These size effects in CdSe QDs were the focus of Paper III, where QDs with different sizes were measured and resolved simultaneously through use of 2D spectroscopy. Analysis of a possible size-dependence for optic phonons was also a part of Paper II, but none was found within the resolution of the experiment. Optical phonons do generally have higher frequencies and are therefore expected to be

⁷Usually referred to as the exciton Bohr radius, as it is defined as the most probable electron-hole distance, similar to the proton-electron distance for the Bohr radius in hydrogen and is indeed based on the same model.

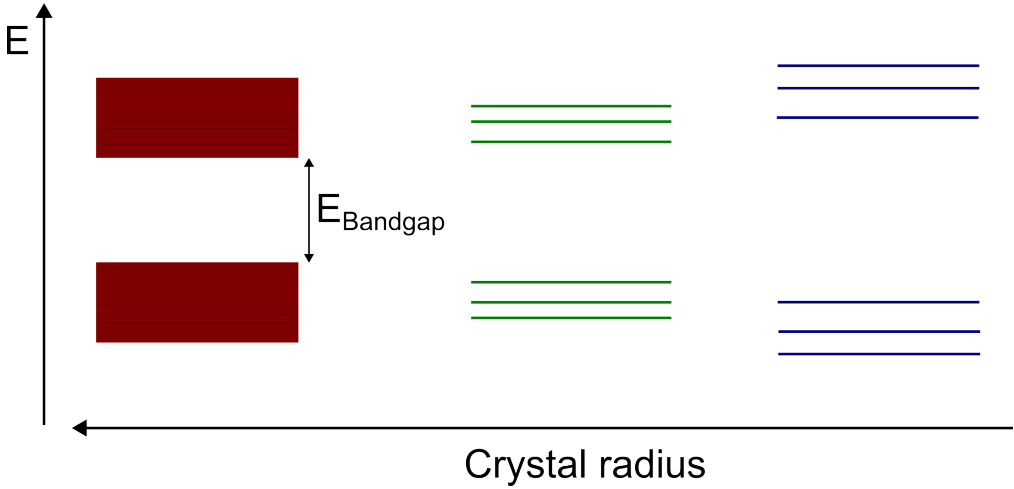


Figure 4.1: A diagrams depicting the band-structure of a bulk material discretizing into energy levels and the increasing separation between ground- and excited states with decreasing QD size, i.e. an increase in confinement.

less affected by QD size than low-frequency acoustic modes which are more easily confined due to their extended wavelengths.

4.2 Vibrations in quantum dots

We previously hinted at vibrations (phonons) in QDs but have not given them a description yet. In an atom, the energy levels are given by the states which the electrons can occupy. When we introduce several bound atoms in the form of a molecule or quantum dot, however, we introduce new parameters. Crucially, the atoms in a molecule are not fixed, but rather in some equilibrium position as determined by the forces attracting and repelling them. It is therefore possible for them to move relative to one another while remaining bound together. In crystalline systems with many atoms, such as bulk materials or quantum dots, these vibrations are usually discussed in terms of phonons, which are normal modes of the lattice vibrations, expressed as waves. In general, there are two main types of phonons, acoustic and optical. These can then be split into subcategories depending on the direction of oscillation, which can be either longitudinal (oscillation along direction of travel) or transverse (oscillation perpendicular to direction of travel). Acoustic phonons are called as such because they consist of atoms oscillating coherently with one another, if not perfectly in phase, forming a collective traveling motion like a sound wave (hence the name). Optical phonons are instead made up of out-of-phase vibrations and are as such often at higher frequencies, implying a lesser extent in space as well. Optical phonons

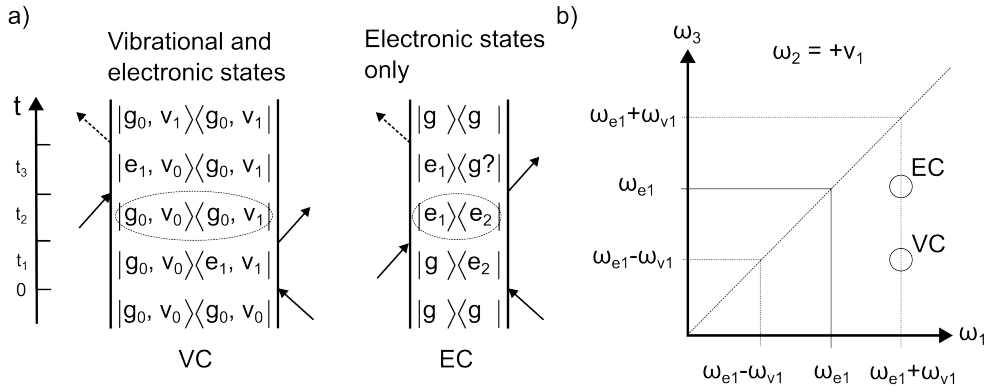


Figure 4.2: Diagram of 2D spectroscopic analysis of the origin of population-time beatings in a QD. a) displays two rephasing Feynman diagrams which attempt to account for a positive population time coherence as explained either by couplings to vibrational states (VC) or a second, near-lying electronic state (EC) with an energy-difference equivalent to the hypothetical vibrational frequency. b) displays a 2D diagram (with the excitation and detection frequencies along the horizontal and vertical axes, respectively) at a given frequency in a Fourier-transformed population time axis including the peaks given by the Feynman diagrams.

get their name from the fact that oscillations between neighboring atoms can give rise to local electric dipoles which can then couple them to the material's electronic transitions. This can mean that an absorption of a photon by a quantum dot can lead to an excitation in both electronic and vibrational modes. Generally conservation of momentum will prevent more than a single phonon excitation per interaction (can also be seen from selection rules for a harmonic oscillator model of vibrations). These excitations can place the system in vibrational coherences, giving so-called quantum beats for spectroscopic pathways where one would otherwise assume the system to be at rest, such as during the population time. Couplings of this nature are the main topic of Paper II. The different phonon modes are well accounted for by a harmonic oscillator description, so that optical phonons may form relatively evenly spaced 'substates' to the electronic states which they are coupled to.

Coherences during population times will primarily be observed through investigating the dynamics of individual peaks in a 2D spectrum over the collected population times. An oscillation of the signal will then indicate a coherence. If enough population-time data has been collected, one can Fourier transform the data with respect to the population time as well. This enables the analysis of these coherences with the same tools used in other 2D spectroscopy (Feynman diagrams, mainly) and the origin of the type of beating observed can be determined. A partial example of this type of analysis is shown in Figure 4.2. It can be found that the electronic coherence model cannot explain all peak

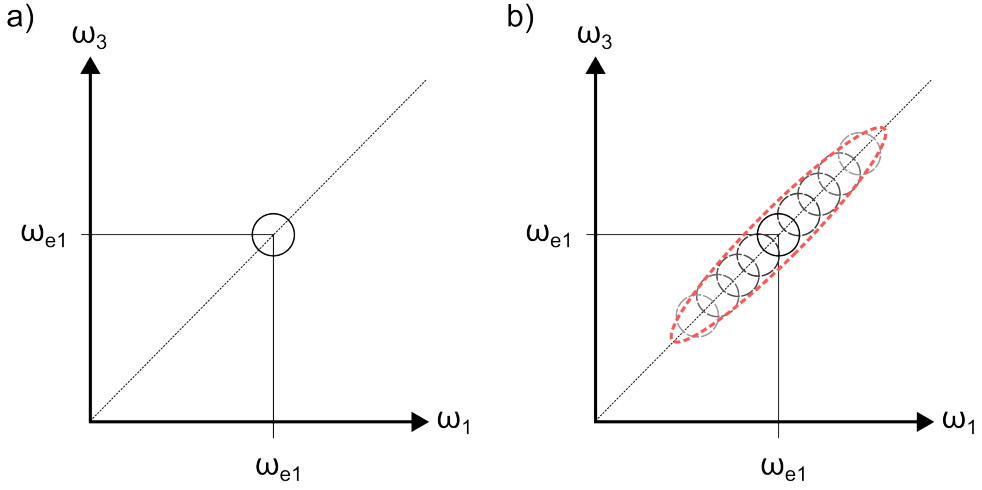


Figure 4.3: Illustration of how size-dependent bandwidth causes inhomogeneous broadening in 2D spectra. Axes are defined the same as in Figure 4.2. a) illustrates a single diagonal peak at a given electronic transition frequency when the QD size distribution is narrow. b) instead illustrates the broadening along the diagonal of that same signal when a large size distribution of QDs is measured, with the QD from the other figure marking the center of the distribution. The dashed oval marks what the broad peak would look like in a 2D spectrum. As can be seen, the homogeneous and inhomogeneous linewidths are simultaneously visible.

positions achieved by vibrational or vibronic^[78] coherences, at least not without some amendment to the ground state not included in the base assumptions (signified by the question mark in Figure 4.2 a)). A complete account of the origins of the coherence signals includes constructing all possible pathways for the cases considered. Then, the theory must be put to the test by comparison with actual 2D measurement data. This can be done by comparing the overlap integrals of the involved states with the amplitude and phase of the equivalent measured peaks^[79]. In this case, the amplitude of the peaks contains information regarding the relative transition strengths and the amount of pathways which contribute. In experiments where differently-sized QDs can be measured and resolved simultaneously, such as in 2D spectroscopy, the phase of the peaks can reveal a dependence (or lack thereof) of the optical phonon modes on the QD size. A phase consistent along the diagonal (the direction along which the inhomogeneous broadening is expressed) for a given peak implies an absence of size-dependence within measurement resolution. A more in-depth discussion of the above topics for CdSe QDs can be found in Paper II.

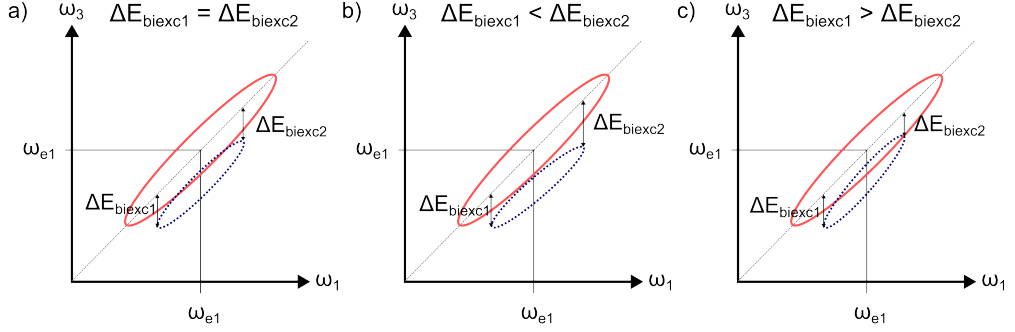


Figure 4.4: Diagram of multiple 2D spectra with inhomogeneous broadening due to a broad QD size distribution, as illustrated in Fig 4.3 b), with the diagonal (SE and GSB, red oval) and the biexciton ESA peaks (blue dashed oval) deconvoluted. a) shows an example where the biexciton binding energy is size-independent, and is therefore parallel to the diagonal. b) and c) show cases where the binding energy increases and decreases monotonously with decreasing QD size (i.e. along with an increasing band gap and therefore higher frequency along the diagonal), respectively.

4.3 Size-dependence and correlations in quantum dots

As mentioned before, in general a QD size-decrease will cause an increase in the band gap. Any size-dependent change in band gap will then cause two simultaneously measured QDs to appear at different frequencies in a spectroscopic measurement. When an ensemble of QDs with a continuous range of sizes is measured, this produces an inhomogeneously broadened QD spectrum. A 2D measurement can simultaneously resolve the homogeneous and inhomogeneous linewidth of a given transition through the separation of excitation and detection axes, as illustrated in Fig. 4.3. This in turn allows for size-labeling of different positions along a single diagonal peak. The position-size labeling may also allow for size-dependent correlation measurements to be carried out as well. This is the focus of Paper III. This position-size labeling is limited by other signals in the spectrum which may overlap, causing either addition or cancellation depending on the relative sign, so care must be taken in their analysis.

When using highly intense laser pulses, such as in 2D spectroscopy, it is possible to create a second exciton in a single quantum dot. When these bind together, they are referred to as biexcitons, and their signature in the spectrum is an increase in absorption which is a type of ESA signal. For a rephasing spectrum in CdSe QDs, this ESA signal will appear just below a diagonal exciton peak along the detection axis^[80–82]. This slight difference in energy is due to the biexciton binding energy $\Delta E_{\text{biexc}} = 2E_{\text{exc}} - E_{\text{biexc}}$, which causes the coherence frequency between the biexciton and exciton state to be slightly lower than the exciton frequency itself, hence it appears 'below' the diagonal. Just like the signal along the diagonal, it can be used to observe size dependence of the

biexciton state. The biexciton peak may not run completely parallel to the diagonal of the spectrum if it is size-dependent, however! As an example, an increase in binding energy with a decrease in QD size would cause the ESA peak to shift further away from the diagonal for higher excitation frequencies, as shown in Figure 4.4. In order to measure any kind of size dependence, one then needs to apply judicious modeling with the relevant lineshapes, especially in a spectrum where multiple peaks are present.

This size dependence need not be monotonous though, and indeed in Paper III a non-monotonous size dependence of the biexciton binding energy was measured, where a minimum binding energy was measured for the ensemble's middle-sized dots! Additionally, for different population times, the binding energy was seen to shift for smaller QDs. This could be partially due to exciton attraction, which has been reported for CdSe quantum dots^[83]. Exciton repulsion has also been reported for certain quantum dot structures^[84]. It is then possible that the time-dependent changes in measured binding energy for the smaller QDs could be due to the equilibrium of repulsive and attractive forces shifting over the population time.

5 Two-photon absorption, Classical and Entangled

With all this done, we are now ready to take our first few steps toward nonlinear entangled-photon spectroscopy! A notable step on the way to our goal is the measurement of two-photon absorption (TPA), a nonlinear (although not in the 2D spectroscopy way) absorption measurement. In most cases when a photon is absorbed by a material, it is due to it being close to, or exactly, resonant with some electronic transition within. TPA is instead the absorption of two non-resonant photons in short succession whose *total* frequency is near-resonant with a given transition, illustrated in Figure 5.1. The likelihood of TPA occurring is extremely small and so to maximize chances of it happening, one needs to focus a laser very tightly and ensure one's laser pulses are very short. Even under ideal circumstances, most photons will not participate in TPA processes.

Historically, this has actually made TPA desirable within biology for sensitive in vivo studies, as it is a very precise way of measuring in an area localized much more sharply than with a focused laser beam of resonant photons^[85] with less tissue damage^[86]. Some samples, however, may be photosensitive even to the point where the residual photons in a typical TPA measurement can cause photodissociation or heating damage^[87]. To avoid this, a more delicate approach is required. There has been some discussion as to whether or not photon entanglement can be used in a realistic way to enhance TPA signals at low photon fluxes with theoretical predictions in the affirmative^[88;89]. These predictions are based on previous findings which indicate that for photons originating from SPDC, TPA processes have two scaling components, one scaling linearly with beam intensity and one with its square, with the linear component dominating at very low photon fluxes^[90–93]. Several studies of entangled two-photon absorption (ETPA) have been made^[94–97], but it has been hard to draw definitive conclusions based on the reported results⁸, especially if there is no measurement of a signal without a photon-pair delay^[98]!

But we have skipped ahead a little here, how does two-photon absorption actually happen? Let us take a few steps back so we can keep going forward later.

⁸In addition, ref.^[97] is 'missing' a background fluorescence signal which to the author's knowledge is yet unexplained (but we believe is due to a phenomenon well-known in other fields). I believe to have found the explanation, and so would recommend the interested reader to read both ref.^[97] and Appendix B.

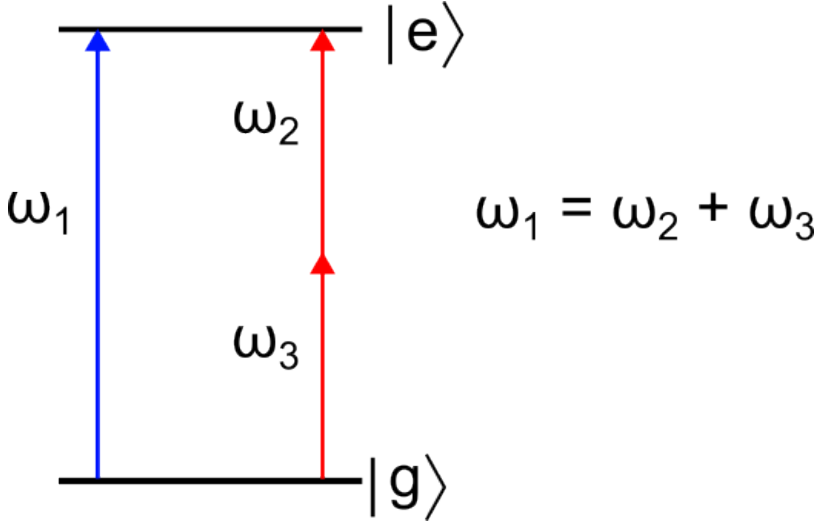


Figure 5.1: Simple illustration of two-photon absorption compared to one-photon absorption. The single exciting photon (blue arrow) has a frequency ω_1 which is resonant with the electronic transition $g \rightarrow e$. It is then possible, though not very probable, that two photons with a sum frequency equal to ω_1 (two red arrows) arriving simultaneously can cause a $g \rightarrow e$ excitation.

5.1 Two-photon absorption, Basics

To begin with, the probability of TPA per unit time can be summarized as^[99]:

$$A_{2p} = \kappa_{2p} \langle a^\dagger a^\dagger a a \rangle, \quad (5.1)$$

where κ_{2p} represents all the collected constants involved in the TPA process. As before $a^\dagger$ and a represent the creation and annihilation operators of our light field respectively, as evaluated at the same point in space and time (i.e. so that all the photons are present at the atom at the same time). If we think about this in terms of classical electric fields, we then use the analytical signals instead of our operators, and so we have:

$$\langle E^{(+)} E^{(+)} E^{*(-)} E^{*(-)} \rangle = \langle I^2 \rangle, \quad (5.2)$$

where I is the instantaneous intensity. We can take the second-order correlation function of the field, expressed in terms of intensity:

$$g^{(2)}(\tau) = \frac{\langle I(t) I(t + \tau) \rangle}{\langle I \rangle^2}. \quad (5.3)$$

The intensity correlation function is constant for a non-fluctuating source, such as a monochromatic laser, and generally gives information on time-dependent

light fluctuations. We can then insert this with $\tau = 0$ into our transition probability expression to get:

$$A_{2p} = \kappa'_{2p} \langle I \rangle^2 g^{(2)}(0). \quad (5.4)$$

This tells us that a classical two-photon absorption is both proportional to the square of the intensity and the second-order field correlation function^[100]. This also tells us that the fluctuations in our intensity have an effect on the TPA efficiency. As an example: let us assume that our light sources have identical average intensities $\langle I \rangle$, and one a thermal source (assumed to be filtered, resonant and focused the same as a laser) and another is a cw-laser. Then, by looking at the correlation functions which are $g^{(2)}(0) = 2$ for the thermal source and $g^{(2)}(0) = 1$ for the cw-laser, we find that the thermal (fluctuating) source has twice the TPA-rate relative to the continuous laser (non-fluctuating)⁹! As pulsed lasers can have even higher values of $g^{(2)}(0)$ ^[102], pulsed lasers are generally the method of choice if one wants to observe TPA.

Wait a minute, this just leads us right back to our conundrum from the start! It seems that the only way to get a good amount of TPA is to have an intense, pulsed laser! So how do we get from here to using entangled photons? Our entangled photons have a $g^{(2)}(0) = 2$ like the thermal light, which is better than a cw-laser, but it's clearly not enough! This means that to understand why, we have to think a little bit harder about the description of our TPA model, to turn it into an ETPA model...

5.2 Entangled two-photon absorption

While the statistics of our individual SPDC-photons may be thermal, recall that the description of an entangled system is fundamentally incomplete without taking all involved parts into account! The correlations *between* photons are then the key to making the distinction between TPA and ETPA. In this way, we can still make the intensity correlation function $g^{(2)}(0)$ work to our advantage if we get to the bottom of our quantum correlations, so let's get digging!

We begin by considering our SPDC state, much in the same way as defined by 3.27, where we mostly ignore the directionality of the fields, other than that we assume them to be spatially separate. If we then consider that we have some

⁹The degree to which TPA is dependent on intensity fluctuations is quite interesting. It can also be seen that TPA has a strong effect on the outgoing light fluctuations as well! The curious reader is referred to refs.^[99] and^[101] in particular, though many references in this section make for good reading on the topic.

detector in the path of one of our beams, we get the following expression for the average number of photons over our detection window t_w ^[103]:

$$n_j = s \int_{-t_w/2}^{t_w/2} d\tau \langle \Psi_{\text{si}} | a_j^\dagger(\tau) a_j(\tau) | \Psi_{\text{si}} \rangle = s t_w A_D \Phi, \quad (5.5)$$

where A_D is the surface area of the detector, j refers to either the signal or idler modes, and Φ is our photon flux (number of photons per time and area). Then, if our detection time window t_w is significantly larger than the coherence length of our downconverted photons, but short relative to the average time between pair emissions, we can be reasonably sure we only detect a single photon at a time¹⁰, we can get the expression:

$$n_j \approx s A_D / A_{\text{spdc}}, \quad (5.6)$$

where A_{spdc} is the beam area of our downconverted photons. This also gives us:

$$\Phi \approx \frac{1}{t_w A_{\text{spdc}}}. \quad (5.7)$$

Using these assumptions, we can get the following expression for coincidence detection of our photon pairs:

$$\begin{aligned} G^{(2)}(t) &= s^2 \int_{-t_w/2}^{t_w/2} d\tau \langle \Psi_{\text{si}} | a_s^\dagger(\tau) a_i^\dagger(\tau + t) a_i(\tau + t) a_s(\tau) | \Psi_{\text{si}} \rangle \\ &= s^2 f(t) t_w A_{D_1} A_{D_2} \Phi + \dots, \end{aligned} \quad (5.8)$$

where $f(t)$ is an overlap function which peaks at $t = 0$ and is determined by the coherence time of our downconverted photons. A_{D_1} and A_{D_2} are the detector areas for detector 1 and 2 respectively. We can see here, that as we have taken the expectation value with respect to the same state as before, we are still linearly dependent on the photon flux! If our photon flux is so great that our previous assumption of one pair per detection window on average no longer holds, we do have to include a term dependent on the square of the flux as well though, this term is the equivalent of our classical term for thermal coincidence detection.

If we then consider that our detectors are instead a molecular system, which may be sensitive to two photons absorbed simultaneously, we can think of this as our entangled two-photon cross section! This may seem like a bold declaration, but bear with me just a little while longer! If you consider the coincidence

¹⁰This requirement is rather easy to achieve with a narrow-band pump laser and detectors with sub-microsecond time resolutions, due to the low efficiency of SPDC.

detection expression again, you may notice that we have cheekily renamed it $G^{(2)}(t)$. This is not coincidental, as it is in fact our non-normalized intensity correlation function! So that, recalling equations 5.1-5.3:

$$G^{(2)}(0) = \langle I \rangle^2 \cdot g^{(2)}(0), \quad (5.9)$$

where we generalize our expression to account for overlapped pairs to get:

$$G^{(2)}(0) = \alpha \sigma_e \Phi + \beta \sigma_c \Phi^2, \quad (5.10)$$

where σ_e represents our ETPA cross-section, and σ_c our classical TPA cross-section. α and β are constants which depend on our photon modes^[98]. We can then insert this into our expression for the TPA rate, as given by Equation 5.4:

$$A_{2p} \propto \alpha \sigma_e \Phi + \beta \sigma_c \Phi^2. \quad (5.11)$$

Here we have omitted our prefactor κ'_{2p} , for brevity. We can also find, in the cases where the photon time-correlation satisfies $\sigma_t < \tau_p$ and the spatial correlation of our signal and idler is greater than our pump beam area, so that $A_{\text{spdc}} < A_{\text{pump}}$, we have the relationship^[104]:

$$\sigma_e \approx \frac{\sigma_c}{\sigma_t \cdot A_{\text{spdc}}}. \quad (5.12)$$

This expression then tells us that a stronger downconversion photon correlation, i.e. a minimized σ_t and A_{spdc} , gives the strongest possible 'quantum advantage' and gives the highest likelihood of successfully measuring ETPA.

If one can then make some (well motivated!) assumptions about one's photon modes, it is possible to get exact values for α and β . In so doing, it becomes possible to measure σ_e exactly! Additionally, with good knowledge of one's entanglement parameters, it becomes possible to determine the contribution of ETPA and classical TPA to a total TPA count. For narrow-band pumped SDPC photons, the ETPA contribution will generally be orders of magnitude stronger at the photon fluxes of downconverted photons that can be produced. The question then remains whether or not it is possible to measure ETPA with these types of measurement? The crucial points are then a high downconverted photon flux (which will still be significantly lower than the classical photon flux required for classical TPA) and good entanglement conditions, so that the downconverted photons are maximally entangled/correlated in time-frequency. A way to delay signal- and idler photons relative to one another so that one can observe a time-dependence in the ETPA would also be a good, if not necessary, part of an ETPA experiment. A way to measure at different laser powers would

also be good, as this would be able to measure any flux-dependence in one's signal, which should be present for any true TPA measurement.

In an ideal scenario, these requirements can all be met when using an SPDC-source feeding into a Franson interferometer. The complete separation of photons, followed by recombination on a sample and transmission-mode coincidence detection allows a fine time resolution. The absorption measurement then has enhanced contrast thanks to the Franson interference, which also acts as a shorthand for the quality of our entanglement¹¹!

By encoding our ETPA-signal in the Franson interference this way, we can use a relatively simple absorption model to calculate an ETPA cross-section σ_e from our results, which will be linear in coincidence counts. The Franson geometry and coincidence detection additionally allows us to exclude single-photon losses from our measurement results, since single-photon losses will be independent of the relative long-arm delay ΔT (barring any alignment-dependent losses, which can be corrected for) and will therefore not produce a time-dependent loss. The only time-dependent signal will then be one which requires a photon overlap, which for proper alignment will be at the center of the Franson interference pattern, and as such is guaranteed to be a two-photon effect (though not necessarily ETPA, but other candidates are unlikely). This is the focus of Paper IV, which is in many ways the culmination of this entire project, it also serves as a proof-of-concept for Franson interference as a platform for nonlinear spectroscopy going forward! For more information regarding the experimental setup and details, please refer to Paper IV (and its supplementary material) as well as Appendix A.

¹¹A perfect storm, is it not?

6 Conclusions and Outlook

We have here studied theoretical nonlinear spectroscopy in Paper I. The aim here was to test the theoretical (nevermind practical!) limitations of multidimensional spectroscopy in the case of weak and short-lived correlations. We found that even in an ideal case, artifact signals are extremely strong even in the presence of a real signal. Any signal that is then expected to not last longer than the pulse overlap needs to have its decay carefully analyzed to verify it is not a pure artifact. This artifact is unavoidable when pulses are overlapped, but could potentially be reduced with lower photon fluxes. Unfortunately, in classical spectroscopy high photon fluxes are often required to observe these signals.

In Papers II and III we instead analyze information produced in multidimensional spectroscopy measurements. The main purpose of these measurements were to investigate the signal origins of coherences and to investigate biexciton correlations through size-dependence measurements. We were successfully able to determine the origins of population-time coherences thanks to pathway analysis. Additionally we were able to find that biexciton binding energies were non-monotonously dependent on QD size. This demonstrates the wealth of information contained in these types of measurements, which are nonetheless constrained by peak overlap and that they need to be carefully analyzed in order to not draw incorrect conclusions.

The outcomes of the above papers are successful and demonstrate the benefits of multidimensional spectroscopy, which nevertheless has its own drawbacks and limitations. We then believe that the next step, which can alleviate some of the problems with measurement artifacts and congested spectra would be the use of entangled photons for the purposes of nonlinear spectroscopy.

We have taken an early step in this process by using the Franson interferometer as a platform for the measurement of ETPA in Paper IV. We believe narrow-band pumped entangled photon spectroscopy can be developed further, with the Franson interferometer being a particularly strong platform for this type of experiment. Narrow-band pumping additionally enables full utilization of the strong frequency-anticorrelation of the generated time-frequency entangled photons.

Future development of this project would involve a renovation of the setup to perform further ETPA measurements and to adapt it for the requirements of nonlinear spectroscopy. There are already theoretical conceptions of what such an experiment may look like^[103;105;106], and these could serve well to guide ex-

perimental design going forward. Many modern proposals within the field of entangled 2D spectroscopy suggest the use of pulsed pump lasers, which trades the strong frequency correlation for a strong measurable signal. We remain optimistic about the use of the narrow-band pumping in nonlinear entangled-photon spectroscopy, as we believe the ETPA-measurements carried out in Paper IV demonstrate the ability to measure signals requiring high sensitivity even under sub-optimal conditions, yielding a solid upper bound for the ETPA cross-section. Thus we expect that a refurbished setup with a higher downconversion flux, though still within the photon counting regime, has a strong potential going forward, especially with regards to collinear SPDC generation. This would ideally be carried out either with Type-II downconversion or a 'reverse HOM'-style generation geometry which allows clean separation of signal and idler photons while increasing effective photon flux, as shown in Appendix B. Alternatives to single-mode lasers can also be considered. High-quality Fabry-Perot cavities could be considered for the filtering of pump light, to ensure a controlled pump bandwidth as well.

In short, the potential of entangled-photon spectroscopy remains to a large extent untapped, in part because there is a mismatch between theoretical and experimental developments so far. However, with continued experimental work, we strongly believe that this gap can be bridged and are eager to see interesting developments in the field in the future.

Appendices

A Interferometry setup

Most of the interferometric setup is displayed in Figure 1 of Paper IV, but a more detailed version of the pump setup is described here in Figure A.1. The SPDC downconversion stages (everything after and including f_3 in Figure A.1) and Franson interferometer were initially designed and constructed by our collaborators from Innsbruck (Luis Matheis, Sebastian Gstyr, Robert Keil, in Gregor Weihs group).

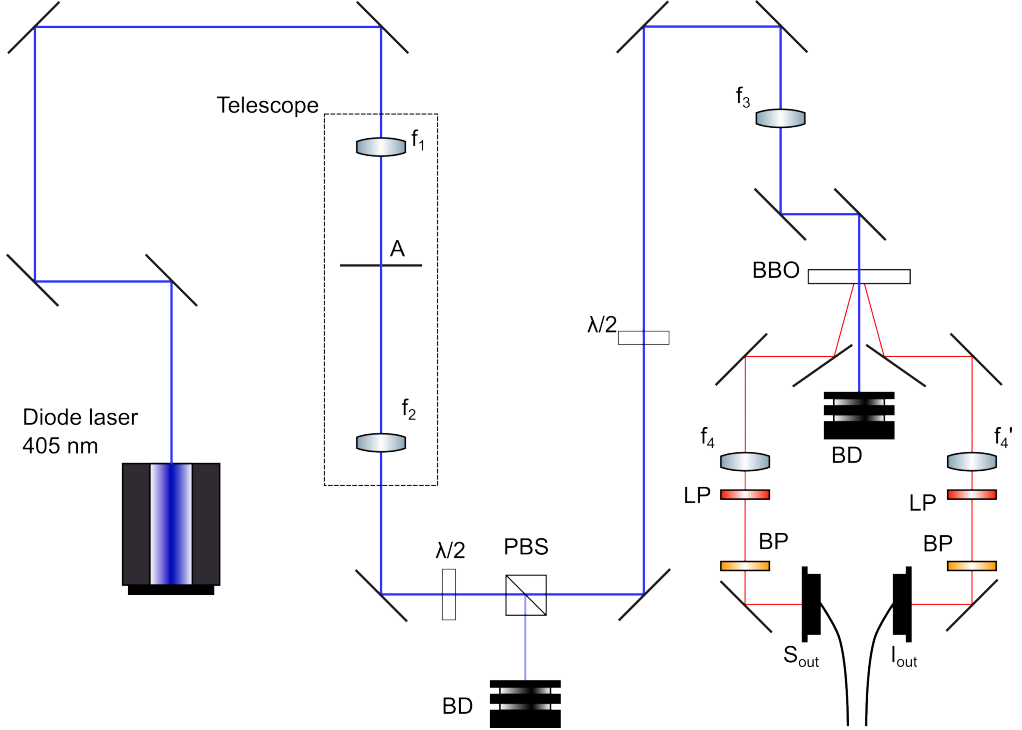


Figure A.1: A diagram of the full entangled photon source, including pump laser. The pump laser is a single-mode continuous-wave diode laser which emits at 405 nm (LM-405-PLR-40-4K Surelock, Coherent). Lenses f_1 and f_2 have focal lengths $f = 175$ mm and 100 mm, respectively. A represents an aperture in the telescope. Half-wave plates are marked with $\lambda/2$, and a polarizing beamsplitter, marked PBS, is located between them. f_3 is a focusing lens with focal length $f = 175$ mm. The nonlinear crystal is marked as BBO (Beta-Barium Borate, Newlight, NCBBO5200-404(I)-HA6-M12.7, 2 mm thickness). Lenses f_4 and f_4' both have focal length $f = 250$ mm. LP and BP are long-pass and band-pass filters, respectively. LP transmits wavelengths longer than 650 nm, while BP is a notch filter which transmits wavelengths centered at 800 nm with a width of 40 nm (780 - 820 nm). Beam dumps (BD) are placed to block the residual pump beam after the PBS and BBO crystal. S_{out} and I_{out} are the outcoupling fiber collimators for the signal and idler, respectively.

The pump beam light is reflected and aligned to pass straight through the telescope in order to collimate the beam and clean up the beam profile, which is divergent and asymmetric coming directly from the laser. A half-wave plate is then used in conjunction with the PBS to both adjust the outgoing power of

the pump beam, and to ensure the pump is fully linearly polarized. A second half-wave plate is then used to fine-tune the polarization of the beam to ensure it is perfectly vertical. The focusing lens f_3 focuses the pump beam on the BBO crystal where the SPDC pairs are generated. Lenses f_4 and f'_4 collimate the signal and idler beams, which then pass through the LP and BP, long-pass and band-pass filters, respectively. The signal and idler beams are coupled out through S_{out} and I_{out} and are then passed to the Franson interferometer (see Figure 3.5 in this work or Figure 1 b) in Paper IV).

Initially the delays inside the Franson interferometer were operated with retroreflectors mounted on stepper motors. This worked well for HOM measurements with strongly filtered spectra (which yield a large dip width, due to longer coherence times), but eventually had to be modified through the addition of phase plates in the long paths of both interferometer arms (just before the retroreflectors). One of these phase plates (200 μm thickness) was rotated with a rotation stage (OSMS-40YAW from OptoSigma), which allowed for time-domain resolution of approximately 0.2 femtoseconds.

While initially working well, late in the project, we had issues with the pump laser becoming unstable, as it had at that point reached the end of its stable lifetime. With instability we here refer both to beam drift and multimode emission. Beam drift is simply that the direction of pump laser emission changes randomly with time, causing alignment conditions in the BBO to change. This naturally interferes with any measurement being carried out. The most deleterious effect, however, was the breakdown of the single-mode emission into multi-mode emission. This meant that the laser no longer only emitted a single cavity mode, meaning that the SPDC conditions change drastically, so that the hierarchy of time-scales required for good Franson interference as discussed in Section 3 were no longer satisfied. In turn, this led to a great loss in Franson interference visibility which made the measurements largely useless.

We managed a temporary fix after consulting with a technician from the company which supplied the laser, Coherent, which simply involved lowering the current in the laser, which allowed it to operate stably for longer. This did allow us to make a few more measurements until ultimately laser power was too low to produce usable amounts of SPDC-pairs.

A.1 HOM measurements

In the early stages of the project, we carried out HOM interference measurements, one of these measurements can be observed in Figure 3.4. But a Franson

interferometer is rather more involved than what is required by a HOM measurement, so how does one carry out a HOM measurement with a Franson interferometer without taking it apart?

I will here be referring to names from Figure 3.5, for reference. In general the output ports at D_2 and D'_2 were not used for Franson measurements, so the fiber couplers at these outputs were instead put into different ends of a 50:50 fiber beamsplitter (FBS) and the short paths in each interferometer arm were blocked. By coupling the outputs of the FBS into the coincidence-counting circuit (Time Tagger Ultra, Swabian instruments) via the APD detectors (Excelitas Technologies, SPCM-NIR-12-FC) it was possible to adjust the delays T_A and T_B so that one could carry out a HOM measurement.

B Reverse Hong-Ou-Mandel and Missing Fluorescence

Among the ETPA measurements that have been carried out, there is an interesting result which, according to the authors, is missing a background in a delay-dependent ETPA signal^[97]. In this appendix, I attempt to explain a possible reason why this is, and how this could potentially be applied to a future narrow-band pump experimental design.

Introducing the problem of the missing background: The result reported in Figure 5 in ref.^[97] is missing a constant background fluorescence signal which should be independent of the delay used in their Michelson interferometer, which is illustrated in Figure B.1 a). The interferometer is fed with a stream of collinear SPDC-photon pairs through the port N_{out} , which is both an input and output port of the interferometer.

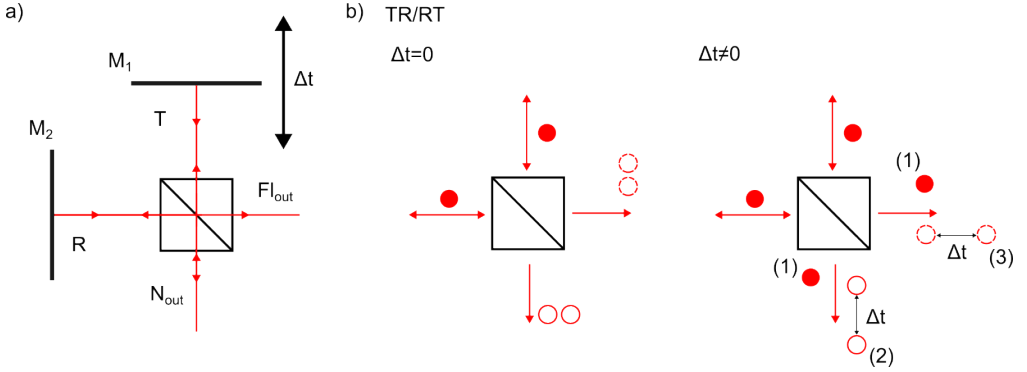


Figure B.1: The Michelson interferometer as set up in ref.^[97] with entangled photon pairs entering through N_{out} . a) shows the interferometer itself, with the different photon directions. R and T represents the photon directions of the photons reflected or transmitted when entering the interferometer, respectively. The 'T' arm has a delay which is achieved by moving mirror M_1 relative to the static position of mirror M_2 . Photons exit the interferometer either through output port F_{out} or N_{out} , where F_{out} leads to the TPA-absorbing sample. b) illustrates the directions photons can take for different delays in the case where photons are separated upon entering the interferometer, with TR for transmission-reflection and RT for reflection-transmission of the signal and idler, respectively (these cases are indistinguishable). When delay is zero, HOM interference occurs and the RT/TR cases always lead to a photon pair exiting the same port (here marked as empty circles for N_{out} and dashed empty circles for F_{out}). When the delay is nonzero, photons either exit through different ports at with a relative delay (case marked as 1, filled circle, notably case 1 has twice the probability of occurring relative to cases 2 or 3), or through the N_{out} , F_{out} , with the same delay, respectively (case 2, empty circle and case 3, dashed empty circle, respectively). In cases (2) and (3) the photons travel in the same direction, but if Δt is too large for photon overlap, no ETPA can occur.

To summarize, fluorescence from ETPA is expected whenever a pair of photons exit the port F_{out} simultaneously. One then expects to have a fluorescence signal peak when relative path delays in the interferometer are equal ($\Delta t = 0$), as HOM interference will then occur and photons which are initially separated will always exit the interferometer simultaneously and in the same direction,

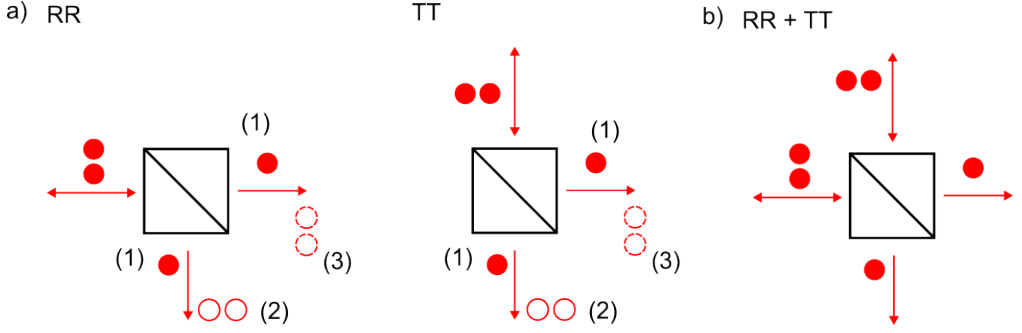


Figure B.2: Diagram of the cases where photons in the SPDC pairs are both reflected or transmitted upon entering the interferometer (RR and TT respectively), which means outcomes are completely delay-independent. a) displays the RR and TT separately, but both have the same possible outcomes: (1) photons exit separately (filled circle), (2) photons exit N_{out} together (empty circles) and (3) photons exit F_{out} together (dashed empty circles). One might expect case (3) to lead to a constant background in the fluorescence signal (which should be equal to half the maximal amplitude of the fluorescence peak from the zero-delay case), but in fact this background does not appear! This is because, as shown in b), the RR and TT paths create the perfect conditions for time-reversed HOM interference^[107]. Since RR and TT are equally probable to occur, the two are indistinguishable and this leads to pathway interference identical, though time-reversed, to that seen in HOM interference! Crucially, this occurs no matter what the delay Δt is, since it is not important when the photon pair arrives at the beamsplitter, only that both paths are equally probable and will lead to the photons returning to the beamsplitter together!

illustrated in Figure B.1 b). This also means that when the delay is nonzero ($\Delta t \neq 0$, or at least long enough away that photons cannot overlap at all), these pathways do not give rise to any fluorescence, as there is never more than one photon at the sample position at any given time. This also leads to one expecting background fluorescence, originating in the cases where signal and idler photons enter the Michelson interferometer and are both reflected or transmitted through the beamsplitter, meaning that regardless of the delay set in the experiment, they will arrive at the beamsplitter simultaneously when exiting as well, this case is illustrated in Figure B.2 a).

Looking at the probabilities of all the pathways involved, this seems like it should lead to a constant background fluorescence at half the rate of the peak delay-dependent fluorescence rate, independent of the delay set in the interferometer, but it does not. This seems to imply that there is something preventing the interferometer from outputting two photons from the same port, except in the equal-delay case.

I would posit that this occurs because this scenario represents a true ‘time-reversal’^[108;109] of the HOM interference case. To explain what we mean by this: the photon pair always arrives at the same input port of the beamsplitter at the same time, but it is always a priori impossible to determine which port the pair will exit, even though the path they take might cause the potential pairs to arrive at the beamsplitter at different times. This gives rise to a similar pathway

indistinguishability as that which is present in HOM interference, but in reverse. The same does not occur when the photon pair first enters the interferometer, as there is no input indistinguishability (the photons are always entering through N_{out}). The photon pairs always enter through the same input port and are split into four cases: TT, TR, RT and RR, where R and T represent reflection and transmission respectively, and in this case there is an indistinguishability between the TT and RR case which makes the ‘reverse HOM’ possible and results in these cases always outputting a single photon in each output port, making any two-photon fluorescence impossible from these cases, thus leading to the ‘missing’ background fluorescence which should by all other accounts be there.

This ‘reverse HOM’ effect is not completely unknown^[107], but is rather obscure and could serve as an explanation to the missing background here. The reverse HOM also potentially has applications which can allow one to separate a collinear Type-I or Type-0 SPDC-beam into signal and idler through use of a polarizing beamsplitter, though this is done much simpler with collinear Type-II SPDC instead. It could, however, prove advantageous if collinear Type-II SPDC has too narrow phase-matching conditions to generate strongly entangled broadband photons from a narrow pump laser.

In practice, this implementation would use a narrow-band CW pump laser with a vertical or horizontal polarization to pump collinear SPDC processes in two subsequent nonlinear crystals, such as BBO’s. Importantly, these nonlinear crystals must be oriented so that they each produce downconverted photons at diagonal polarizations relative to the pump, which are orthogonal to one another. After this, one must filter out the pump beam from the downconverted photons with either long-pass filters or dielectric mirrors, ideally in a way which disperses the downconverted photons minimally. The beam of superposed SPDC-pairs can then be incident on a single input port of a PBS. This superposition will ensure that each photon pair will be split at the PBS, causing a kind of ‘reverse HOM’ which allows a clean split of time-frequency entangled photons, a basic sketch of the proposed setup can be seen in Figure B.3. To show this, we introduce the diagonal and antidiagonal creation operators in the basis of their horizontal and vertical counterparts:

$$a_d^\dagger = (a_h^\dagger + a_v^\dagger)/\sqrt{2}, \quad a_a^\dagger = (a_h^\dagger - a_v^\dagger)/\sqrt{2}, \quad (\text{B.1})$$

where the subscripts h, v, d, a refer to horizontal, vertical, diagonal and antidiagonal polarization modes of their creation operators, respectively. For this split to be fully efficient, the diagonal and anti-diagonal pairs must have a phase

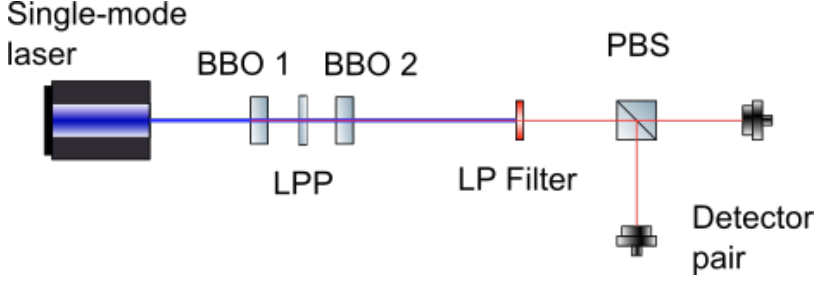


Figure B.3: A diagram of a proposed 'reverse HOM' setup which would allow for collinear generation of entangled photons through Type-0 or Type-I SPDC while still able to cleanly separate signal and idler with a PBS.

difference $\varphi = \pi$, so that the identity for the creation operators:

$$a_h^\dagger a_v^\dagger = \frac{(a_d^\dagger)^2 - (a_a^\dagger)^2}{2}, \quad (\text{B.2})$$

can be assumed to hold^[107;110;111]. Practically, this can be ensured by optimizing coincidence counts through use of a phase plate between the two crystals or mounting one of the crystals in a sub-wavelength sensitive piezo delay stage, which would introduce less dispersion. The collinear geometry of the setup also allows for a much higher collection efficiency than a non-collinear SPDC process, as these rely on collecting a small portion of downconverted photons but have an assured separation of signal- and idler streams.

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¹²I managed to squeeze another Sting quote in just before the end, haha! Quote from: 'If I Ever Lose My Faith in You', unsurprisingly

Publications

