LIGHT SCATTERING ON SUPERRADIANT ENSEMBLES OF MULTILEVEL QUANTUM EMITTERS

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ABSTRACT

This thesis presents a theoretical investigation of the optical properties of ensembles of ultracold multilevel quantum emitters. The theoretical model is based on the coarse-grained master equation which includes the interatomic dipole-dipole interference. We consider here complicated internal atomic structure, including several energy levels. The presence of additional energy levels leads to vacuum-induced interference between the non-degenerate dipole transitions. These processes lead to the formation of the cross-interference terms, which are usually neglected. In this work we investigate the impact of the cross-interference terms on the interatomic dipole-dipole interaction, their effect on the shapes of spectral lines, cooperative Lamb shift and cooperative decay rate.

ZUSAMMENFASSUNG

Diese Arbeit befasst sich mit der theoretischen Erforschung der optischen Eigenschaften von Ensembles ultrakalter Quantenemitter mit mehreren Energieniveaus. Das theoretische Modell basiert auf grobgranularen Mastergleichungen unter Berücksichtigung interatomarer Dipol-Dipol-Wechselwirkungen. Die Arbeit berücksichtigt komplexe atomare Strukturen einschließlich verschiedener Energieniveaus. Das Vorhandensein der zusätzlichen Energieniveaus führt zu vakuuminduzierten Interferenzphänomenen zwischen nicht-entarteten Dipolübergängen. Diese Prozesse haben die Bildung von sogenannten Cross-Interferenztermen zur Folge, welche normalerweise vernachlässigt werden. Diese Arbeit untersucht den Einfluss dieser Cross-Interferenzterme auf die interatomare Dipol-Dipol-Wechselwirkung, ihren Effekt auf die Form von Spektrallinien, kooperative Lambverschiebung und kooperative Zerfallsrate.

INTRODUCTION

One of the most remarkable phenomena in quantum optics is superradiance [1]. It originates from interatomic dipole-dipole interference, when dipolar transitions of individual atoms are coupled via modes of electromagnetic field, forming collective states. Optical properties of these states can significantly deviate from the ones of individual atoms, leading for example to the enhancement of radiation emission [1, 2] and broadening of spectral lines and their frequency shifts. Thus, superradiant light scattering plays the key role for spectroscopy of dense cold atomic gases.

The phenomenon of superradiance can be consequently described via the Born-Markov master equation. First theoretical works on superradiance, based on the master equation formalism [2–4], considered atomic media as ensembles of simple 2-level atoms, where each atom has unique ground and excited states. Later theoretical work [5] demonstrated the importance of Zeeman degeneracy of atomic levels. Master equations also have been developed for quantum emitters with several energy gaps [6, 7]. The presence of various energy levels leads to several types of dipolar transitions, which in principle can interfere, leading to so-called cross-interference terms [7–12]. These terms have been discussed in [12–15] in terms of their relevance for high-precision spectroscopy of single atoms. The cross-interference terms, formed by non-degenerate dipolar transitions, are the in the focus of the presented work. We investigate their impact on the dipole-dipole interaction in a superradiant medium and their effect on the spectral lines of cold atomic ensembles.

The master equation preserves all necessary properties of the density matrix, such as trace preservation, hermiticity and positivity, if it has the so-called *Lindblad* form [16]. Consequent incorporation of the cross-interference terms between non-degenerate dipoles is a theoretical issue, their presence in the master equation might violate the Lindblad form. In the presented thesis we use the coarse-graining formalism [17, 18] to derive the coarse-grained master equation for an ensemble of multilevel atoms [19], the resulting master equation preserves the Lindblad form without any phenomenological assumptions.

This thesis consists of two chapters. In the first chapter we present a derivation of master equation for ensembles of multilevel atoms, using the Born-Markov approximation in its traditional form [2, 20–22]. We discuss the physical meaning of all the components of the equation and the problem of the Lindblad form preservation, related to cross-interference terms and the Born-Markov approximation.

The second chapter is based on Ref. [19], we present a derivation of the coarse-grained master equation, which involves the cross-interference terms resulting from non-degenerate dipole, while preserving the Lindblad form. We apply the derived coarse-grained master equation to simulate the optical properties of a simple superradiant system, consisting of two 3-level atoms. We investigate how the cross-interference terms affect the superradiant line broadening, the dipole-dipole induced line shift and the robustness of the solution to fluctuations of the coarse-graining time, which is a free parameter in the developed theory.

CONTENTS

1

MASTER EQUATION FOR AN ENSEMBLE OF MULTI-LEVEL QUANTUM EMITTERS

In this chapter we present a derivation of a Born-Markov master equation for an ensemble of multi-level quantum emitters. The equation describes dissipative dynamics of an atomic ensemble, coupled with the electromagnetic field (EMF) via electric-dipole coupling. The coupling of the individual atomic transitions with the modes of the EMF mediates effective interactions that give rise to collective dynamics. As a consequence, the optical properties might significantly differ from an ensemble of independent atoms.

Most of the theoretical approaches of these dynamics are based on a simplified model of two-level atoms [1–4, 23], some of them include Zeeman degeneracy of the relevant energy levels [5, 24–26]. The multi-level internal atomic structure considers multiple excitations, which may interfere and increase the complexity of interatomic dipole–dipole interference. One aspect, the center of this investigation, is the phenomenon of interchannel vacuum-induced interference. The master equation derived below systematically includes all this variety of interference processes.

1.1 SYSTEM MODELING

We consider an ensemble of N atoms, coupled with the quantized electromagnetic field. The center of mass of each atom is pinned at point $\vec{R}_\alpha$ ($\alpha = 1, 2, .., N$), excitations of electron are described by a discrete spectrum, we discard the ionization spectrum. We also discard any interaction between the atoms, and solely consider the interaction of the atomic dipolar transitions with the electromagnetic field. Here we specifically talk about atoms, but one should keep in mind that it might be any kind of quantum emitters: molecules, atomic clusters [27] or nanostructures in a crystal [28–33], as long as their spectra fulfill the general properties considered here.

The entire system's state is characterised by the density matrix $\hat{\chi}(t)$. It is a Hermitian operator and acts on a Hilbert space $\mathcal{H} = \mathcal{H}_\mathrm{A} \otimes \mathcal{H}_\mathrm{R}$. Here $\mathcal{H}_\mathrm{R}$ is the subspace of the EMF reservoir and $\mathcal{H}_\mathrm{A}$ is the N-atom

system subspace: $\mathcal{H}_A = \bigotimes_{\alpha=1}^{N} \mathcal{H}_\alpha^A$. The density matrix is further a semi-positive Hermitian operator with a trace equal to one:

$$\hat{\chi} \geq 0; \qquad \hat{\chi}^\dagger = \hat{\chi}; \qquad \mathrm{Tr}(\hat{\chi}) = 1. \tag{1.1}$$

The dynamics of the density matrix is governed by the von Neumann equation:

$$\frac{\partial \hat{\chi}}{\partial t} = \frac{1}{i\hbar}\left[\hat{H}, \hat{\chi}\right], \tag{1.2}$$

where the Hamiltonian reads:

$$\hat{H} = \hat{H}_A + \hat{H}_R + \hat{V}. \tag{1.3}$$

The first term $\hat{H}_A = \sum_{\alpha=1}^{N} \hat{H}_\alpha^A$ includes the spectral information of each atom: $\hat{H}_\alpha^A = \sum_n E_\alpha^n |n\rangle_\alpha \langle n|$, where $|n\rangle_\alpha$ and E_α^n are the eigenstates and eigenvalues of the atom α, they fulfill the eigenvalue equation: $\hat{H}_\alpha^A |n\rangle_\alpha = E_\alpha^n |n\rangle_\alpha$. Here n indicates a set of quantum numbers, which characterise the electronic bound state. The second term on the right-hand side of equation (1.3) is the reservoir Hamiltonian, which in our case is the quantized electromagnetic field

$$\hat{H}_R = \sum_\lambda \hbar\omega_\lambda \left(\hat{a}_\lambda^\dagger \hat{a}_\lambda + \frac{1}{2}\right). \tag{1.4}$$

Here λ labels the mode of the EMF, $\hat{a}_\lambda$ and $\hat{a}_\lambda^\dagger$ are the annihilation and creation operators of photons in mode λ, fulfilling the commutation relations [34]:

$$[\hat{a}_\lambda, \hat{a}_{\lambda'}^\dagger] = \delta_{\lambda\lambda'}, \qquad [\hat{a}_\lambda^\dagger, \hat{a}_{\lambda'}^\dagger] = [\hat{a}_\lambda, \hat{a}_{\lambda'}] = 0. \tag{1.5}$$

For simplicity, we have restricted the electromagnetic field to a box with the quantization volume V, imposing periodic boundary conditions [35]. The mode λ of the EMF is characterised by its wave vector $\vec{k}_\lambda$ and transverse polarization $\vec{e}_\mu$ with $\mu = \pm 1$, so $\vec{e}_\mu(\vec{k}) \perp \vec{k}_\lambda$ and $\vec{e}_\mu \cdot \vec{e}_{\mu'} = \delta_{\mu\mu'}$. The wave vector and the frequency are related by the dispersion relation $|\vec{k}_\lambda| c = \omega_k$ with the speed of light c. The third term of Hamiltonian (1.3) is the interaction operator $\hat{V}$, it is given in the long wavelength electric dipole approximation[1] [36]

$$\hat{V} = \sum_{\alpha=1}^{N} \hat{V}_\alpha = -\sum_{\alpha=1}^{N} \hat{\vec{d}}_\alpha \cdot \hat{\vec{E}}(\vec{R}_\alpha). \tag{1.6}$$

It contains the operator of the quantized electric field, which reads (in Gaussian units)

$$\hat{\vec{E}}(\vec{R}_\alpha) = i \sum_{\vec{k},\mu} \sqrt{\frac{2\pi\hbar\omega_k}{V}} \left(\hat{a}_\lambda \vec{e}_{\vec{k},\mu} e^{i\vec{k}\vec{R}_\alpha} + \hat{a}_\lambda^\dagger \vec{e}_{\vec{k},\mu}^{\,*} e^{-i\vec{k}\vec{R}_\alpha}\right), \tag{1.7}$$

1 The form of the interaction operator (1.6) in the long wavelength dipole approximation is justified by the fact that the linear size of low excited atomic orbitals ($\sim 10^{-10}$m) is much smaller than the optical wavelengths $\sim 10^{-7}$m.

where V is the quantization volume. The dipole operator reads

$$\hat{\vec{d}}_\alpha = \sum_{m,n} \vec{d}_{mn} \hat{\sigma}_\alpha^{mn} = \sum_{m<n} \vec{d}_{mn} \hat{\sigma}_\alpha^{mn} + \text{H.c.}, \tag{1.8}$$

where $\hat{\sigma}_\alpha^{mn} = |m\rangle_\alpha \langle n|$, $\hat{\sigma}_\alpha^{mn} = \hat{\sigma}_\alpha^{nm\,\dagger}$ and $\vec{d}_{mn}$ is the matrix element of the atomic dipole moment [37]. Hereafter, for shortness, we label the transition between a pair of coupled states (m, n) with a single index i. In the following we insert (1.8) and (1.7) in (1.6) and get an expression for the interaction operator

$$\hat{V} = \hbar \sum_{\alpha,i} \hat{\Gamma}_{i\alpha}^\dagger \hat{\sigma}_\alpha^i + \hat{\Gamma}_{i\alpha} \hat{\sigma}_\alpha^{i\,\dagger}. \tag{1.9}$$

Here we have introduced the coupling operators [20]

$$\hat{\Gamma}_{i\alpha} = \sum_\lambda g_{i\alpha}^\lambda \hat{a}_\lambda + (\bar{g}_{i\alpha}^\lambda)^* \hat{a}_\lambda^\dagger, \tag{1.10}$$

written via the coupling constants

$$g_{i\alpha}^\lambda = -\mathrm{i}\sqrt{\frac{2\pi\omega_\lambda}{\hbar V}} (\vec{d}_\alpha^{\,i\,*} \cdot \vec{e}_\lambda) e^{\mathrm{i}\vec{k}\vec{R}_\alpha}, \tag{1.11a}$$

$$\bar{g}_{i\alpha}^\lambda = -\mathrm{i}\sqrt{\frac{2\pi\omega_\lambda}{\hbar V}} (\vec{d}_\alpha^{\,i} \cdot \vec{e}_\lambda) e^{\mathrm{i}\vec{k}\vec{R}_\alpha}. \tag{1.11b}$$

We want to derive an effective equation for the atomic variables by appropriately eliminating the EMF degrees of freedom in equation (1.2). For this purpose we consider the von Neumann equation in the interaction picture

$$\frac{\partial \tilde{\chi}}{\partial t} = \frac{1}{\mathrm{i}\hbar} \left[\tilde{V}, \tilde{\chi}\right], \tag{1.12}$$

where

$$\tilde{\chi}(t) = \hat{U}_I(t) \hat{\chi}(t) \hat{U}_I^\dagger(t), \tag{1.13}$$
$$\tilde{V}(t) = \hat{U}_I(t) \hat{V} \hat{U}_I^\dagger(t), \tag{1.14}$$

and $\hat{U}_I(t) = e^{\frac{\mathrm{i}}{\hbar}(\hat{H}_\mathrm{A} + \hat{H}_\mathrm{R})t}$.

The atomic operators transform as $\tilde{\sigma}_\alpha^i = \hat{\sigma}_\alpha^i e^{-\mathrm{i}\omega^i t}$, with ω^i being the frequency of i^{th} transition $\omega^i = \omega^{mn} = (E_m - E_n)/\hbar$, and the photon field operators as $\tilde{a}_\lambda = \hat{a}_\lambda e^{-\mathrm{i}\omega_\lambda t}$. Now we formally integrate the von Neumann equation (1.12) and get the integral equation for the density matrix:

$$\tilde{\chi}(t) = \tilde{\chi}(0) - \frac{\mathrm{i}}{\hbar} \int_0^t dt_1 \left[\tilde{V}(t_1), \tilde{\chi}(t_1)\right], \tag{1.15}$$

and by inserting it in the right-hand side of 1.12 we obtain

$$\frac{\partial \tilde{\chi}(t)}{\partial t} = \frac{1}{\mathrm{i}\hbar} \left[\tilde{V}(t), \tilde{\chi}(0)\right] - \frac{1}{\hbar^2} \int_0^t dt_1 \left[\tilde{V}(t), \left[\tilde{V}(t_1), \tilde{\chi}(t_1)\right]\right]. \tag{1.16}$$

The atomic density matrix $\hat{\rho}(t)$ can be obtained from the one of the composite system $\hat{\chi}(t)$ by tracing out the EMF's degrees of freedom

$$\begin{aligned}\hat{\rho} &= \mathrm{Tr}_{\mathrm{R}}(\hat{\chi}) \\ &= \sum_{r,m,n} |m\rangle\langle n|\langle r \otimes m|\hat{\chi}|r \otimes n\rangle,\end{aligned} \tag{1.17}$$

where $\{|r\rangle\}$ is an orthonormal basis of $\mathcal{H}_{\mathrm{R}}$, $\{|n\rangle\}$ is an orthonormal basis of $\mathcal{H}_{\mathrm{A}}$ and $\{|r \otimes n\rangle\}$ is an orthonormal basis of the complete Hilbert space $\mathcal{H}$. We implement the partial trace over the reservoir degrees of freedom to equation (1.16), yielding

$$\frac{\partial\tilde{\rho}(t)}{\partial t} = \frac{1}{\mathrm{i}\hbar}\mathrm{Tr}_{\mathrm{R}}\left(\left[\tilde{V}(t), \tilde{\chi}(0)\right]\right) - \frac{1}{\hbar^2}\int_0^t dt_1 \mathrm{Tr}_{\mathrm{R}}\left(\left[\tilde{V}(t), \left[\tilde{V}(t_1), \tilde{\chi}(t_1)\right]\right]\right). \tag{1.18}$$

1.2 BORN-MARKOV MASTER EQUATION

The integro-differential equation (1.18) is so far exact. We now make the so-called Born approximation. For this purpose we assume that initially the EMF and the atoms are uncorrelated, such that the total density matrix $\hat{\chi}(0) = \tilde{\chi}(0)$ can be factorized

$$\hat{\chi}(0) = \hat{\rho}(0) \otimes \hat{R}, \tag{1.19}$$

where $\hat{R}$ describes the state of the EMF. Correlations between the atoms and the EMF will be created by the interactions as time progresses. Assuming weak coupling between atoms and field, the density matrix $\tilde{\chi}(t)$ will keep a separable form up to the zeroth order in the interaction. We further assume that the EMF state is stationary. As a result, the density matrix $\tilde{\chi}(t)$ takes the form

$$\tilde{\chi}(t) = \tilde{\rho}(t) \otimes \hat{R} + \mathcal{O}(\tilde{V}), \tag{1.20}$$

where the last term is non-separable. We now choose a specific form of the photon reservoir - a thermal reservoir

$$\hat{R} = \frac{1}{Z} e^{-\frac{\hat{H}_{\mathrm{R}}}{k_B T}}. \tag{1.21}$$

Here $\hat{H}_{\mathrm{R}}$ is the reservoir Hamiltonian (1.4), T is the reservoir temperature, k_B is the Boltzmann constant and Z is the partition function: $Z = \mathrm{Tr}\left(e^{-\frac{\hat{H}_{\mathrm{R}}}{k_B T}}\right)$. We now use (1.19) and (1.21) in equation (1.18). The first term of the right-hand side (1.18) vanishes as

$$\mathrm{Tr}_{\mathrm{R}}\left(\tilde{V}(t)\hat{R}\right) = \langle\tilde{V}(t)\rangle_{\mathrm{R}} = 0, \tag{1.22}$$

because $\langle\tilde{V}(t)\rangle_{\mathrm{R}} = -\tilde{d}(t) \cdot \langle\tilde{E}(t)\rangle_{\mathrm{R}}$ and for the thermal reservoir $\langle\tilde{E}(t)\rangle_{\mathrm{R}} = 0$ [35]. Now we plug (1.20) into the second term of the

right-hand side of (1.18) and keep only the terms up to the second order over the interaction $\sim (\tilde{V})^2$, the equation reads

$$\frac{\partial\tilde{\rho}(t)}{\partial t} = -\frac{1}{\hbar^2}\int_0^t dt_1 \mathrm{Tr}_\mathrm{R}\left(\left[\tilde{V}(t),\left[\tilde{V}(t_1),(\tilde{\rho}(t_1)\otimes\hat{R})\right]\right]\right). \tag{1.23}$$

After inserting the explicit form of the interaction operator (1.9) into (1.23) and tracing out the EMF degrees of freedom (see Appendix 1.4.1 for details) we obtain

$$\begin{aligned}\frac{\partial\tilde{\rho}(t)}{\partial t} = \sum_{\alpha,\beta}\sum_{i,j}\int_0^t dt_1 d_\alpha^i d_\beta^j C_{\alpha\beta}^{ij}(t-t_1)\left[\tilde{\sigma}_\beta^j(t_1)\tilde{\rho}(t_1),\tilde{\sigma}_\alpha^i(t)\right]\\ +d_\alpha^i d_\beta^{j*} C_{\alpha\beta}^{ij}(t-t_1)\left[\tilde{\sigma}_\beta^{j\dagger}(t_1)\tilde{\rho}(t_1),\tilde{\sigma}_\alpha^i(t)\right]\\ +d_\alpha^{i*} d_\beta^j C_{\alpha\beta}^{ij}(t-t_1)\left[\tilde{\sigma}_\beta^j(t_1)\tilde{\rho}(t_1)\tilde{\sigma}_\alpha^{i\dagger}(t)\right]\\ +d_\alpha^{i*} d_\beta^{j*} C_{\alpha\beta}^{ij}(t-t_1)\left[\tilde{\sigma}_\beta^{j\dagger}(t_1)\tilde{\rho}(t_1),\tilde{\sigma}_\alpha^{i\dagger}(t)\right]+\mathrm{H.c.},\end{aligned} \tag{1.24}$$

where $C_{\alpha\beta}^{ij}(t-t_1)$ is a correlation function. With $t-t_1=\tau$ it reads

$$\begin{aligned}C_{\alpha\beta}^{ij}(\tau) = \frac{1}{(2\pi)^2\hbar c^3}\int_0^{\omega_\mathrm{cut}} d\omega\,\omega^3 F_{\alpha\beta}^{ij}(kR_{\alpha\beta})(1+n(\omega,T))e^{-\mathrm{i}\omega\tau}\\ +\omega^3 F_{\alpha\beta}^{ij}(kR_{\alpha\beta})n(\omega,T)e^{\mathrm{i}\omega\tau},\end{aligned} \tag{1.25}$$

where

$$n(\omega,T) = \frac{1}{\exp(\tau_R\omega)-1}, \tag{1.26}$$

is the mean number of photons of one of the mode at frequency ω at the photon reservoir temperature T and $\tau_R = \frac{\hbar}{k_B T}$. The quantity $F_{\alpha\beta}^{ij}(kR_{\alpha\beta})$ is a so-called diffraction type function [2], which describes the dipole–dipole coupling between a pair of atoms α and β, separated by a distance $R_{\alpha\beta} = |\vec{R}_\alpha - \vec{R}_\beta|$:

$$\begin{aligned}F_{\alpha\beta}^{ij}(kR_{\alpha\beta}) = 4\pi\left\{\frac{\sin(kR_{\alpha\beta})}{kR_{\alpha\beta}}\left((\vec{e}_\alpha^{\,i*}\cdot\vec{e}_\beta^{\,j})-\hat{\varepsilon}_{\alpha\beta}^{i*}\hat{\varepsilon}_{\alpha\beta}^{j}\right)\right.\\ \left.+\left(\frac{\cos(kR_{\alpha\beta})}{(kR_{\alpha\beta})^2}-\frac{\sin(kR_{\alpha\beta})}{(kR_{\alpha\beta})^3}\right)\left((\vec{e}_\alpha^{\,i*}\cdot\vec{e}_\beta^{\,j})-3\hat{\varepsilon}_{\alpha\beta}^{i*}\hat{\varepsilon}_{\alpha\beta}^{j}\right)\right\},\end{aligned} \tag{1.27}$$

here $\vec{e}_\alpha^{\,i} = \frac{\vec{d}_\alpha^{\,i}}{d_\alpha^i}$ is a unit vector of a corresponding dipole moment and the quantity $\hat{\varepsilon}_{\alpha\beta}^i = \frac{\vec{d}_\alpha^{\,i}\cdot\vec{R}_{\alpha\beta}}{d_\alpha^i R_{\alpha\beta}}$ is the dipole's projection on the interatomic axis. The single-atom case $\alpha=\beta$ corresponds to the limit $kR_{\alpha\beta}\to 0$ and (1.27) reads

$$\begin{aligned}F_{\alpha\alpha}^{ij} &= \lim_{kR_{\alpha\beta}\to 0} F_{\alpha\beta}^{ij}(kR_{\alpha\beta})\\ &= \frac{8\pi}{3}(\vec{e}_\alpha^{\,i*}\cdot\vec{e}_\alpha^{\,j}).\end{aligned} \tag{1.28}$$

The integral over frequencies (1.25) is truncated at $\omega_{\text{cut}} < \infty$ for certain reasons. The cut-off frequency is estimated as [37] $\omega_{\text{cut}} \sim \frac{mc^2}{\hbar} \sim 10^{21}$ Hz, m here is the electron's mass.

Further actions on equation (1.24) depend on the properties of the correlation function (1.25). Particularly, one needs to quantify τ_{corr}, the reservoir correlation time. It is a parameter, which determines the time-scale of decay of the atom-reservoir correlation function (1.25). We can estimate the width of the correlation function as [20]

$$\tau_{\text{corr}} = \max\left\{\omega_{\text{cut}}^{-1}, \tau_R\right\}. \tag{1.29}$$

In this thesis we always assume that the photon reservoir is at room temperature $T = 300$ K, so $\tau_R \approx 10^{-13}$ sec, while $\omega_{\text{cut}}^{-1} \sim 10^{-21}$ sec, so the reservoir correlation time is implicitly assumed always to be $\tau_{\text{corr}} = \tau_R$.

The typical time scale for the time-evolution of the atomic variables is $\tau_A \sim 10^{-8}$ sec (for optical transitions), such that $\tau_R \ll \tau_A$ holds. The variable change $t - t_1 = \tau$ in the time integral (1.24) also enters in the density matrix $\rho(t_1) \to \rho(t - \tau)$, thus we can consider the atomic density matrix in the integrand as a function of events in the past. The whole considered period of time evolution of the system can be analysed in the coarse-grained grid with step Δt, fulfilling the inequality: $\tau_R \ll \Delta t \ll \tau_A$. The width of the correlation function defines a characteristic time, over which the reservoir memory is relevant and might impact the atomic variables. Since the atomic variables evolve very slowly over Δt we approximate $\rho(t - \tau) \approx \rho(t)$. This is equivalent to an assumption that the reservoir is memoryless for $\tau_R \to 0$, which is known as the Markov approximation, widely used in quantum optics [2, 20, 21]. A case of a finite-time light propagation $\tau_L = \frac{|\vec{R}_1 - \vec{R}_2|}{c} > 0$ is investigated in [38] for a pair of two-level atoms.

After we make the variable change $\tau = t - t_1$ in equation (1.24) the integration limits remain the same, $\int_0^t dt_1 \to \int_0^t d\tau$. Given $\tau_R \ll \tau_A$ we can extend the integration limit to infinity in the spirit of the Markov approximation. The equation becomes:

$$\begin{aligned}
\frac{\partial \tilde{\rho}}{\partial t} = \sum_{\alpha,\beta}\sum_{i,j}\Bigg(&\int_0^\infty d\tau C_{\alpha\beta}^{ij}(\tau)e^{i\omega_j\tau}\Bigg) \\
&\times \left(d_\alpha^i d_\beta^j[\tilde{\sigma}_\beta^j(t)\tilde{\rho}(t), \tilde{\sigma}_\alpha^i(t)] + d_\alpha^{i*} d_\beta^j[\tilde{\sigma}_\beta^j(t)\tilde{\rho}(t), \tilde{\sigma}_\alpha^{i\,\dagger}(t)]\right) \\
&+ \left(\int_0^\infty d\tau C_{\alpha\beta}^{ij}(\tau)e^{-i\omega_j\tau}\right) \\
&\times \left(d_\alpha^i d_\beta^{j*}[\tilde{\sigma}_\beta^{j\,\dagger}(t)\tilde{\rho}(t), \tilde{\sigma}_\alpha^i(t)] + d_\alpha^{i*} d_\beta^{j*}[\tilde{\sigma}_\beta^{j\,\dagger}(t)\tilde{\rho}(t), \tilde{\sigma}_\alpha^{i\,\dagger}(t)]\right) \\
&+ \text{H.c.}
\end{aligned} \tag{1.30}$$

The correlation function $C^{ij}_{\alpha\beta}(\tau)$ still contains the integration over the photon frequencies. We now use the following relation:

$$\int_0^\infty d\tau e^{-\mathrm{i}(\omega-\omega_j)\tau} = \pi\delta(\omega-\omega_j) - \mathrm{i}\mathcal{P}\left(\frac{1}{\omega-\omega_j}\right), \tag{1.31}$$

for the time integral. The first term on the right-hand side of (1.31) contains the so-called Dirac delta-function[2] and the second term is the Cauchy principal value[3].

Using the expression (1.31) we can easily get the final form of the master equation (see more details in 1.4.1.1)

$$\frac{\partial\tilde{\rho}}{\partial t} = \frac{1}{\mathrm{i}\hbar}\sum_\alpha^N\left[\tilde{H}^{\mathrm{LS}}_\alpha,\tilde{\rho}\right] + \mathcal{L}^{\mathrm{D}}\tilde{\rho} + \frac{1}{\mathrm{i}\hbar}\sum_{\alpha,\beta(\neq\alpha)}^N\left[\tilde{H}^{\mathrm{CLS}}_{\alpha\beta},\tilde{\rho}\right] + \\ + \overline{\mathcal{L}}^{\mathrm{D}}\tilde{\rho} + \overline{\mathcal{L}}^{\mathrm{S}}\tilde{\rho}. \tag{1.34}$$

The quantity $\mathcal{L}^{\mathrm{D}}\tilde{\rho} + \overline{\mathcal{L}}^{\mathrm{D}}\tilde{\rho}$ is the so-called *dissipator*, which describes dissipative dynamics. One can distinguish the secular part

$$\mathcal{L}^{\mathrm{D}}\tilde{\rho} = \sum_{\alpha,\beta}\sum_{i,j}(1+n(\omega_j,T))\left(\frac{\Gamma^{ij}_{\alpha\beta}}{2}[\tilde{\sigma}^j_\beta\tilde{\rho},\tilde{\sigma}^{i\dagger}_\alpha] + \frac{\Gamma^{ij*}_{\alpha\beta}}{2}[\tilde{\sigma}^i_\alpha,\tilde{\rho}\,\tilde{\sigma}^{j\dagger}_\beta]\right) \\ + n(\omega_j,T)\left(\frac{\Gamma^{ij*}_{\alpha\beta}}{2}[\tilde{\sigma}^{j\dagger}_\beta\tilde{\rho},\tilde{\sigma}^i_\alpha] + \frac{\Gamma^{ij}_{\alpha\beta}}{2}[\tilde{\sigma}^{i\dagger}_\alpha,\tilde{\rho}\,\tilde{\sigma}^j_\beta]\right), \tag{1.35}$$

and the non-secular one

$$\overline{\mathcal{L}}^{\mathrm{D}}\tilde{\rho} = \sum_{\alpha,\beta}\sum_{i,j}(1+n(\omega_j,T))\left(\frac{\overline{\Gamma}^{ij}_{\alpha\beta}}{2}[\tilde{\sigma}^j_\beta\tilde{\rho},\tilde{\sigma}^i_\alpha] + \frac{\overline{\Gamma}^{ij*}_{\alpha\beta}}{2}[\tilde{\sigma}^{i\dagger}_\alpha,\tilde{\rho}\,\tilde{\sigma}^{j\dagger}_\beta]\right) \\ + n(\omega_j,T)\left(\frac{\overline{\Gamma}^{ij*}_{\alpha\beta}}{2}[\tilde{\sigma}^{j\dagger}_\beta\tilde{\rho},\tilde{\sigma}^{i\dagger}_\alpha] + \frac{\overline{\Gamma}^{ij}_{\alpha\beta}}{2}[\tilde{\sigma}^i_\alpha,\tilde{\rho}\tilde{\sigma}^j_\beta]\right), \tag{1.36}$$

2 For $a,b,c\in\mathbb{R}$:

$$\int_a^b dx\,\delta(x-c) = \begin{cases}1, & \text{if } c\in[a,b];\\ 0, & \text{otherwise.}\end{cases} \tag{1.32}$$

3 Let an integrand of $\int_a^b f(x)/(x-c)dx$ have a singularity point $c\in[a,b]$ ($f(x)$ is a smooth function on the considered interval), then we write the integral as follows:

$$\int_a^b\frac{f(x)}{x-c}dx \to \int_a^{c-\delta_1}\frac{f(x)}{x-c}dx + \int_{c+\delta_2}^b\frac{f(x)}{x-c}dx \quad (\delta_1,\delta_2>0),$$

and take a limit for both δ_1 and δ_2 to zero:

$$\int_a^b f(x)dx = \lim_{\delta_1,\delta_2\to0}\left(\int_a^{c-\delta_1}\frac{f(x)}{x-c}dx + \int_{c+\delta_2}^b\frac{f(x)}{x-c}dx\right). \tag{1.33}$$

If the limit (1.33) exists, then it is called the Cauchy principle value of integral:

$$\lim_{\delta_1,\delta_2\to0}\left(\int_a^{c-\delta_1}\frac{f(x)}{x-c}dx + \int_{c+\delta_2}^b\frac{f(x)}{x-c}dx\right) = \mathcal{P}\int_a^b\frac{f(x)}{x-c}dx.$$

where the coefficients read

$$\Gamma^{ij}_{\alpha\beta} = \frac{d^{i*}_{\alpha} d^{j}_{\beta} F^{ij}_{\alpha\beta}(k_j R_{\alpha\beta})}{4\pi\hbar c^3}\omega_j^3, \tag{1.37a}$$

$$\overline{\Gamma}^{ij}_{\alpha\beta} = \frac{d^{i}_{\alpha} d^{j}_{\beta} F^{ij}_{\alpha\beta}(k_j R_{\alpha\beta})}{4\pi\hbar c^3}\omega_j^3. \tag{1.37b}$$

The coefficients (1.37) contain the diffraction type function (1.27). The single-atom case ($\alpha = \beta$) corresponds to the limit of vanishing interatomic distance $k_j R_{\alpha\beta} \to 0$ (1.28) and these coefficients read

$$\Gamma^{ij}_{\alpha\alpha} = \frac{4}{3}\frac{\vec{d}^{\,i*}_{\alpha} \cdot \vec{d}^{\,j}_{\alpha}}{\hbar c^3}\omega_j^3, \tag{1.38a}$$

$$\overline{\Gamma}^{ij}_{\alpha\alpha} = \frac{4}{3}\frac{\vec{d}^{\,i}_{\alpha} \cdot \vec{d}^{\,j}_{\alpha}}{\hbar c^3}\omega_j^3. \tag{1.38b}$$

In the case $i \neq j$ the coefficients do not vanish when the dipoles of the corresponding transitions are parallel, so that their scalar product does not vanish.

The operator $\tilde{H}^{\mathrm{LS}}(t)$ takes the form

$$\tilde{H}^{\mathrm{LS}}_{\alpha}(t) = -\hbar \sum_{i,j} \tilde{\sigma}^{i\dagger}_{\alpha}\tilde{\sigma}^{j}_{\alpha}(\Delta^{-}_{ij} + \Delta^{T}_{ij}) + \tilde{\sigma}^{j}_{\alpha}\tilde{\sigma}^{i\dagger}_{\alpha}(\Delta^{+}_{ij} - \Delta^{T}_{ij}), \tag{1.39}$$

with coefficients

$$\Delta^{\pm}_{ij} = \frac{2\vec{d}^{\,i*}_{\alpha}\vec{d}^{\,j}_{\alpha}}{3\pi\hbar c^3}\mathcal{P}\int_0^{\omega_{\mathrm{cut}}} d\omega\, \frac{\omega^3}{\omega \pm \omega_j}, \tag{1.40a}$$

$$\Delta^{T}_{ij} = \frac{2\vec{d}^{\,i*}_{\alpha}\vec{d}^{\,j}_{\alpha}}{3\pi\hbar c^3}\mathcal{P}\int_0^{\omega_{\mathrm{cut}}} d\omega\, n(\omega, T)\left(\frac{\omega^3}{\omega - \omega_j} - \frac{\omega^3}{\omega + \omega_j}\right). \tag{1.40b}$$

The diagonal elements of (1.40a) ($i = j$) correspond to a shift of an atomic state energy due to the electron's interaction with the virtual photons of the vacuum. The integral over the photon's frequencies diverges, but it can be treated using the procedure of renormalization, described for example in [39]. For the Hydrogen atom, this contribution is different from zero for S states and is known as the Lamb-shift [37].

The off-diagonal elements (1.40a) ($i \neq j$) are the $cross - shift$ terms [21], [7], result from the interference between parallel dipoles of different transitions of an individual atom. We can estimate them using corresponding diagonal terms [15]:

$$\Delta^{\pm}_{ij} \approx \frac{1}{2}\vec{d}^{\,i*}_{\alpha}\vec{d}^{\,j}_{\alpha}\left(\frac{\Delta^{\pm}_{ii}}{|\vec{d}^{\,i}_{\alpha}|^2} + \frac{\Delta^{\pm}_{jj}}{|\vec{d}^{\,j}_{\alpha}|^2}\right). \tag{1.41}$$

The coefficients (1.40b) are contributions due to thermal fluctuations. Their impact on high-precision atomic measurements is investigated,

for example, in [40]. The Hamiltonian $\tilde{H}^{\mathrm{CLS}}_{\alpha\beta}$ describes an effective interaction between dipolar transitions of different atoms:

$$\tilde{H}^{\mathrm{CLS}}_{\alpha\beta} = \sum_{i,j} \hbar \Lambda^{ij}_{\alpha\beta} \tilde{\sigma}^{i\,\dagger}_{\alpha}(t) \tilde{\sigma}^{j}_{\beta}(t), \tag{1.42}$$

with the coefficients

$$\begin{aligned}\Lambda^{ij}_{\alpha\beta} = \frac{d^{i*}_{\alpha} d^{j}_{\beta}}{\hbar c^3} \omega_j^3 \Bigg\{ &- \frac{\cos(k_j R)}{k_j R} \left((\vec{e}^{\,i*}_{\alpha} \cdot \vec{e}^{\,j}_{\beta}) - \hat{\varepsilon}^{i*}_{\alpha\beta} \hat{\varepsilon}^{j}_{\alpha\beta} \right) \\ &+ \left(\frac{\sin(k_j R)}{(k_j R)^2} + \frac{\cos(k_j R)}{(k_j R)^3} \right) \left((\vec{e}^{\,i*}_{\alpha} \cdot \vec{e}^{\,j}_{\beta}) - 3 \hat{\varepsilon}^{i*}_{\alpha\beta} \hat{\varepsilon}^{j}_{\alpha\beta} \right) \Bigg\},\end{aligned} \tag{1.43}$$

it results in the so-called cooperative Lamb shift, which namely, a shift of spectral lines observed in optically dense media [3]. The off-diagonal terms ($i \neq j$) are the *interatomic cross − shift* terms, they are schematically shown in Fig. 2.1c. The last quantity $\overline{\mathcal{L}}^{\mathrm{S}} \tilde{\rho}$ of (1.75) is the non-secular part of the Lamb shift:

$$\begin{aligned}\overline{\mathcal{L}}^{\mathrm{S}} \tilde{\rho} = -\mathrm{i} \sum_{\alpha,\beta} \sum_{i,j} &\left(\overline{\Delta}^{-\,ij}_{\alpha\beta} + \overline{\Delta}^{T\,ij}_{\alpha\beta} \right) [\tilde{\sigma}^{j}_{\beta}(t) \tilde{\rho}(t), \tilde{\sigma}^{i}_{\alpha}(t)] \\ &+ \left(\overline{\Delta}^{+\,ij}_{\alpha\beta} - \overline{\Delta}^{T\,ij}_{\alpha\beta} \right)^{*} [\tilde{\sigma}^{j\,\dagger}_{\beta}(t) \tilde{\rho}(t), \tilde{\sigma}^{i\,\dagger}_{\alpha}(t)] \\ &- \left(\overline{\Delta}^{+\,ij}_{\alpha\beta} - \overline{\Delta}^{T\,ij}_{\alpha\beta} \right) [\tilde{\sigma}^{i}_{\alpha}(t), \tilde{\rho}(t) \tilde{\sigma}^{j}_{\beta}(t)] \\ &- \left(\overline{\Delta}^{-\,ij}_{\alpha\beta} + \overline{\Delta}^{T\,ij}_{\alpha\beta} \right)^{*} [\tilde{\sigma}^{i\,\dagger}_{\alpha}(t), \tilde{\rho}(t) \tilde{\sigma}^{j\,\dagger}_{\beta}(t)].\end{aligned} \tag{1.44}$$

The fast-oscillating terms $\overline{\mathcal{L}}^{\mathrm{D}} \hat{\rho}$ and $\overline{\mathcal{L}}^{\mathrm{S}} \hat{\rho}$ omitted within the rotating-wave approximation (RWA) [20], [23].

1.2.1 *Validity of the master equation*

We now analyse whether the master equation (1.34) is a valid master equation. The master equation must satisfy a few criteria (1.1): it must preserve the trace, hermiticity and positivity of the density matrix. All these features of density matrix are preserved if master equation has the so-called *Lindblad form* [16, 35].

Lindblad theorem states that the most general form of a time-local master equation that preserves both trace and positivity of the density matrix is

$$\partial_t \hat{\rho} = \frac{1}{\mathrm{i}\hbar} \left[\hat{h}, \hat{\rho} \right] + \sum_{n,m}^{N^2-1} a_{nm} \left(\hat{F}_m \hat{\rho} \hat{F}_n^{\dagger} - \frac{1}{2} \{ \hat{F}_n^{\dagger} \hat{F}_m, \hat{\rho} \} \right), \tag{1.45}$$

where $\hat{h}$ is a Hermitian operator which acts on elements of the Hilbert space $\mathcal{H}_{\mathrm{A}}$, $N = \dim \mathcal{H}_{\mathrm{A}}$ and $\{\hat{F}_m\}$ is an orthonormal basis of the space of operators acting on elements of $\mathcal{H}_{\mathrm{A}}$. If the matrix $\overleftrightarrow{A} = (a_{nm})$ is semi-positive and the operators $\hat{h}$, $\hat{F}_m$ are bounded (which always

holds in the case of a finite dimensional Hilbert space $\mathcal{H}_A$), then the Lindblad theorem guarantees that for any density matrix $\hat{\rho}(t)$ the time propagated density matrix $\hat{\rho}(t')$, $t' > t$, determined from (1.45), is semi-positive, Hermitian and has trace one.

We now compare the master equation (1.45) with the derived one (1.34) without the fast-oscillating terms (1.36) and (1.44), assuming that the RWA holds. The Hermitian operator $\hat{h}$ in the Liouvillian of (1.45) is equvalent to $\hat{H} = \sum_{\alpha=1}^{N} \hat{H}_{\alpha}^{A} + \hat{H}_{\alpha}^{LS} + \sum_{\beta(\neq\alpha)=1}^{N} \hat{H}_{\alpha\beta}^{CLS}$ in the derived master equation (1.34). However, the Lamb shift (1.39) and the imaginary dipole-dipole interaction (1.42) hamiltonians contain the cross-shift terms in form (1.40) and (1.43), which violate the hermiticity of the operators when the cross-shift terms are formed by non-degenerate dipole transitions $\omega_j \neq \omega_i$. Thus, when non-degenerate transitions are involved and form the cross-interference terms, one violates the Lindblad form preservation and one cannot guarantee positivity of the evolved density matrix as well.

Thus, one may conclude that the master equation (1.34) in general does not preserve the Lindblad form. The derived equation is valid only in the particular case when the atomic structure is taken only with a single energy gap and all transitions are degenerate, i.e. $\Gamma_{\alpha\beta}^{ij}(\omega_j) = \Gamma_{\beta\alpha}^{ji}(\omega_i)$ for $\forall\, i, j$.

1.3 SOLUTION OF THE MASTER EQUATION FOR A FEW SIMPLE SYSTEMS

Here we solve the derived the Born-Markov master equation for a few simple systems in order to give an insight into the processes described by the different terms.

1.3.1 *Single two-level atom*

Here we discuss the decay dynamics of an atom, composed by the ground and excited states $|g\rangle$ and $|e\rangle$ with transition frequency ω_0. The coupling with the electromagnetic field leads to the master equation

$$\partial_t \hat{\rho} + \frac{\mathrm{i}}{\hbar}\left[\hat{H}^{A} + \hat{H}^{LS}, \hat{\rho}\right] - \mathcal{L}^{D}\hat{\rho} - \overline{\mathcal{L}}^{D}\hat{\rho} - \overline{\mathcal{L}}^{S}\hat{\rho} = 0, \tag{1.46}$$

where the last two terms are the non-secular ones, we discard them from consideration for now. The Hamiltonian in the commutator reads:

$$H^{A} + H^{LS} = \begin{pmatrix} 0 & 0 \\ 0 & \hbar(\omega_0 + \Omega_{LS}) \end{pmatrix}$$

with ω_0 being the atomic transition frequency and $\Omega_{LS} = \Delta^{+} - \Delta^{-} - 2\Delta^{T}$ is the Lamb shift. The part $\Delta^{+} - \Delta^{-}$ is due to the coupling with the vacuum and $2\Delta^{T}$ is the ac Stark effect by the blackbody radiation

(BBR), the coefficients $\Delta^{\pm}$ and Δ^{T} are given in (1.40). The dissipator reads:

$$\mathcal{L}^{\mathrm{D}}\hat{\rho} = \frac{\Gamma}{2}(1+\bar{n})\left(2\hat{\sigma}\hat{\rho}\hat{\sigma}^{\dagger} - \hat{\sigma}^{\dagger}\hat{\sigma}\hat{\rho} - \hat{\rho}\hat{\sigma}^{\dagger}\hat{\sigma}\right) + \frac{\Gamma}{2}\bar{n}\left(2\hat{\sigma}^{\dagger}\hat{\rho}\hat{\sigma} - \hat{\sigma}\hat{\sigma}^{\dagger}\hat{\rho} - \hat{\rho}\hat{\sigma}\hat{\sigma}^{\dagger}\right), \quad (1.47)$$

with $\bar{n} = n(\omega_0, T)$ being the mean number of photons of a mode at frequency ω_0 at temperature T. The current master equation can be solved straightforward, particularly the coherences have the following form:

$$\begin{aligned}\rho_{ge}(t) &= \rho_{ge}(0)e^{\mathrm{i}(\omega_0+\Omega_{LS})t-\frac{\Gamma}{2}(1+2\bar{n})t},\\ \rho_{eg}(t) &= \rho_{eg}(0)e^{-\mathrm{i}(\omega_0+\Omega_{LS})t-\frac{\Gamma}{2}(1+2\bar{n})t}.\end{aligned} \quad (1.48)$$

One can see that the transition frequency parameter is shifted by the value Ω_{LS} and the decay rate includes the mean-photon number $\bar{n}$. The temperature-dependent mean photon number $\bar{n}$ arises from the BBR, it leads to line broadening and a shift of the line position by the coefficient Δ^{T} (1.40b). The BBR corrections for the Lamb shift and for the line broadening were studied, for example, in [41]. It was shown that they might be relevant for transitions between the high-excited Rydberg states [42, 43]. For transitions with frequency in the optical or ultraviolet regime, at room temperature $\omega_0\tau_R \gg 1$ and consequently $n(\omega_0, T) \ll 1$, see Fig. 1.1a. The BBR affects the atomic state populations. The results below are the solution of (1.46) for diagonal elements with initial conditions $\rho_{ee}(0) = 1$, $\rho_{gg}(0) = 0$:

$$\begin{aligned}\rho_{ee}(t) &= \frac{(1+\bar{n})e^{-\Gamma t(2n+1)} + \bar{n}}{1+2\bar{n}},\\ \rho_{gg}(t) &= \frac{(1+\bar{n}) - e^{-\Gamma t(2\bar{n}+1)}(1+\bar{n})}{1+2\bar{n}},\end{aligned} \quad (1.49)$$

At the time limit $t \to \infty$ the magnitudes of the level populations are determined by the value of $\bar{n}$, Fig. 1.1(b). The larger the value $\bar{n}$, the more one can observe the tendency for equal population as it shown in Fig. 1.1(c). In the limit $\bar{n} \to \infty$: $\rho_{ee}(t) = \rho_{gg}(t) = \frac{1}{2}$.

One may conclude that the diagonal terms of (1.40) lead to the energy shifts of the considered atomic excited states, while the diagonal terms of (1.37a) $\Gamma_{\alpha\alpha} = \Gamma$ correspond to the lifetime of an excited state. The BBR factor $n(\omega_0, T)$ is not relevant for the optical transition frequencies ω_0 at a room temperature $T = 300\mathrm{K}$.

The solution of the master equation (1.46) with the non-secular terms $\overline{\mathcal{L}}^{\mathrm{D}}\hat{\rho}$ and $\overline{\mathcal{L}}^{\mathrm{S}}\hat{\rho}$ was discussed in [44] in the limit $\bar{n} \to 0$. The incorporation of the non-secular terms in the master equation gives a frequency shift $\sim \frac{\Gamma^2}{\omega_0}$, which is the analog of the Bloch-Siegert shift [45]. If we take $\Gamma = 2\pi \times 6$ MHz and $\omega_0 = 2\pi \times 384$ THz, which are

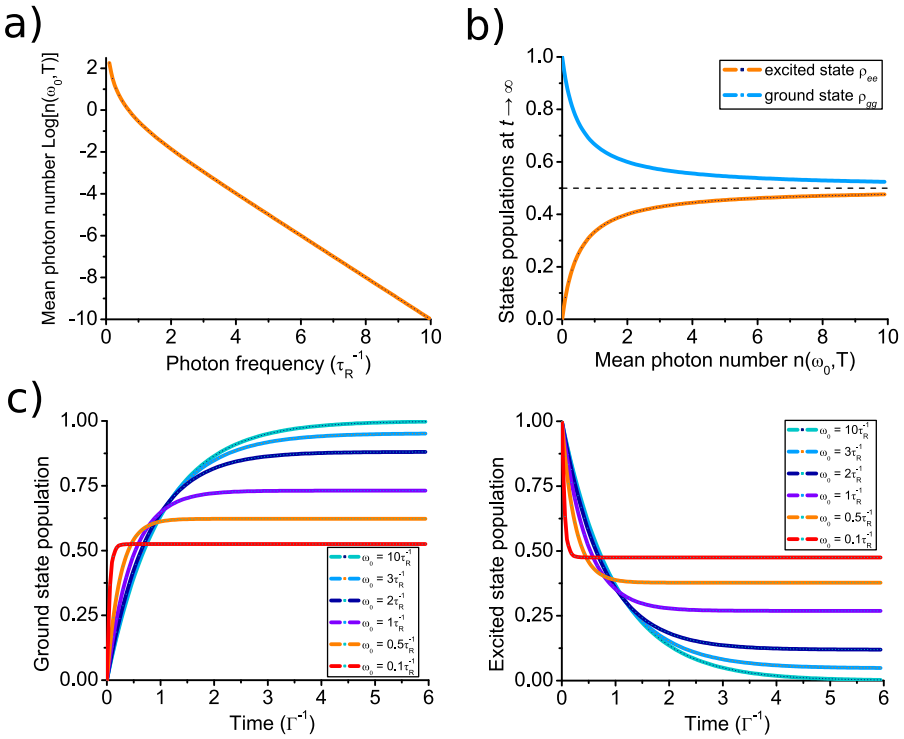

Figure 1.1: (a) The mean-photon number value $n(\omega, T)$ (1.26) at room temperature $T = 300$ versus the photon frequency ω, (b) the atomic states populations (1.49) in the limit $t \to \infty$ for a two-level atom, (c) the time dynamics of the atomic states populations (1.49) for various values of $n(\omega_0, T)$.

the parameters of line D2 for Rb^{87} [46], the value of this correction is $\frac{\Gamma^2}{\omega_0} = 2\pi \times 0.094$ Hz. Thus, for optical transition parameters the non-secular terms give a correction which is negligibly small, and the non-secular terms $\overline{\mathcal{L}}^{\mathrm{D}}\hat{\rho}$ and $\overline{\mathcal{L}}^{\mathrm{S}}\hat{\rho}$ are usually skipped within the RWA. Moreover, the presence of the non-secular terms might be in conflict with the Markov approximation, it is discussed for example in [47].

1.3.2 *Single two-level atom with Zeeman degeneracy*

Here we assume a level structure with a single energy gap, but a degenerate ground state: the unique excited state can decay into 3 channels, Fig. 1.2(a). The master equation for such a system reads:

$$\partial\hat{\rho} = \frac{1}{i\hbar}\left[\hat{H}^{\mathrm{A}}, \hat{\rho}\right] + \sum_{i=1,2,3} \frac{\Gamma^{ii}}{2}\left(2\hat{\sigma}^i\hat{\rho}\hat{\sigma}^{i\dagger} - \hat{\sigma}^{i\dagger}\hat{\sigma}^i\hat{\rho} - \hat{\rho}\hat{\sigma}^{i\dagger}\hat{\sigma}^i\right), \qquad (1.50)$$

here we discarded the non-secular terms and the BBR factors $n(\omega_0, T)$, considering the optical transition frequencies and the room temperature of the photon reservoir. Note that we do not have any cross-damping terms involved in the equation Γ^{ij} $(i \neq j)$, because they

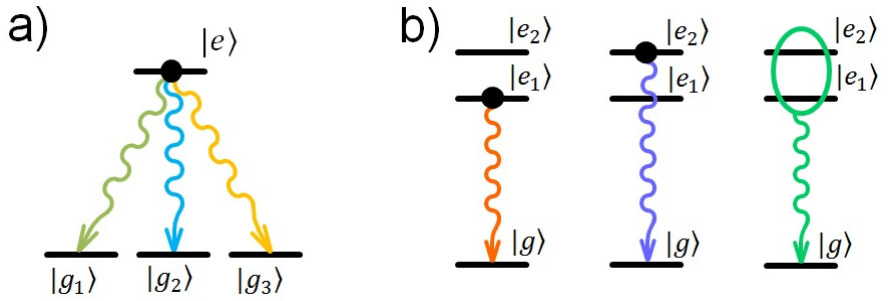

Figure 1.2: Schematic representation of the processes: (a) relevant for the problem 1.3.2, decay of a unique excited state into degenerate ground state, (b) relevant for the problem 1.3.3, decay of each excited state and the coherence between the decay processes, formed by the cross-damping terms, leading to the quantum beats.

vanish for orthogonal dipoles within a single atom. The equation for the excited state population reads:

$$\partial_t \rho_{ee} = -\rho_{ee} \sum_{i=1,2,3} \frac{\Gamma^{ii}}{2} = -\rho_{ee} \sum_{i=1,2,3} \frac{\Gamma^{e-g_i, e-g_i}}{2}, \tag{1.51}$$

with the solution

$$\rho_{ee}(t) = \rho_{ee}(0) e^{-\frac{\gamma t}{2}}, \tag{1.52}$$

where $\gamma = \sum_{i=1,2,3} \Gamma^{e-g_i, e-g_i}$. Thus, the quantity γ describes the lifetime of the excited state, while each individual term Γ^{ii} has the meaning of a decay rate into a certain decay channel.

1.3.3 *Single three-level atom: problem of hermiticity preservation, quantum beat spectroscopy*

Let our system be a single three-level atom, a unique ground state $|g\rangle$ is coupled to two non-degenerate excited states $|e_1\rangle$ and $|e_2\rangle$ by electric dipole transitions $\hat{\vec{d}}_{ge_1} = \hat{\vec{d}}_1$ and $\hat{\vec{d}}_{ge_2} = \hat{\vec{d}}_2$. The dipole moments are parallel, i.e. they have the same polarisation. The master equation for such a system reads

$$\frac{\partial \hat{\rho}}{\partial t} = \frac{1}{i\hbar} \left[\hat{H}^{\mathrm{A}}, \hat{\rho} \right] + \sum_{i,j=1}^{2} \Gamma^{ij} \left(2\hat{\sigma}_j \hat{\rho} \hat{\sigma}_i^{\dagger} - \left\{ \hat{\sigma}_i^{\dagger} \hat{\sigma}_j, \hat{\rho} \right\}_+ \right), \tag{1.53}$$

with the atomic Hamiltonian

$$\hat{H}^{\mathrm{A}} = \hbar\omega_1 |e_1\rangle\langle e_1| + \hbar\omega_2 |e_2\rangle\langle e_2|. \tag{1.54}$$

The dissipator is written via the atomic operators

$$\hat{\sigma}_1 = |g\rangle\langle e_1|, \tag{1.55}$$

$$\hat{\sigma}_2 = |g\rangle\langle e_2|. \tag{1.56}$$

The coefficients (1.37a) in the single-atom case (1.97) read

$$\Gamma^{ij} = \frac{4}{3}\frac{d_i^* d_j}{\hbar c^3}\omega_j^3.$$

Our master equation (1.53) includes the cross-damping terms and it gives a system of 9 linear differential equations for elements of the density matrix. Let us compare the two of them:

$$\begin{aligned}\dot{\rho}_{ge_2} &= -\frac{1}{2}\Gamma^{12}\rho_{ge_1} - \left(\frac{1}{2}\Gamma^{22} - i\omega_2\right)\rho_{ge_2},\\ \dot{\rho}_{e_2g} &= -\frac{1}{2}\Gamma^{21}\rho_{e_1g} - \left(\frac{1}{2}\Gamma^{22} + i\omega_2\right)\rho_{e_2g}.\end{aligned} \tag{1.57}$$

These are the equations for coherences and one should transform into another via hermitian conjugation, but this is not fulfilled because of the cross-damping terms $\Gamma^{12} \neq \Gamma^{21}$. Thus, $\rho_{ge_2} \neq \rho^*_{e_2g}$ and the solution of the master equation might lead to unphysical results. For degenerate transitions, $\Gamma^{12} = \Gamma^{21}$ and hermiticity is naturally restored. For the non-degenerate transition, hermiticity can be restored artificially by setting

$$\omega_j \to \omega_{ij} = \sqrt{\omega_i \omega_j}, \tag{1.58}$$

in (1.37a) [21]. In this way the coefficients become $\Gamma^{ij} = \frac{4}{3}\frac{\vec{d}_i^* \vec{d}_j}{\hbar c^3}\omega_{ij}^3 = \Gamma^{ji}$ with $\omega_{ij} = \sqrt{\omega_i \omega_j}$. However, the step (1.58) is done in a non-systematic way, which causes a question about the validity of such procedure. Particularly one may ask a practical question: how large can be the energy gap between the transitions $\delta\omega = \omega_2 - \omega_1$ in order to justify the action (1.58)?

The cross-damping terms Γ^{ij} are important for spectroscopy. Let us assume that the atom is excited to one of the upper states or their linear superposition by a short laser pulse. The atom will decay to the ground state, emitting a photon. The intensity of emitted light can be written via atomic coherences ρ_{ge_i} [21]:

$$I(t) \sim \Gamma_{11}|\rho_{ge_1}(t)|^2 + \Gamma_{22}|\rho_{ge_2}(t)|^2 + 2\Gamma_{12}\mathrm{Re}(\rho_{ge_1}(t)\rho_{ge_2}(t)). \tag{1.59}$$

If we neglect the damping rates, then the coherences can be approximately written as $\rho_{ge_1}(t) \approx \rho_{ge_1} e^{i\omega_i t}$ and, thus, the light intensity reads:

$$I(t) \sim \Gamma_{11}|\rho_{ge_1}|^2 + \Gamma_{22}|\rho_{ge_2}|^2 + 2\Gamma_{12}\mathrm{Re}(\rho_{ge_1}\rho_{ge_2})\cos(t\delta\omega). \tag{1.60}$$

The light intensity (1.60) clearly exhibits oscillations in time with the period $\delta\omega$, they are also called quantum beats [48]. These intensity oscillations can be measured and from their period we can extract the magnitude $\delta\omega$ [49]. Note that if the cross-damping terms, entering the expression for emission light intensity, are at the basis of the phenomena of quantum beats. The interference process between parallel dipoles for a single atom, leading to the single-atom cross-interference terms, is illustrated in Fig. 2.1(a).

1.3.4 *A pair of two-level atoms*

Now we consider two emitters, composed each by two levels, coupled via dipole-dipole interaction, pinned at positions $\vec{R}_1$ and $\vec{R}_2$. The single-atom Lamb shift value is included in the transition eigenfrequency, we do not include the non-secular parts and the temperature-dependent coefficients here. The master equation reads:

$$\partial_t \hat{\rho} = \frac{1}{\mathrm{i}\hbar} \sum_{\alpha=1,2} \left[\hat{H}^{\mathrm{A}}_{\alpha} + \sum_{\beta(\neq\alpha)=1}^{2} \hat{H}^{\mathrm{CLS}}_{\alpha\beta}, \hat{\rho} \right] + \sum_{\alpha,\beta=1}^{2} \frac{\Gamma_{\alpha\beta}}{2} \left(2\hat{\sigma}_\beta \hat{\rho} \hat{\sigma}^\dagger_\alpha - \hat{\sigma}^\dagger_\alpha \hat{\sigma}_\beta \hat{\rho} - \hat{\rho} \hat{\sigma}^\dagger_\alpha \hat{\sigma}_\beta \right). \quad (1.61)$$

The Hamiltonian matrix in the commutator is not diagonal in the basis $\{|gg\rangle, |ge\rangle, |eg\rangle, |ee\rangle\}$ due to the dipole-dipole interaction terms:

$$\sum_{\alpha=1,2} \hat{H}^{\mathrm{A}}_{\alpha} + \sum_{\beta(\neq\alpha)=1}^{2} \hat{H}^{\mathrm{CLS}}_{\alpha\beta} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & \hbar\omega_0 & \hbar\Lambda_{12} & 0 \\ 0 & \hbar\Lambda_{12} & \hbar\omega_0 & 0 \\ 0 & 0 & 0 & 2\hbar\omega_0 \end{pmatrix}.$$

The coefficients Λ_{12} are functions of the interatomic distance $R_{12} = |\vec{R}_1 - \vec{R}_2|$ (1.43). These coefficients vanish in the limit $R_{12} \to \infty$ and diverge when $R_{12} \to 0$ as shown in Fig. 1.3(b). The Hamiltonian matrix is diagonal in the so-called "molecular eigenstates" basis [21]:

$$\begin{aligned} |g\rangle &= |gg\rangle, \\ |s\rangle &= \frac{1}{\sqrt{2}} \left(|eg\rangle + |ge\rangle \right), \\ |a\rangle &= \frac{1}{\sqrt{2}} \left(|eg\rangle - |ge\rangle \right), \\ |e\rangle &= |ee\rangle, \end{aligned} \quad (1.62)$$

where $|s\rangle$ and $|a\rangle$ are the symmetric and antisymmetric states respectively, we also have a set of eigenenergies:

$$E_g = 0, \quad E_s = \hbar(\omega_0 + \Lambda_{12}), \quad E_a = \hbar(\omega_0 - \hbar\Lambda_{12}), \quad E_e = 2\hbar\omega_0.$$

In the basis (1.62) the master equation (1.61) is solved straightforward, solutions for coherencies $\rho_{sg}(t)$ and $\rho_{ag}(t)$ read

$$\begin{aligned} \rho_{sg}(t) &= \rho_{sg}(0) e^{-\mathrm{i}(\omega_0 + \Lambda_{12})t - \frac{\Gamma + \Gamma_{12}}{2} t}, \\ \rho_{ag}(t) &= \rho_{ag}(0) e^{-\mathrm{i}(\omega_0 - \Lambda_{12})t - \frac{\Gamma - \Gamma_{12}}{2} t}. \end{aligned} \quad (1.63)$$

We see that the dipole–dipole interaction causes an energy gap $2\hbar\Lambda_{12}$ between the symmetric and antisymmetric states and also modifies

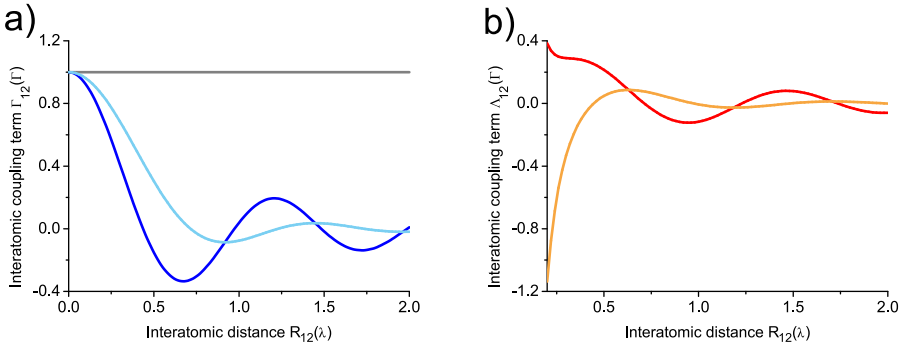

Figure 1.3: Interatomic coupling term (1.37a) for two-level limit Γ_{12} versus the interatomic distance R_{12} (a): light blue curve corresponds to the case $\hat{\varepsilon}_{12} = 0$, blue curve is for $\hat{\varepsilon}_{12} = 1$, grey line is the single-atom spontaneous decay rate Γ. Interatomic coupling term (1.43) for two-level limit Λ_{12} versus the interatomic distance R_{12} (b): red curve corresponds to the case $\hat{\varepsilon}_{12} = 0$, orange curve is for $\hat{\varepsilon}_{12} = 1$.

their lifetimes. The symmetric state with the enhanced decay rate is also called superradiant, while the antisymmetric one is called subradiant. In the limit $R_{12} \to 0$ we have $\Gamma_{12} \to \Gamma$ (it is shown in Fig. 1.3(a)) and the linewidth of the superradiant state is twice larger than for a single atom, while the subradiant state becomes stable.

Assuming that the atomic pair is driven by a laser field we can add the driving laser Hamiltonian

$$\hat{H}_{\mathrm{L}} = \hbar \sum_{\alpha=1,2} \Omega\, e^{i(\vec{k}_L \vec{R}_\alpha - \omega_L t)} \hat{\sigma}_\alpha^\dagger + \mathrm{H.c.}, \tag{1.64}$$

in the Liouvillian of (1.61), where $\vec{k}_L$ is the laser wave-vector, $\omega_L = c|\vec{k}_L|$, and Ω is the Rabi frequency, the derivation of (1.64) is given in Appendix 1.4.5. The explicit time-dependence of the complete hamiltonian $\hat{H} = \sum_{\alpha=1,2} \hat{H}_\alpha^{\mathrm{A}} + \hat{H}_\alpha^{\mathrm{L}} + \sum_{\beta(\neq\alpha)=1}^{2} \hat{H}_{\alpha\beta}^{\mathrm{CLS}}$ ($\hat{H}_\alpha^{\mathrm{L}}$ corresponds to a single term on the RHS of (1.64)) disappears in a reference frame oscillating with a laser frequency $\omega_L = \omega_0 + \delta_L$, where δ_L is a laser detuning defined with respect to transition frequency of a single atom ω_0. In the rotating frame the full hamiltonian reads

$$\hat{H} = \hbar \begin{pmatrix} 0 & \Omega_2^* & \Omega_1^* & 0 \\ \Omega_2 & -\delta_L & \Lambda_{12} & \Omega_1^* \\ \Omega_1 & \Lambda_{12} & -\delta_L & \Omega_2^* \\ 0 & \Omega_1 & \Omega_2 & -2\delta_L \end{pmatrix},$$

where $\Omega_\alpha = \Omega\, e^{i\vec{k}_L \vec{R}_\alpha}$ and further in molecular basis (1.62) $\{|g\rangle, |s\rangle, |a\rangle, |e\rangle\}$

$$\hat{H} = \hbar \begin{pmatrix} 0 & \Omega_s^* & \Omega_a^* & 0 \\ \Omega_s & -(\delta_L - \Lambda_{12}) & 0 & \Omega_s^* \\ \Omega_a & 0 & -(\delta_L + \Lambda_{12}) & -\Omega_a^* \\ 0 & \Omega_s & -\Omega_a & -2\delta_L \end{pmatrix}.$$

We see that the ground state $|g\rangle$ is coupled with the symmetric $|s\rangle$ and antisymmetric $|a\rangle$ states by certain Rabi frequencies

$$\Omega_s = \Omega \frac{e^{i\vec{k}_L\vec{R}_1} + e^{i\vec{k}_L\vec{R}_2}}{\sqrt{2}}, \tag{1.65}$$

$$\Omega_a = \Omega \frac{e^{i\vec{k}_L\vec{R}_1} - e^{i\vec{k}_L\vec{R}_2}}{\sqrt{2}}. \tag{1.66}$$

From (1.66) we can see that if the atoms are illuminated with the same phase, i.e. when $\vec{k}_L\vec{R}_1 = \vec{k}_L\vec{R}_2$, the coupling between the ground and antisymmetric states vanishes. We solve numerically the master equation (1.61) with the driving laser Hamiltonian (1.64) for various laser detunings $\delta_L = \omega_L - \omega_0$. We pin the atoms at a relative distance $|\vec{R}_{12}| = 0.025\lambda$ and drive them as shown in Fig 1.4(a), the laser field is always kept such that $\vec{E}_L \perp \vec{R}_{12}$ and $\Omega = 20\Gamma$.

We use the numeric solution to construct the photon-count signal [15] as a function of the laser detuning

$$S(\delta_L) = \sum_{\alpha,\beta=1}^{N=2} \Gamma_{\alpha\beta} \mathrm{Tr}\left[\hat{\sigma}_\beta \hat{\rho}\, \hat{\sigma}_\alpha^\dagger\right], \tag{1.67}$$

the results of the calculations are given in Figs 1.4(b)-(f). In Figs. 1.4(b)-(e) we can see that the system's spectrum consists of three lines: the red-shifted narrow peak and the blue-shifted broadened peak are associated with transitions to symmetric and antisymmetric states, respectively, the central peak is associated with the double-excited state $|ee\rangle$. Note that, the smaller the angle between the vectors $\vec{k}_L$ and $\vec{R}_{12}$, the smaller the intensity of the red-shifted subradiant peak. This is because, as the angle decreases, we approach to the case where the atoms are illuminated by the laser in the same phase, which means vanishing of the corresponding Rabi frequency (1.66). In the limit $\vec{k}_L \perp \vec{R}_{12}$ shown in Fig. 1.4(f) the subradiant peak disappears. Thus, as already noted, the excitation spectra show both symmetric and antisymmetric collective states, except for the special case when the atoms are driven in-phase. In this particular case the subradiant component disappears.

One may conclude that the interatomic dipole–dipole interaction forms collective states, their spectral properties depend on the coefficients $\Gamma_{\alpha\beta}^{ii}$ (1.37a) and $\Lambda_{\alpha\beta}^{ii}$ (1.43) ($\alpha \neq \beta$), these coefficients are schematically shown in Fig. 2.1(b). The interatomic dipole–dipole interference can occur also between different types of dipoles, these processes correspond to the terms $\Gamma_{\alpha\beta}^{ij}$, $\Lambda_{\alpha\beta}^{ij}$ ($\alpha \neq \beta$, $i \neq j$) in the master equation, they are schematically displayed in Fig. 2.1(c). These terms are relevant, for example, for quantum beats between non-identical two-level atoms [21]. Their impact has also been studied in superradiant atomic ensembles in the case of interfering degenerate orthogonal dipoles [5, 24].

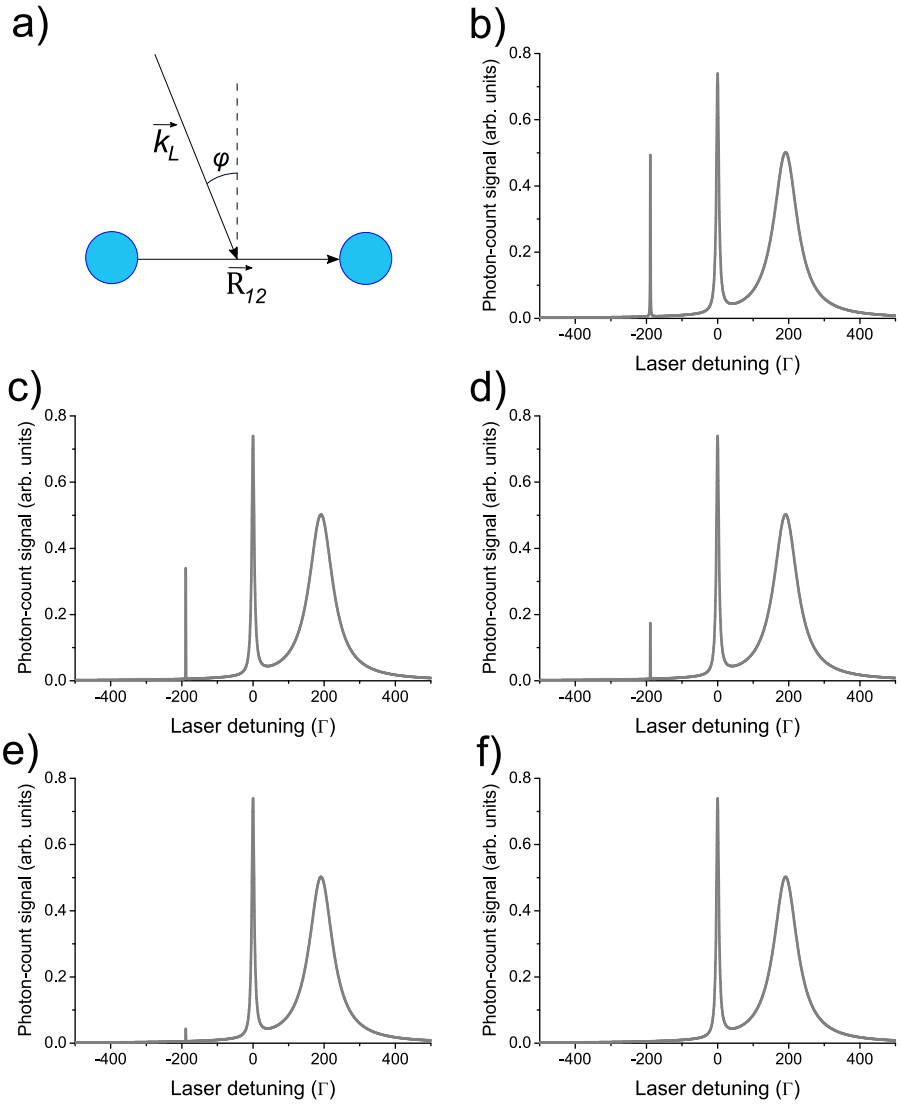

Figure 1.4: Spatial orientation of the driving laser wave vector $\vec{k}_L$ and the interatomic axis vector $\vec{R}_{12} = \vec{R}_1 - \vec{R}_2$ (a). The photon-count signals are given for angles $\varphi = 0.025\pi$ (b), $\varphi = 0.005\pi$ (c), $\varphi = 0.0025\pi$ (d), $\varphi = 0.001\pi$ (e), $\varphi = 0$ (f). All calculations are performed for $\Omega = 20\Gamma$ and $|\vec{R}_{12}| = 0.025\lambda$, atomic dipole moments are taken oriented perpendicularly to the interatomic axis. The laser detuning δ_L is taken with respect to the transition frequency of a single atom ω_0: $\omega_L = \omega_0 + \delta_L$.

1.4 APPENDIX

Here we present some arithmetic details of the derivation of the master equation, which we removed from the main text in order to improve its readability.

1.4.1 *Combination of various terms in the von Neumann equation*

After we explicitly write the double commutator from (1.23) we get:

$$\begin{aligned}\frac{\partial\tilde{\rho}(t)}{\partial t} = -\frac{1}{\hbar^2}\sum_{\alpha,\beta}\int_0^t dt_1 \mathrm{Tr}_R\left[\tilde{V}_\alpha(t)\tilde{V}_\beta(t_1)(\tilde{\rho}(t_1)\otimes\hat{R})\right]\\ -\mathrm{Tr}_R\left[\tilde{V}_\beta(t_1)(\tilde{\rho}(t_1)\otimes\hat{R})\tilde{V}_\alpha(t)\right]\\ -\mathrm{Tr}_R\left[\tilde{V}_\alpha(t)(\tilde{\rho}(t_1)\otimes\hat{R})\tilde{V}_\beta(t_1)\right]\\ +\mathrm{Tr}_R\left[(\tilde{\rho}(t_1)\otimes\hat{R})\tilde{V}_\beta(t_1)\tilde{V}_\alpha(t)\right]. \qquad (1.68)\end{aligned}$$

Now we insert the explicit form of the interaction operator into (1.68):

$$\begin{aligned}\frac{\partial\tilde{\rho}(t)}{\partial t} = -\sum_{\alpha,\beta}\sum_{i,j}\int_0^t dt_1 \langle\tilde{\Gamma}^\dagger_{i\alpha}(t)\tilde{\Gamma}^\dagger_{j\beta}(t_1)\rangle_R\,\tilde{\sigma}^i_\alpha(t)\tilde{\sigma}^j_\beta(t_1)\tilde{\rho}(t_1) \qquad (1.69a)\\ +\langle\tilde{\Gamma}^\dagger_{i\alpha}(t)\tilde{\Gamma}_{j\beta}(t_1)\rangle_R\,\tilde{\sigma}^i_\alpha(t)\tilde{\sigma}^{j\dagger}_\beta(t_1)\tilde{\rho}(t_1) \qquad (1.69b)\\ +\langle\tilde{\Gamma}_{i\alpha}(t)\tilde{\Gamma}^\dagger_{j\beta}(t_1)\rangle_R\,\tilde{\sigma}^{i\dagger}_\alpha(t)\tilde{\sigma}^j_\beta(t_1)\tilde{\rho}(t_1) \qquad (1.69c)\\ +\langle\tilde{\Gamma}_{i\alpha}(t)\tilde{\Gamma}_{j\beta}(t_1)\rangle_R\,\tilde{\sigma}^{i\dagger}_\alpha(t)\tilde{\sigma}^{j\dagger}_\beta(t_1)\tilde{\rho}(t_1) \qquad (1.69d)\\ -\langle\tilde{\Gamma}^\dagger_{i\alpha}(t)\tilde{\Gamma}^\dagger_{j\beta}(t_1)\rangle_R\,\tilde{\sigma}^j_\beta(t_1)\tilde{\rho}(t_1)\tilde{\sigma}^i_\alpha(t) \qquad (1.69e)\\ -\langle\tilde{\Gamma}_{i\alpha}(t)\tilde{\Gamma}^\dagger_{j\beta}(t_1)\rangle_R\,\tilde{\sigma}^j_\beta(t_1)\tilde{\rho}(t_1)\tilde{\sigma}^{i\dagger}_\alpha(t) \qquad (1.69f)\\ -\langle\tilde{\Gamma}^\dagger_{i\alpha}(t)\tilde{\Gamma}_{j\beta}(t_1)\rangle_R\,\tilde{\sigma}^{j\dagger}_\beta(t_1)\tilde{\rho}(t_1)\tilde{\sigma}^i_\alpha(t) \qquad (1.69g)\\ -\langle\tilde{\Gamma}_{i\alpha}(t)\tilde{\Gamma}_{j\beta}(t_1)\rangle_R\,\tilde{\sigma}^{j\dagger}_\beta(t_1)\tilde{\rho}(t_1)\tilde{\sigma}^{i\dagger}_\alpha(t) \qquad (1.69h)\\ -\langle\tilde{\Gamma}^\dagger_{j\beta}(t_1)\tilde{\Gamma}^\dagger_{i\alpha}(t)\rangle_R\,\tilde{\sigma}^i_\alpha(t)\tilde{\rho}(t_1)\tilde{\sigma}^j_\beta(t_1) \qquad (1.69i)\\ -\langle\tilde{\Gamma}_{j\beta}(t_1)\tilde{\Gamma}^\dagger_{i\alpha}(t)\rangle_R\,\tilde{\sigma}^i_\alpha(t)\tilde{\rho}(t_1)\tilde{\sigma}^{j\dagger}_\beta(t_1) \qquad (1.69j)\\ -\langle\tilde{\Gamma}^\dagger_{j\beta}(t_1)\tilde{\Gamma}_{i\alpha}(t)\rangle_R\,\tilde{\sigma}^{i\dagger}_\alpha(t)\tilde{\rho}(t_1)\tilde{\sigma}^j_\beta(t_1) \qquad (1.69k)\\ -\langle\tilde{\Gamma}_{j\beta}(t_1)\tilde{\Gamma}_{i\alpha}(t)\rangle_R\,\tilde{\sigma}^{i\dagger}_\alpha(t)\tilde{\rho}(t_1)\tilde{\sigma}^{j\dagger}_\beta(t_1) \qquad (1.69l)\\ +\langle\tilde{\Gamma}^\dagger_{j\beta}(t_1)\tilde{\Gamma}^\dagger_{i\alpha}(t)\rangle_R\,\tilde{\rho}(t_1)\tilde{\sigma}^j_\beta(t_1)\tilde{\sigma}^i_\alpha(t) \qquad (1.69m)\\ +\langle\tilde{\Gamma}^\dagger_{j\beta}(t_1)\tilde{\Gamma}_{i\alpha}(t)\rangle_R\,\tilde{\rho}(t_1)\tilde{\sigma}^j_\beta(t_1)\tilde{\sigma}^{i\dagger}_\alpha(t) \qquad (1.69n)\\ +\langle\tilde{\Gamma}_{j\beta}(t_1)\tilde{\Gamma}^\dagger_{i\alpha}(t)\rangle_R\,\tilde{\rho}(t_1)\tilde{\sigma}^{j\dagger}_\beta(t_1)\tilde{\sigma}^i_\alpha(t) \qquad (1.69o)\\ +\langle\tilde{\Gamma}_{j\beta}(t_1)\tilde{\Gamma}_{i\alpha}(t)\rangle_R\,\tilde{\rho}(t_1)\tilde{\sigma}^{j\dagger}_\beta(t_1)\tilde{\sigma}^{i\dagger}_\alpha(t). \qquad (1.69p)\end{aligned}$$

We have 16 terms in the current equation, we combine them as follows: (1.69a) with (1.69e), (1.69b) with (1.69g), (1.69c) with (1.69f), (1.69d) with (1.69h), (1.69i) with (1.69m), (1.69j) with (1.69o), (1.69k) with (1.69n), (1.69l) with (1.69p). The result reads

$$\frac{\partial\tilde{\rho}(t)}{\partial t} = \sum_{\alpha,\beta}\sum_{i,j}\int_0^t dt_1 \langle\tilde{\Gamma}^\dagger_{i\alpha}(t)\tilde{\Gamma}^\dagger_{j\beta}(t_1)\rangle_{\mathrm{R}}\,[\tilde{\sigma}^j_\beta(t_1)\tilde{\rho}(t_1),\tilde{\sigma}^i_\alpha(t)]$$
$$+\langle\tilde{\Gamma}^\dagger_{i\alpha}(t)\tilde{\Gamma}_{j\beta}(t_1)\rangle_{\mathrm{R}}\,[\tilde{\sigma}^{j\,\dagger}_\beta(t_1)\tilde{\rho}(t_1),\tilde{\sigma}^i_\alpha(t)]$$
$$+\langle\tilde{\Gamma}_{i\alpha}(t)\tilde{\Gamma}^\dagger_{j\beta}(t_1)\rangle_{\mathrm{R}}\,[\tilde{\sigma}^j_\beta(t_1)\tilde{\rho}(t_1),\tilde{\sigma}^{i\,\dagger}_\alpha(t)]$$
$$+\langle\tilde{\Gamma}_{i\alpha}(t)\tilde{\Gamma}_{j\beta}(t_1)\rangle_{\mathrm{R}}\,[\tilde{\sigma}^{j\,\dagger}_\beta(t_1)\tilde{\rho}(t_1),\tilde{\sigma}^{i\,\dagger}_\alpha(t)] \qquad (1.70a)$$

$$+\langle\tilde{\Gamma}^\dagger_{j\beta}(t_1)\tilde{\Gamma}^\dagger_{i\alpha}(t)\rangle_{\mathrm{R}}\,[\tilde{\sigma}^i_\alpha(t),\tilde{\rho}(t_1)\tilde{\sigma}^j_\beta(t_1)]$$
$$+\langle\tilde{\Gamma}_{j\beta}(t_1)\tilde{\Gamma}^\dagger_{i\alpha}(t)\rangle_{\mathrm{R}}\,[\tilde{\sigma}^i_\alpha(t),\tilde{\rho}(t_1)\tilde{\sigma}^{j\,\dagger}_\beta(t_1)]$$
$$+\langle\tilde{\Gamma}^\dagger_{j\beta}(t_1)\tilde{\Gamma}_{i\alpha}(t)\rangle_{\mathrm{R}}\,[\tilde{\sigma}^{i\,\dagger}_\alpha(t),\tilde{\rho}(t_1)\tilde{\sigma}^j_\beta(t_1)]$$
$$+\langle\tilde{\Gamma}_{j\beta}(t_1)\tilde{\Gamma}_{i\alpha}(t)\rangle_{\mathrm{R}}\,[\tilde{\sigma}^{i\,\dagger}_\alpha(t),\tilde{\rho}(t_1)\tilde{\sigma}^{j\,\dagger}_\beta(t_1)]. \qquad (1.70b)$$

The quantity (1.70a) is hermitian conjugated of (1.70b). Here we introduce correlation functions:

$$C^{++}_{(i\alpha)(j\beta)}(t-t_1) = \langle\tilde{\Gamma}^\dagger_{i\alpha}(t)\tilde{\Gamma}^\dagger_{j\beta}(t_1)\rangle_{\mathrm{R}};\quad C^{-+}_{(i\alpha)(j\beta)}(t-t_1) = \langle\tilde{\Gamma}_{i\alpha}(t)\tilde{\Gamma}^\dagger_{j\beta}(t_1)\rangle_{\mathrm{R}};$$
$$C^{+-}_{(i\alpha)(j\beta)}(t-t_1) = \langle\tilde{\Gamma}^\dagger_{i\alpha}(t)\tilde{\Gamma}_{j\beta}(t_1)\rangle_{\mathrm{R}};\quad C^{--}_{(i\alpha)(j\beta)}(t-t_1) = \langle\tilde{\Gamma}_{i\alpha}(t)\tilde{\Gamma}_{j\beta}(t_1)\rangle_{\mathrm{R}}. \qquad (1.71)$$

Let it be $t_1 = t-\tau$, then:

$$C^{++}_{(i\alpha)(j\beta)}(\tau) = \sum_\lambda (g^\lambda_{i\alpha})^* \bar{g}^\lambda_{j\beta} e^{i\omega_\lambda\tau} n(\omega_\lambda,T) + \bar{g}^\lambda_{i\alpha}(g^\lambda_{j\beta})^* e^{-i\omega_\lambda\tau}(1+n(\omega_\lambda,T)), \qquad (1.72a)$$

$$C^{-+}_{(i\alpha)(j\beta)}(\tau) = \sum_\lambda g^\lambda_{i\alpha}(g^\lambda_{j\beta})^* e^{-i\omega_\lambda\tau}(1+n(\omega_\lambda,T)) + (\bar{g}^\lambda_{i\alpha})^* \bar{g}^\lambda_{j\beta} e^{i\omega_\lambda\tau} n(\omega_\lambda,T), \qquad (1.72b)$$

$$C^{+-}_{(i\alpha)(j\beta)}(\tau) = \sum_\lambda (g^\lambda_{i\alpha})^* g^\lambda_{j\beta} e^{i\omega_\lambda\tau} n(\omega_\lambda,T) + \bar{g}^\lambda_{i\alpha}(\bar{g}^\lambda_{j\beta})^* e^{-i\omega_\lambda\tau}(1+n(\omega_\lambda,T)), \qquad (1.72c)$$

$$C^{--}_{(i\alpha)(j\beta)}(\tau) = \sum_\lambda g^\lambda_{i\alpha}(\bar{g}^\lambda_{j\beta})^* e^{-i\omega_\lambda\tau}(1+n(\omega_\lambda,T)) + (\bar{g}^\lambda_{i\alpha})^* \bar{g}^\lambda_{j\beta} e^{i\omega_\lambda\tau} n(\omega_\lambda,T). \qquad (1.72d)$$

Here above we have used the following relations:

$$\langle\hat{a}^\dagger_\lambda\hat{a}_{\lambda'}\rangle = \delta_{\lambda\lambda'} n(\omega_\lambda,T), \qquad \langle\hat{a}_\lambda\hat{a}^\dagger_{\lambda'}\rangle = \delta_{\lambda\lambda'}(1+n(\omega_\lambda,T)), \qquad (1.73)$$

where $n(\omega_\lambda,T) = \frac{1}{\exp(\hbar\omega_\lambda/(k_B T))-1}$ is a mean number of photons at mode λ of the thermal reservoir, a detailed derivation of quantities (1.73) is given in Appendix 1.4.2. Now we make some additional assumptions. We assume that the photon reservoir has a very large quantisation volume and, thus, the spectra of photon modes is continuous. It allows us to go from the discrete sum to the integral form:

$$\sum_\lambda \to \frac{V}{(2\pi)^3 c^3}\int_0^{\omega_{\mathrm{cut}}} d\omega\,\omega^2 \int_{4\pi} d\Omega \sum_{\mu=\pm1}, \qquad (1.74)$$

explicit integration over the angular variables is given in Appendix 1.4.3.

1.4.1.1 *Coefficients of the master equation*

After we implement the formula (1.31) to the equation (1.30) we obtain:

$$
\begin{aligned}
\frac{\partial\tilde{\rho}}{\partial t} = &\sum_{\alpha,\beta}\sum_{i,j} \\
&\left(\frac{1}{2}\overline{\Gamma}^{ij}_{\alpha\beta}(n(\omega_j,T)+1) - \mathrm{i}\overline{\Delta}_{\alpha\beta}{}^{-\,ij} - \mathrm{i}\overline{\Delta}_{\alpha\beta}{}^{T\,ij}\right)[\tilde{\sigma}^j_\beta(t)\tilde{\rho}(t),\tilde{\sigma}^i_\alpha(t)] \\
+&\left(\frac{1}{2}\Gamma^{ij}_{\alpha\beta}(n(\omega_j,T)+1) - \mathrm{i}\Delta_{\alpha\beta}{}^{-\,ij} - \mathrm{i}\Delta_{\alpha\beta}{}^{T\,ij}\right)[\tilde{\sigma}^j_\beta(t)\tilde{\rho}(t),\tilde{\sigma}^{i\,\dagger}_\alpha(t)] \\
+&\left(\frac{1}{2}\Gamma^{ij\,*}_{\alpha\beta}n(\omega_j,T) - \mathrm{i}\left(\Delta_{\alpha\beta}{}^{+\,ij}\right)^* + \mathrm{i}\left(\Delta_{\alpha\beta}{}^{T\,ij}\right)^*\right)[\tilde{\sigma}^{j\,\dagger}_\beta(t)\tilde{\rho}(t),\tilde{\sigma}^i_\alpha(t)] \\
+&\left(\frac{1}{2}\overline{\Gamma}^{ij\,*}_{\alpha\beta}n(\omega_j,T) - \mathrm{i}\left(\overline{\Delta}^{+\,ij}_{\alpha\beta}\right)^* + \mathrm{i}\left(\overline{\Delta}^{T\,ij}_{\alpha\beta}\right)^*\right)[\tilde{\sigma}^{j\,\dagger}_\beta(t)\tilde{\rho}(t),\tilde{\sigma}^{i\,\dagger}_\alpha(t)] \\
\\
+&\left(\frac{1}{2}\overline{\Gamma}^{ij}_{\alpha\beta}n(\omega_j,T) + \mathrm{i}\overline{\Delta}_{\alpha\beta}{}^{+\,ij} - \mathrm{i}\overline{\Delta}_{\alpha\beta}{}^{T\,ij}\right)[\tilde{\sigma}^i_\alpha(t),\tilde{\rho}(t)\tilde{\sigma}^j_\beta(t)] \\
+&\left(\frac{1}{2}\Gamma^{ij\,*}_{\alpha\beta}(n(\omega_j,T)+1) + \mathrm{i}\left(\Delta_{\alpha\beta}{}^{-\,ij}\right)^* + \mathrm{i}\left(\Delta_{\alpha\beta}{}^{T\,ij}\right)^*\right)[\tilde{\sigma}^i_\alpha(t),\tilde{\rho}(t)\tilde{\sigma}^{j\,\dagger}_\beta(t)] \\
+&\left(\frac{1}{2}\Gamma^{ij}_{\alpha\beta}n(\omega_j,T) + \mathrm{i}\Delta_{\alpha\beta}{}^{+\,ij} - \mathrm{i}\Delta_{\alpha\beta}{}^{T\,ij}\right)[\tilde{\sigma}^{i\,\dagger}_\alpha(t),\tilde{\rho}(t)\tilde{\sigma}^j_\beta(t)] \\
+&\left(\frac{1}{2}\overline{\Gamma}^{ij\,*}_{\alpha\beta}(n(\omega_j,T)+1) + \mathrm{i}\left(\overline{\Delta}^{-\,ij}_{\alpha\beta}\right)^* + \mathrm{i}\left(\overline{\Delta}_{\alpha\beta}{}^{T\,ij}\right)^*\right)[\tilde{\sigma}^{i\,\dagger}_\alpha(t),\tilde{\rho}(t)\tilde{\sigma}^{j\,\dagger}_\beta(t)].
\end{aligned}
\tag{1.75}
$$

The coefficients of (1.75) contain both real and imaginary parts. Collecting the real coefficients is quite straightforward and we focus on the imaginary ones, their expressions read

$$\Delta^{\pm\,ij}_{\alpha\beta} = \frac{d^{i*}_\alpha d^j_\beta}{(2\pi)^2\hbar c^3}\mathcal{P}\int_0^{\omega_{\mathrm{cut}}} d\omega\,\frac{\omega^3 F^{ij}_{\alpha\beta}(kR)}{\omega\pm\omega_j}, \tag{1.76a}$$

$$\overline{\Delta}^{\pm\,ij}_{\alpha\beta} = \frac{d^i_\alpha d^j_\beta}{(2\pi)^2\hbar c^3}\mathcal{P}\int_0^{\omega_{\mathrm{cut}}} d\omega\,\frac{\omega^3 F^{ij}_{\alpha\beta}(kR)}{\omega\pm\omega_j}, \tag{1.76b}$$

$$\Delta^{T\,ij}_{\alpha\beta} = \frac{d^{i*}_\alpha d^j_\beta}{(2\pi)^2\hbar c^3}\mathcal{P}\int_0^{\omega_{\mathrm{cut}}} d\omega\, n(\omega,T)F^{ij}_{\alpha\beta}(kR)\left(\frac{\omega^3}{\omega-\omega_j} - \frac{\omega^3}{\omega+\omega_j}\right), \tag{1.76c}$$

$$\overline{\Delta}^{T\,ij}_{\alpha\beta} = \frac{d^i_\alpha d^j_\beta}{(2\pi)^2\hbar c^3}\mathcal{P}\int_0^{\omega_{\mathrm{cut}}} d\omega\, n(\omega,T)F^{ij}_{\alpha\beta}(kR)\left(\frac{\omega^3}{\omega-\omega_j} - \frac{\omega^3}{\omega+\omega_j}\right). \tag{1.76d}$$

Here below we focus on the secular imaginary terms of (1.75):

$$\begin{aligned}\mathrm{i}\,\mathrm{Im}\left(\partial_t\tilde{\rho}\right)_{\mathrm{sec}} = \mathrm{i}\sum_{\alpha,\beta}\sum_{i,j}&\left(-{\Delta_{\alpha\beta}}^{-ij} - {\Delta_{\alpha\beta}}^{Tij}\right)\left[\tilde{\sigma}_\beta^j(t)\tilde{\rho}(t),\tilde{\sigma}_\alpha^{i\dagger}(t)\right]\\ &+\left(-\left({\Delta_{\alpha\beta}}^{+ij}\right)^* + \left({\Delta_{\alpha\beta}}^{Tij}\right)^*\right)\left[\tilde{\sigma}_\beta^{j\dagger}(t)\tilde{\rho}(t),\tilde{\sigma}_\alpha^{i}(t)\right]\\ &+\left(\left({\Delta_{\alpha\beta}}^{-ij}\right)^* + \left({\Delta_{\alpha\beta}}^{Tij}\right)^*\right)\left[\tilde{\sigma}_\alpha^{i}(t),\tilde{\rho}(t)\tilde{\sigma}_\beta^{j\dagger}(t)\right]\\ &+\left({\Delta_{\alpha\beta}}^{+ij} - {\Delta_{\alpha\beta}}^{Tij}\right)\left[\tilde{\sigma}_\alpha^{i\dagger}(t),\tilde{\rho}(t)\tilde{\sigma}_\beta^{j}(t)\right].\end{aligned}$$

We can rewrite it in a more compact form if we exchange indexes for the third and the fourth terms $i \leftrightarrow j$, $\alpha \leftrightarrow \beta$:

$$\begin{aligned}\mathrm{i}\,\mathrm{Im}\left(\partial_t\tilde{\rho}\right)_{\mathrm{sec}} = \frac{1}{\mathrm{i}\hbar}\sum_{\alpha,\beta}\sum_{i,j}&(-\hbar)\left({\Delta_{\alpha\beta}}^{-ij} + {\Delta_{\alpha\beta}}^{Tij}\right)\left[\tilde{\sigma}_\alpha^{i\dagger}(t)\tilde{\sigma}_\beta^{j}(t),\tilde{\rho}(t)\right]+\\ &+(-\hbar)\left(\left({\Delta_{\alpha\beta}}^{+ij}\right)^* - \left({\Delta_{\alpha\beta}}^{Tij}\right)^*\right)\left[\tilde{\sigma}_\alpha^{i}(t)\tilde{\sigma}_\beta^{j\dagger}(t),\tilde{\rho}(t)\right].\end{aligned} \tag{1.77}$$

Further arithmetic actions significantly depend on whether the atomic operators in commutators (1.77) refers to the same atom ($\alpha = \beta$) or not ($\alpha \neq \beta$) because of the commutation relationship for the atomic operators. For a single atom ($\alpha = \beta$) we can write the expression (1.77) in the form:

$$\mathrm{i}\,\mathrm{Im}\left(\partial_t\tilde{\rho}\right)_{\mathrm{sec},(\alpha=\beta)} = \frac{1}{\mathrm{i}\hbar}\sum_{\alpha}\left[\tilde{H}_\alpha^{\mathrm{LS}}(t),\tilde{\rho}(t)\right], \tag{1.78}$$

the expression of operator $\tilde{H}_\alpha^{\mathrm{LS}}(t)$ is given by (1.39). In the second case ($\alpha \neq \beta$ in (1.77)) we can swap the operator's order in the second commutator $\tilde{\sigma}_\alpha^i\tilde{\sigma}_\beta^{j\dagger} = \tilde{\sigma}_\beta^{j\dagger}\tilde{\sigma}_\alpha^i$ and change the indexes, then the equation (1.77) reads:

$$\mathrm{i}\,\mathrm{Im}\left(\partial_t\tilde{\rho}\right)_{\mathrm{sec},(\alpha\neq\beta)} = \frac{1}{\mathrm{i}\hbar}\left[(-\hbar)\sum_{\alpha,\beta(\neq\alpha)}\sum_{i,j}\tilde{\sigma}_\alpha^{i\dagger}(t)\tilde{\sigma}_\beta^{j}(t)\left(\Delta_{\alpha\beta}^{-ij} + \Delta_{\alpha\beta}^{+ij}\right),\tilde{\rho}(t)\right], \tag{1.79}$$

with the sum in the parentheses

$$\begin{aligned}&(-\hbar)\left(\Delta_{\alpha\beta}^{-ij} + \Delta_{\alpha\beta}^{+ij}\right) =\\ &= (-\hbar)\frac{d_\alpha^{i*}d_\beta^j}{(2\pi)^2\hbar c^3}\left\{\mathcal{P}\int_0^{\omega_{\mathrm{cut}}}\frac{\omega^3 F_{\alpha\beta}^{ij}(k_jR)}{\omega-\omega_j} + \frac{\omega^3 F_{\alpha\beta}^{ij}(k_jR)}{\omega+\omega_j}d\omega\right\}.\end{aligned} \tag{1.80}$$

We can make a variable change in the second term $\omega \to -\omega$ and set $\omega_{\mathrm{cut}} \to \infty$, then:

$$(-\hbar)\left(\Delta_{\alpha\beta}^{-ij} + \Delta_{\alpha\beta}^{+ij}\right) = (-\hbar)\left\{\frac{d_\alpha^{i*}d_\beta^j}{(2\pi)^2\hbar c^3}\mathcal{P}\int_{-\infty}^{\infty}\frac{\omega^3 F_{\alpha\beta}^{ij}(k_jR)}{\omega-\omega_j}d\omega\right\}. \tag{1.81}$$

Note, that the quantity in the figure brackets and the dissipator's coefficient $\Gamma^{ij}_{\alpha\beta}$ (1.37a) are connected by the Kramers–Kronig relation. The integral over frequencies can be calculated and the final expression for (1.80) reads:

$$\hbar\Lambda^{ij}_{\alpha\beta} = \hbar\frac{d^{i*}_{\alpha}d^{j}_{\beta}}{\hbar c^3}\omega_j^3\left\{-\frac{\cos(k_jR)}{k_jR}\left((\vec{e}^{\,i*}_{\alpha}\cdot\vec{e}^{\,j}_{\beta})-\hat{\varepsilon}^{i*}_{\alpha\beta}\hat{\varepsilon}^{j}_{\alpha\beta}\right)\right.$$
$$\left.+\left(\frac{\sin(k_jR)}{(k_jR)^2}+\frac{\cos(k_jR)}{(k_jR)^3}\right)\left((\vec{e}^{\,i*}_{\alpha}\cdot\vec{e}^{\,j}_{\beta})-3\hat{\varepsilon}^{i*}_{\alpha\beta}\hat{\varepsilon}^{j}_{\alpha\beta}\right)\right\} \quad (1.82)$$

and finally we can write for (1.79):

$$\mathrm{i}\,\mathrm{Im}\,(\partial_t\tilde{\rho})_{\mathrm{sec},(\alpha\neq\beta)} = \frac{1}{\mathrm{i}\hbar}\sum_{\alpha\neq\beta}\left[\tilde{H}^{\mathrm{CLS}}_{\alpha\beta},\tilde{\rho}\right], \quad (1.83)$$

where Hamiltonian $\tilde{H}^{\mathrm{CLS}}_{\alpha\beta}$ describes an effective interaction between dipolar transitions of different atoms (1.42).

1.4.2 *Mean values of the field operators for the thermal reservoir*

During derivation of the master equation we take a specific form of the photon reservoir - a thermal reservoir [35]:

$$\hat{R} = \frac{1}{Z}e^{-\frac{\hat{H}_R}{k_BT}} = \prod_{\lambda}\left\{e^{-\hbar\omega_\lambda\hat{a}^\dagger_\lambda\hat{a}_\lambda/(k_BT)}\left(1-e^{-\hbar\omega_\lambda/(k_BT)}\right)\right\}, \quad (1.84)$$

where $\hat{H}_R$ is defined by (1.4). We use this photon state for calculation of mean values $\langle\hat{a}^\dagger_\lambda\hat{a}_{\lambda'}\rangle$ and $\langle\hat{a}_\lambda\hat{a}^\dagger_{\lambda'}\rangle$

$$\langle\hat{a}^\dagger_\lambda\hat{a}_{\lambda'}\rangle_R = \delta_{\lambda\lambda'}\left[\prod_{\nu(\neq\lambda)}\left(\sum_{n_\nu=0}^{\infty}e^{-\hbar\omega_\nu n_\nu/(k_BT)}(1-e^{-\hbar\omega_\nu/(k_BT)})\right)\right]$$
$$\times\left(\sum_{n_\lambda=0}^{\infty}n_\lambda e^{-\hbar\omega_\lambda n_\lambda/(k_BT)}(1-e^{-\hbar\omega_\lambda/(k_BT)})\right)$$
$$= \delta_{\lambda\lambda'}\sum_{n_\lambda=0}^{\infty}n_\lambda e^{-\hbar\omega_\lambda n_\lambda/(k_BT)}(1-e^{-\hbar\omega_\lambda/(k_BT)}), \quad (1.85)$$

the sum can be cast into geometric series:

$$\sum_{n=0}^{\infty}ne^{-an} = -\frac{\partial}{\partial a}\sum_{n=0}^{\infty}e^{-an} = -\frac{\partial}{\partial a}\frac{1}{1-e^{-a}} = \frac{e^{-a}}{(1-e^{-a})^2}.$$

Thus, the final result reads

$$\langle\hat{a}^\dagger_\lambda\hat{a}_{\lambda'}\rangle = \delta_{\lambda\lambda'}n(\omega_\lambda,T), \quad (1.86)$$

with the mean photon number in mode λ:

$$n(\omega_\lambda,T) = \frac{1}{e^{\hbar\omega_\lambda/(k_BT)}-1}.$$

Similarly it is easy to show that

$$\langle \hat{a}_\lambda \hat{a}^\dagger_{\lambda'} \rangle_R = \delta_{\lambda\lambda'}(1 + n(\omega_\lambda, T)), \tag{1.87}$$

$$\langle \hat{a}^\dagger_\lambda \hat{a}^\dagger_{\lambda'} \rangle_R = \langle \hat{a}_\lambda \hat{a}_{\lambda'} \rangle_R = 0, \tag{1.88}$$

using the commutators (1.5).

1.4.3 *Angular integration of the correlation function*

When we perform the procedure of reduction, we consider the limit of large quantisation volume, and we can cast the sum over the reservoir's modes into an integral, where the sum over photon polarisations is included. Let vectors $\vec{a}$ and $\vec{b}$ represent the dipole moments, then:

$$\int_\Omega d\Omega \sum_{\mu=\pm1} (\vec{a} \cdot \vec{e}_{\vec{k},\mu})(\vec{b} \cdot \vec{e}^*_{\vec{k},\mu}) e^{i\vec{k}\vec{R}_{\alpha\beta}} = \frac{8\pi}{3} \vec{a} \overleftrightarrow{D}^{\Omega}_{\alpha\beta} \vec{b}, \tag{1.89}$$

where the integration region should involve all photon modes $\Omega = 4\pi$. The sum over the polarisations and the angular integration are included in a matrix:

$$\begin{aligned} \overleftrightarrow{D}^{4\pi}_{\alpha\beta} &= \frac{3}{8\pi} \int_{\Omega=4\pi} d\Omega\, e^{i\vec{k}\vec{R}_{\alpha\beta}} \underbrace{\sum_{\mu=\pm1} \vec{e}_{\vec{k},\mu} \vec{e}^{\,\mathrm{T}}_{\vec{k},\mu}}_{\text{matr}} \\ &= \frac{3}{8\pi} \int_{\Omega=4\pi} d\Omega\, e^{i\vec{k}\vec{R}_{\alpha\beta}} \left(\hat{\mathbf{I}}_3 - \vec{e}_k \vec{e}^{\,\mathrm{T}}_k \right), \end{aligned} \tag{1.90}$$

where $\vec{e}_k = \vec{k}/|\vec{k}|$ and $\hat{\mathbf{I}}_3$ is a unit matrix of size 3×3. Let us chose the unit wave vector as follows

$$\vec{e}_k = \begin{pmatrix} \sin(\theta)\cos(\phi) \\ \sin(\theta)\sin(\phi) \\ \cos(\theta) \end{pmatrix}, \tag{1.91}$$

where the polar angle θ is defined with respect to vector $\vec{R}_{\alpha\beta}$ (we chose vector $\vec{R}_{\alpha\beta}$ in the integrand of (1.90) as $\vec{R}_{\alpha\beta} = \{0, 0, R_{\alpha\beta}\}$ in cartesian coordinate system). The angular integrals can be calculated straightforwardly, the answer reads

$$\begin{aligned} \overleftrightarrow{D}^{4\pi}_{\alpha\beta} &= \frac{3}{8\pi} \begin{pmatrix} D_1(kR_{\alpha\beta}) & 0 & 0 \\ 0 & D_1(kR_{\alpha\beta}) & 0 \\ 0 & 0 & D_1(kR_{\alpha\beta}) - D_2(kR_{\alpha\beta}) \end{pmatrix} \\ &= \frac{3}{8\pi} \left(D_1(kR_{\alpha\beta}) \hat{\mathbf{I}}_3 - D_2(kR_{\alpha\beta}) \vec{e}_R \vec{e}^{\,T}_R \right), \end{aligned} \tag{1.92}$$

where $\vec{e}_R = \frac{\vec{R}_{\alpha\beta}}{R_{\alpha\beta}}$ and

$$D_1 = 4\pi \left(\frac{\sin(x)}{x} + \frac{\cos(x)}{x^2} - \frac{\sin(x)}{x^3} \right), \tag{1.93}$$

$$D_2 = 4\pi \left(\frac{\sin(x)}{x} + 3\frac{\cos(x)}{x^2} - 3\frac{\sin(x)}{x^3} \right). \tag{1.94}$$

Now the product in the RHS of (1.89) reads

$$\frac{8\pi}{3}\vec{a}\overset{\leftrightarrow 4\pi}{D}_{\alpha\beta}\vec{b} = |\vec{a}||\vec{b}| \times F^{ab}_{\alpha\beta}(kR_{\alpha\beta}), \tag{1.95}$$

here $F^{ab}_{\alpha\beta}(kR_{\alpha\beta})$ is so-called diffraction type function [2]

$$F^{ab}_{\alpha\beta}(kR_{\alpha\beta}) = 4\pi\left\{\frac{\sin(kR_{\alpha\beta})}{kR_{\alpha\beta}}\left((\vec{e}_a\cdot\vec{e}_b) - \hat{\varepsilon}^a_{\alpha\beta}\hat{\varepsilon}^b_{\alpha\beta}\right)\right.$$
$$\left. + \left(\frac{\cos(kR_{\alpha\beta})}{(kR_{\alpha\beta})^2} - \frac{\sin(kR_{\alpha\beta})}{(kR_{\alpha\beta})^3}\right)\left((\vec{e}_a\cdot\vec{e}_b) - 3\hat{\varepsilon}^a_{\alpha\beta}\hat{\varepsilon}^b_{\alpha\beta}\right)\right\}, \tag{1.96}$$

it describes the strength of the interatomic dipole–dipole coupling versus the interatomic distance. The symbol $\hat{\varepsilon}^a_{\alpha\beta}$ denotes a projection of vector $\vec{a}$ on the interatomic distance $R_{\alpha\beta}$: $\hat{\varepsilon}^a_{\alpha\beta} = \frac{\vec{a}\cdot\vec{R}_{\alpha\beta}}{|\vec{a}||\vec{R}_{\alpha\beta}|}$. For short distances the RHS of (1.96) reads

$$F^{ab}_{\alpha\beta}(x) \xrightarrow{x\to 0} 4\pi\left\{1\times\left((\vec{e}_a\cdot\vec{e}_b) - \hat{\varepsilon}^a_{\alpha\beta}\hat{\varepsilon}^b_{\alpha\beta}\right)\right.$$
$$\left. + \left(\frac{1-\frac{1}{2}x^2}{x^2} - \frac{x-\frac{1}{6}x^3}{x^3}\right)\left((\vec{e}_a\cdot\vec{e}_b) - 3\hat{\varepsilon}^a_{\alpha\beta}\hat{\varepsilon}^b_{\alpha\beta}\right)\right\} =$$
$$= \frac{8\pi}{3}(\vec{e}_a\cdot\vec{e}_b). \tag{1.97}$$

1.4.4 *About atomic dipole moments*

Here below we present a general expression for a dipole moment, which correspond to transition between two given atomic states $|n, L, S, J, F, M_F\rangle \rightarrow |n', L', S', J', F', M'_F\rangle$. We consider the following momentum coupling scheme:

$$\vec{F} = \vec{I} + \vec{J}, \tag{1.98}$$
$$\vec{J} = \vec{L} + \vec{S}, \tag{1.99}$$

where $\vec{S}$, $\vec{L}$ and $\vec{J}$ are the spin, the orbital angular momentum and the total angular momentum of an electron, $\vec{I}$ is the angular momentum of an atomic nuclei (individual for specific isotopes), $\vec{F}$ is the total angular momentum of the atom. The general expression for the dipole moment can be construct form a consequence of the following identities:

$$\langle n, F, M_F|\hat{d}_q|n', F', M'_F\rangle = (-1)^{F-M_F}\begin{pmatrix} F & 1 & F' \\ -M_F & q & M'_F\end{pmatrix}\langle n, F|\hat{d}|n', F'\rangle, \tag{1.100}$$

where M_F is the magnetic quantum number $M_F = -F, -F+1, ..., F-1, F$ and $\langle n, F|\hat{d}|n', F'\rangle = \langle n, J, I, F|\hat{d}|n', J', I', F'\rangle$, where

$$\langle n, J, I, F|\hat{d}|n', J', I', F'\rangle =$$
$$= (-1)^{I+1-J'-F}\sqrt{(2F+1)(2F'+1)}W(JFJ'F'; I1)\,\langle n, J|\hat{d}|n', J'\rangle, \tag{1.101}$$

where $\langle n, J|\hat{d}|n', J'\rangle = \langle n, L, S, J|\hat{d}|n', L', S', J'\rangle$ and

$$\begin{aligned}&\langle n, L, S, J|\hat{d}|n', L', S', J'\rangle = \\ &= (-1)^{S+1-L'-J}\sqrt{(2J+1)(2J'+1)}W(LJL'J';S1) \times \langle n, L|\hat{d}|n', L'\rangle,\end{aligned} \tag{1.102}$$

with

$$\langle n, L|d|n', L'\rangle = \sqrt{(2L+1)(2L'+1)}\begin{pmatrix} L & 1 & L' \\ 0 & 0 & 0\end{pmatrix}\underbrace{\int_0^\infty dr\, r^3 R_{nL}R_{n'L'}}_{d_R(n'L', nL)}. \tag{1.103}$$

Note that the 3j-symbols obey the following selection rule: $|F-1| \leq F' \leq F+1$, $M_F - M'_F = q$, where $q = 0, \pm 1$ corresponds to π and $\sigma^\pm$ polarisations, respectively. Dipole moments with the same value of q are called parallel. The expressions (1.101) and (1.102) follow the momentum couplings, $W(j_1, j_2, l_1, l_2; J, L)$ is the Racah W-coefficient, which is related with Wigner's 6-j symbols:

$$W(j_1, j_2, l_1, l_2; J, L) = (-1)^{j_1+j_2+l_1+l_2}\begin{Bmatrix} j_1 & j_2 & J \\ l_2 & l_1 & L\end{Bmatrix}.$$

The radial integral in (1.103) can be computed exactly only for hydrogen and the hydrogen-like single-electron ions. For many-electron atoms one can use the Hartree-Fock approach and its generalizations, such as MCHF [52] or RPAE [53], to calculate the radial integrals with satisfactory precision. However, in practise the values of radial integrals are extracted from available experimental data. The final expression for an atomic dipole moment reads:

$$\begin{aligned}\langle n, F, M_F|\hat{d}_q|n', F', M'_F\rangle = (-1)^{M_F+I-J'+S-L'-J}&\begin{pmatrix} F & 1 & F' \\ -M_F & q & M_F\end{pmatrix} \times \\ \times \sqrt{[F][F'][J][J'][L][L']}\, W(JFJ'F';I1)\, &W(LJL'J';S1) \times \\ \times \begin{pmatrix} L & 1 & L' \\ 0 & 0 & 0\end{pmatrix} d_R(n'L', nL),&\end{aligned} \tag{1.104}$$

where $[k] = 2k+1$.

1.4.5 *Laser field hamiltonian*

Here we present detailed derivation of the driving laser hamiltonian. A quantized laser field state could be considered as a coherent state $|\alpha_\lambda\rangle \in \mathcal{H}_R$, which defined as follows [35]:

$$|\alpha_\lambda\rangle = \hat{\mathcal{D}}_\lambda(\alpha)|\text{vac}\rangle, \tag{1.105}$$

where $\hat{\mathcal{D}}_\lambda(\alpha)$ is a displacement operator:

$$\hat{\mathcal{D}}_\lambda(\alpha) = e^{\alpha\hat{a}_\lambda^\dagger + \alpha^*\hat{a}_\lambda}, \tag{1.106}$$

with $\alpha \in \mathcal{C}$. Let us assume laser at a certain mode λ and freequency ω_L. Then the density matrix of the laser field state reads

$$\hat{R} = \hat{\mathcal{D}}_{\lambda_L}(\alpha e^{-i\omega_L t})|\text{vac}\rangle\langle\text{vac}|\hat{\mathcal{D}}_{\lambda_L}^\dagger(\alpha e^{-i\omega_L t}). \tag{1.107}$$

Now we perform a unitary transformation in order to simplify the basis of the reservoir state. The transformation reads

$$\hat{U}_L = \hat{\mathcal{D}}_{\lambda_L}^\dagger(\alpha e^{-i\omega_L t}) = \hat{\mathcal{D}}_{\lambda_L}(-\alpha e^{-i\omega_L t}). \tag{1.108}$$

After we apply the transformation (1.108) to (1.107) we get transformed density matrix for reservoir

$$\hat{R}' = |\text{vac}\rangle\langle\text{vac}|. \tag{1.109}$$

The next step is apply the transformation (1.108) to the hamiltonian (1.3)

$$\hat{H}' = \hat{U}_L\hat{H}\hat{U}_L^\dagger - i\hbar\,\hat{U}_L\frac{\partial\hat{U}_L^\dagger}{\partial t}. \tag{1.110}$$

In order to obtain the transformed hamiltonian we have to evaluate all the terms of the original hamiltonian. First of all let us evaluate the creation and annihilation field operators of photons $\hat{a}$ and $\hat{a}^\dagger$ using so-called the Baker-Haussdorf lemma [54]

$$e^{\hat{A}}\hat{B}e^{-\hat{A}} = \hat{B} + [\hat{A},\hat{B}] + \frac{1}{2!}[\hat{A},[\hat{A},\hat{B}]] + \frac{1}{3!}[\hat{A},[\hat{A},[\hat{A},\hat{B}]]] + \ldots \tag{1.111}$$

Using lemma (1.111) the transformed creation operator reads

$$\begin{aligned}\hat{U}_L(t)\hat{a}_\lambda^\dagger\hat{U}_L^\dagger(t) &= \hat{\mathcal{D}}_{\lambda_L}^\dagger(\alpha e^{-i\omega_L t})\hat{a}_\lambda^\dagger\hat{\mathcal{D}}_{\lambda_L}(\alpha e^{-i\omega_L t}) \\ &= \hat{a}_\lambda^\dagger + [-\alpha e^{-i\omega_L t}\hat{a}_L^\dagger + \alpha^* e^{i\omega_L t}\hat{a}_L, \hat{a}_\lambda] \\ &= \hat{a}_\lambda^\dagger + \alpha^* e^{i\omega_L t}\delta_{L\lambda}1_{\text{R}}.\end{aligned} \tag{1.112}$$

Analogiously transformed annihilation operator

$$\hat{U}_L(t)\hat{a}_\lambda\hat{U}_L^\dagger(t) = \hat{a}_\lambda + \alpha e^{-i\omega_L t}\delta_{L\lambda}1_{\text{R}}. \tag{1.113}$$

Equations (1.112) and (1.113) can be generalized for an arbitrary polynomial $G(\hat{a},\hat{a}^\dagger)$ [54], namely

$$\hat{U}_L(t)G(\hat{a},\hat{a}^\dagger)\hat{U}_L^\dagger(t) = G(\hat{a} + \alpha e^{-i\omega_L t}1_{\text{R}}, \hat{a}^\dagger + \alpha^* e^{i\omega_L t}1_{\text{R}}). \tag{1.114}$$

Using the equation (1.114) we can evaluate the reservoir hamiltonian (1.4) as

$$\begin{aligned}\hat{U}_L(t)\hat{H}_{\text{R}}\hat{U}_L^\dagger(t) &= \sum_\lambda \hbar\omega_\lambda\left(\hat{U}_L\hat{a}_\lambda^\dagger\hat{a}_\lambda\hat{U}_L^\dagger + \frac{1}{2}\right) \\ &= \sum_\lambda \hbar\omega_\lambda\left[(\hat{a}_\lambda^\dagger + \alpha^* e^{i\omega_L t}\delta_{\lambda L}1_{\text{R}})(\hat{a}_\lambda + \alpha e^{-i\omega_L t}\delta_{\lambda L}1_{\text{R}}) + \frac{1}{2}\right] \\ &= \hat{H}_{\text{R}} + \hbar\omega_L\left(\alpha^* e^{i\omega_L t}1_{\text{R}}\hat{a}_L + \alpha e^{-i\omega_L t}1_{\text{R}}\hat{a}_L^\dagger + |\alpha|^2 1_{\text{R}}\right).\end{aligned} \tag{1.115}$$

Atomic system hamiltonian acts in $\mathcal{H}_\mathrm{A}$. It means that it commutes with the transformation operator $\hat{U}_L$ and the transformed atomic Hamiltonian is identical to the original one

$$\hat{U}_L \hat{H}_\mathrm{A} \hat{U}_L^\dagger = \hat{U}_L \hat{U}_L^\dagger \hat{H}_\mathrm{A} = \hat{H}_\mathrm{A}. \tag{1.116}$$

The interaction operator (1.6) contains the sum over all the atoms, the result of the unitary transformation for one of them reads:

$$\hat{V}_\alpha = \hbar \sum_\lambda \sum_i \left(\bar{g}_{i\alpha}^\lambda \hat{a}_\lambda e^{i\vec{k}_\lambda \vec{R}_\alpha} + \left(g_{i\alpha}^\lambda \right)^* \hat{a}_\lambda^\dagger e^{-i\vec{k}_\lambda \vec{R}_\alpha} \right) \hat{\sigma}_\alpha^i + \left(g_{i\alpha}^\lambda \hat{a}_\lambda e^{i\vec{k}_\lambda \vec{R}_\alpha} + \left(\bar{g}_{i\alpha}^\lambda \right)^* \hat{a}_\lambda^\dagger e^{-i\vec{k}_\lambda \vec{R}_\alpha} \right) \hat{\sigma}_\alpha^{i\,\dagger}.$$

It contains single creation and annihilation operators, thus we can use results (1.112) and (1.113) to evaluate the interaction operator

$$\begin{aligned} \hat{U}_L \hat{V}_\alpha \hat{U}_L^\dagger = \hat{V}_\alpha + \\ + \hbar \sum_i \left(\left(g_{i\alpha}^L \right)^* \alpha^* e^{-i(\vec{k}_L \vec{R}_\alpha - \omega_L t)} 1_\mathrm{R} + \bar{g}_{i\alpha}^L \alpha e^{i(\vec{k}_L \vec{R}_\alpha - \omega_L t)} 1_\mathrm{R} \right) \hat{\sigma}_\alpha^i \\ + \left(g_{i\alpha}^L \alpha e^{i(\vec{k}_L \vec{R}_\alpha - \omega_L t)} 1_\mathrm{R} + \left(\bar{g}_{i\alpha}^L \right)^* \alpha^* e^{-i(\vec{k}_L \vec{R}_\alpha - \omega_L t)} 1_\mathrm{R} \right) \hat{\sigma}_\alpha^{i\,\dagger}. \end{aligned} \tag{1.117}$$

Thus, the transformation of the original operator $\hat{V}_\alpha$ gives the same operator plus an additional term, which is called Laser-field hamiltonian

$$\hat{H}_\alpha^L = \hbar \sum_i \bar{\Omega}_\alpha^i e^{i(\vec{k}_L \vec{R}_\alpha - \omega_L t)} 1_\mathrm{R} \hat{\sigma}_\alpha^i + \Omega_\alpha^i e^{i(\vec{k}_L \vec{R}_\alpha - \omega_L t)} 1_\mathrm{R} \hat{\sigma}_\alpha^{i\,\dagger} + \mathrm{H.c.}, \tag{1.118}$$

here $\bar{\Omega}_\alpha^i = \bar{g}_{i\alpha}^L$ and $\Omega_\alpha^i = g_{i\alpha}^L$ are Rabi frequencies. The transformation of original hamiltonian has performed. The terms $\sim \bar{\Omega}_\alpha^i$ are the fast oscillating terms and cn be omitted within the RWA. The last step is to compute the second term in (1.110). The time-derivative reads

$$\begin{aligned} \frac{\partial \hat{U}_L^\dagger}{\partial t} = \frac{\partial}{\partial t} \left(e^{\alpha \exp(-i\omega_L t)\hat{a}_L^\dagger} \cdot e^{-\alpha^* \exp(i\omega_L t)\hat{a}_L} \right) \\ = \alpha e^{-i\omega_L t}(-i\omega_L)\hat{a}_L^\dagger \hat{U}_L^\dagger + e^{\alpha \exp(-i\omega_L t)\hat{a}_L^\dagger}(-\alpha^* e^{i\omega_L t}(i\omega_L)\hat{a}_L) e^{-\alpha^* \exp(i\omega_L t)\hat{a}_L} \\ = (-i\omega_L) \left[\alpha e^{-i\omega_L t} \hat{a}_L^\dagger \hat{U}_L^\dagger + \alpha^* e^{i\omega_L t} \hat{U}_L^\dagger \hat{a}_L \right], \end{aligned} \tag{1.119}$$

we multiply it on $i\hbar\,\hat{U}_L$ from the left side and get

$$i\hbar\,\hat{U}_L \frac{\partial \hat{U}_L^\dagger}{\partial t} = \hbar\omega_L \left(\alpha e^{-i\omega_L t} \hat{a}_L^\dagger + \alpha^* e^{i\omega_L t} \hat{a}_L + |\alpha|^2 1_\mathrm{R} \right). \tag{1.120}$$

The last equation vinishes with the second term of transformed reservoir hamiltonian (1.115). Thus, the whole transformed hamiltonian reads

$$\hat{H}' = \hat{H}_\mathrm{A} + \hat{H}_\mathrm{R} + \hat{V} + \hat{H}_\mathrm{L}. \tag{1.121}$$

It has additional term, which has already been mentioned above, it is the Laser-field hamiltonian

$$\hat{H}_\mathrm{L} = \sum_\alpha \hat{H}_\alpha^\mathrm{L} = \hbar \sum_\alpha \sum_i \Omega_\alpha^i e^{i(\vec{k}_L \vec{R}_\alpha - \omega_L t)} 1_\mathrm{R} \hat{\sigma}_\alpha^{i\,\dagger} + \mathrm{H.c.} \tag{1.122}$$

2

MASTER EQUATION FOR MULTILEVEL INTERFERENCE IN A SUPERRADIANT MEDIUM

Master equation for multilevel interference in a superradiant medium

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The theoretical model was developed by A. Konovalov and G. Morigi. Numerical simulations were designed and performed by A. Konovalov. Analytical results were derived by A. Konovalov. The calculations and results were checked, discussed and analyzed by both authors. The article was written by A. Konovalov and G. Morigi.

2.1 ABSTRACT

We derive a master equation for a superradiant medium which includes multilevel interference between the individual scatterers. The derivation relies on the Born-Markov approximation and implements the coarse-graining formalism. The master equation fulfills the Lindblad form and contains terms describing multilevel interference between parallel transitions of a single atom, multiatom interference between identical transitions, and multiatom interference between different electronic transitions with parallel dipoles. This formalism is then applied to determine the excitation spectrum of two emitters using the parameters of the hydrogen transitions $2S_{1/2} \rightarrow 4P_{1/2}$ and $2S_{1/2} \rightarrow 4P_{3/2}$, where the gap between the parallel dipoles is of the order of GHz. The distortion of the signal due to the interplay of multilevel and multiemitter interference is analyzed as a function of their distance. These results suggest that interference between parallel

dipolar transition can significantly affect the spectroscopic properties of optically dense media.

2.2 INTRODUCTION

Superradiance generally denotes a phenomenon which enhances radiation. In quantum optics, it originates from quantum interference in the light emission by an ensemble of atoms, molecules, or other types of resonant emitters which form an optically-dense medium [1–3]. In free space, this requires that the average interparticle distance is smaller than the wavelength of the scattered radiation. Then, the coupling of the individual atomic transitions with the modes of the electromagnetic field can be effectively described in terms of collective dipoles and the radiative properties depend on the collective spin quantum numbers [1]. Superradiant (and subradiant) scattering plays a relevant role in the spectroscopy of dense atomic gases [25, 55–60], it could enhance transport of light in organic semiconductors [61], and it is the key mechanism of recent realizations of ultranarrow lasers [62, 63].

Superradiant light scattering is often described by means of a perturbative expansion in the atom-photon interactions and using the Born-Markov approximation [2–5, 20, 35, 38, 64–66]. Most theoretical treatments focus on two-level dipolar transitions [2–5, 20, 24, 38, 64–66], some also including the possible degeneracy of the ground or excited state of the transition [5, 24, 66]. These treatments successfully predict experimental measurements at sufficiently low optical densities. Qualitative discrepancies have been found when comparing the predictions of these models with recent experiments with dense atomic media [25, 56, 60]. This requires one to assess the effects of terms which are typically discarded or only partially considered.

In this work we derive a master equation for an optically dense medium and set our focus on vacuum-induced interference [6, 21, 67, 68]. Vacuum-induced interference refers to interference phenomena between electronic transitions coupled to common modes of the electromagnetic field. If the transitions are dipolar, they are denoted by parallel dipoles. Interference also occurs when the electromagnetic field modes are in the vacuum, and is qualitatively different from laser-induced interference [69]. In closed level structures, these effects can be tested by means of quantum beat spectroscopy and are expected to give rise to "steady-state quantum beats" [21, 67]. They are also expected to play an important role in high-precision spectroscopy [10, 15, 70, 71]. In this work, we determine the Born-Markov master equation of multilevel scatterers in an optically dense medium and which includes interference terms between parallel dipoles. For this purpose, we derive the master equation by applying the coarse-graining formalism of Refs. [17, 18]. The master equation that we

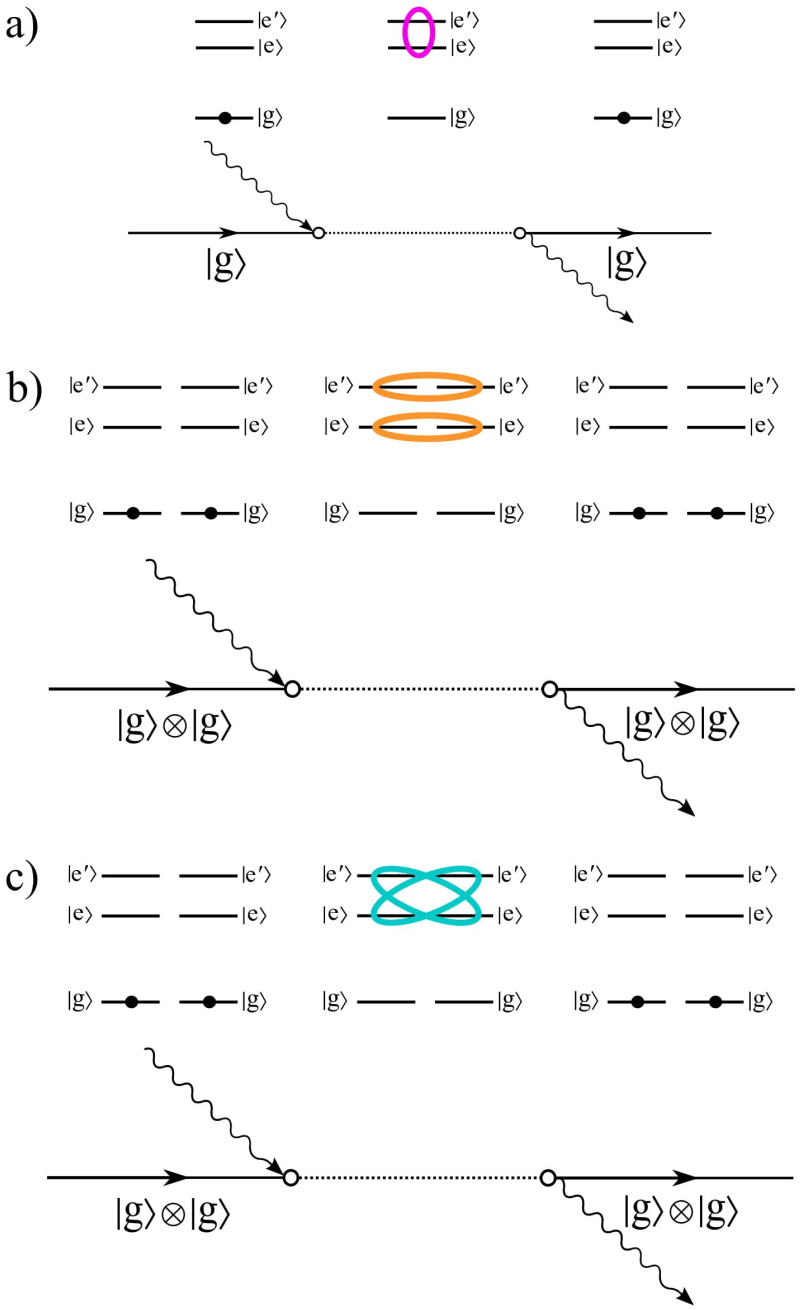

Figure 2.1: Interfering processes leading to photon scattering by resonant emitters. The emitter's relevant states are the ground state $|g\rangle$ and the excited states $|e\rangle$, $|e'\rangle$; the transitions $|g\rangle \rightarrow |e\rangle$ and $|g\rangle \rightarrow |e'\rangle$ have parallel dipole moments. The horizontal lines sketch the scattering processes, the wavy lines the photon, and the level schemes give the corresponding occupation of the emitters' internal levels (dot and circles). The emitters are initially in the ground state (solid line). Photon absorption (first wiggle line) can excite a coherent superposition of (a) the excited states of a single emitter, (b) the resonant states of the two emitters, and (c) different excited states of the two emitters but with parallel dipoles. Photon emission (second wiggle line) projects the emitters in the same final state. In this work, we analyze the spectroscopic features due to the interference of these three processes.

obtain preserves the Lindblad form and, in the limit of one single emitter, it reduces to the coarse-grained master equation of Ref. [15]. We then apply it to determine the excitation spectrum and the light shift of two identical emitters, each composed of two parallel dipoles sharing the same ground state. In this simplified model, we show that collective scattering results from the coherent sum of three processes, which we illustrate in Fig. 2.1: (a) the interference between parallel dipoles of the individual atoms, (b) the interference between resonant transitions of different atoms, and (c) the interference between parallel dipoles of different atoms. Here, we argue that in an optically dense medium, they can give rise to measurable shifts of the spectroscopic lines.

This work is organized as follows. In Sec. 2.3 we present the derivation of the master equation by eliminating the degrees of freedom of the electromagnetic field within the Born-Markov approximation and by implementing the coarse-graining method developed in Ref. [17]. By these means, we obtain a superoperator that fulfills the Lindblad form. This superoperator consistently describes interference processes between parallel dipoles of the individual atoms and interference processes of different atoms. In Sec. 2.4, we then consider the specific example of two emitters, composed of two parallel dipoles sharing the same ground state, and determine their excitation spectrum using the parameters of the transitions $2S_{1/2} \rightarrow 4P_{1/2}$ and $2S_{1/2} \rightarrow 4P_{3/2}$ of a hydrogen atom. By means of a simple fitting function, we argue that the interference effects give rise to measurable shifts of the resonance lines. Finally, in Sec. 2.5, we draw the conclusions and discuss outlooks of this work. The appendices contain details of the calculations in Sec. 2.3 and 2.4.

2.3 DERIVATION OF THE SUPERRADIANT MASTER EQUATION

In this section, we report the derivation of the Born-Markov master equation for an optically dense atomic or molecular medium. Our derivation follows the lines of textbook derivations [2, 6, 20, 35] and we extend it by implementing the coarse-grained method developed in Ref. [17]. This allows us to systematically take into account the interference of parallel dipoles and, at the same time, to preserve the Lindblad form of the master equation. In the single-atom limit, our master equation reproduces the one derived in Ref. [15], which includes the interference processes between parallel dipoles in a single atom.

For convenience, in the following we assume an ensemble of emitters with identical electronic transitions. This formalism, nevertheless, can be straightforwardly extended to ensembles of different particles (which could also be a mixture of atoms and molecules) with quasiresonant transitions. The relevant assumption is that the emitters

are pinned at given positions and are distinguishable particles. Our starting point is the von-Neumann equation governing the coherent dynamics. Below we provide the salient steps leading to the corresponding coarse-grained master equation for the emitters' internal degrees of freedom.

2.3.1 *Multilevel emitters interacting with the quantum electromagnetic field*

We consider N emitters interacting with the modes of the electromagnetic field (EMF) in the volume V. We assume that the particles are pinned at the positions $\vec{R}_\alpha$, with $\alpha = 1, \dots, N$. We denote by $\mathcal{H}$ the Hilbert space of the emitters' internal degrees of freedom and of the EMF's degrees of freedom, $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_R$. The time evolution of the density matrix $\hat{\chi}(t)$, describing the state of photons and emitters, is governed by the von-Neumann equation

$$\partial_t \hat{\chi} = [\hat{H}, \hat{\chi}]/i\hbar\,, \tag{2.1}$$

where $\hat{H}$ is the Hamiltonian determining the dynamics, which we decompose into the sum of the Hamiltonian $\hat{H}_\mathrm{A}$ for the emitters' (internal) degrees of freedom, the Hamiltonian $\hat{H}_\mathrm{R}$ for the free EMF, and the emitter-photon interactions $\hat{V}$:

$$\hat{H} = \hat{H}_\mathrm{A} + \hat{H}_\mathrm{R} + \hat{V}\,. \tag{2.2}$$

We remark here that $\hat{H}_\mathrm{R} \equiv \hat{1}_A \otimes \hat{H}_\mathrm{R}$ and $\hat{H}_\mathrm{A} \equiv \hat{H}_\mathrm{A} \otimes \hat{1}_R$, where $\hat{1}_R$ and $\hat{1}_A$ the identity operators in the Hilbert spaces $\mathcal{H}_\mathrm{R}$ and $\mathcal{H}_\mathrm{A}$, respectively. Thus, we use the same notation for the operator $\hat{H}_{j=A,R}$ defined in the extended Hilbert space $\mathcal{H}$ and in the reduced Hilbert space $\mathcal{H}_j$.

The emitters' Hamiltonian. The emitters Hamiltonian describes the dynamics of the internal degrees of freedom of N emitters,

$$\hat{H}_\mathrm{A} = \sum_{\alpha=1}^{N} \hat{H}_{\mathrm{A}_\alpha}\,,$$

where $\hat{H}_{\mathrm{A}_\alpha}$ is the Hamiltonian of emitter $\alpha = 1, \dots, N$ at position $\vec{R}_\alpha$ and we assume that the size of the center-of-mass wave packet is much smaller than the interparticle distance (in Eq. (2.3), we omit to explicitly write that $\hat{H}_{\mathrm{A}_\alpha}$ is the identity operator in the Hilbert space of the emitters with $\beta \neq \alpha$). We consider here only the lowest electronic bound states assuming that the system is at room temperature. The spectrum of each emitter is discrete and the Hamiltonian in diagonal form reads

$$\hat{H}_{\mathrm{A}_\alpha} = \sum_n E_n |n\rangle_\alpha \langle n|\,, \tag{2.3}$$

with E_n the eigenvalue and $|n\rangle_\alpha$ the corresponding eigenvector for the emitter at the position $\vec{R}_\alpha$. In a more general treatment, where

the emitters might not be identical and/or in the presence of spatial inhomogeneity, the energy also depends on the label α.

The quantum electromagnetic field. We treat the EMF in second quantization and choose the Coulomb gauge. We denote the quantization volume by V and assume periodic boundary conditions. The energy of the field relative to the vacuum energy reads

$$\hat{H}_{\mathrm{R}} = \sum_{\lambda} \hbar\omega_{\lambda} \hat{a}_{\lambda}^{\dagger} \hat{a}_{\lambda} \,, \tag{2.4}$$

where λ denotes the sum over the EMF modes and the sum has an upper cutoff given by the energy $\hbar\omega_{\mathrm{cut}} \sim mc^2$, with m the electron mass. The modes here are traveling waves and are fully characterized by the wave vector $\vec{k}_{\lambda}$ and by the transverse polarization $\vec{e}_{\lambda}$, with the frequency $\omega_{\lambda} = c|\vec{k}_{\lambda}|$ and c the speed of light in vacuum. Operators $\hat{a}_{\lambda}$ and $\hat{a}_{\lambda}^{\dagger}$ annihilate and create, respectively, a photon of mode λ, and fulfill the bosonic commutation relations $[\hat{a}_{\lambda}, \hat{a}_{\lambda'}^{\dagger}] = \delta_{\lambda,\lambda'}$ and $[\hat{a}_{\lambda}, \hat{a}_{\lambda'}] = 0$.

The initial state of the EMF field is assumed to be given by the thermal distribution

$$\hat{R} = \exp\left(-\hat{H}_{\mathrm{R}}/k_B T\right)/Z \,, \tag{2.5}$$

where k_B is Boltzmann's constant, T is the temperature, and $Z = \mathrm{Tr}\{\exp\left(-\hat{H}_{\mathrm{R}}/k_B T\right)\}$ is the partition function. Within the validity of the Born approximation, $\hat{R}$ gives the state of the EMF at all times. Here we assume room temperatures, $T \sim 300\,\mathrm{K}$.

Emitter-photon interactions. Here, emitter-photon interactions are treated in the electric-dipole approximation. Operator $\hat{V}$ is the sum of the interactions of the fields with each emitter, $\hat{V} = \sum_{\alpha=1}^{N} \hat{V}_{\alpha}$, with

$$\hat{V}_{\alpha} = \hbar \sum_{n} \hat{\Gamma}_{n}^{\alpha} \hat{\sigma}_{n}^{\alpha} \,, \tag{2.6}$$

where the sum is over all pairs of electronic levels $n = (n_1, n_2)$ coupled by an electric-dipole transition. Here, operator $\hat{\sigma}_{n}^{\alpha}$ describes the transition between $|n_1\rangle_{\alpha}$ and $|n_2\rangle_{\alpha}$:

$$\hat{\sigma}_{n}^{\alpha} \equiv |n_1\rangle_{\alpha}\langle n_2| \,.$$

The corresponding coupling strength is determined by the coupling operator $\hat{\Gamma}_{n}^{\alpha}$, which acts over the degrees of freedom of the electromagnetic field and reads

$$\hat{\Gamma}_{n}^{\alpha} = \sum_{\lambda} \left(g_{n}^{\alpha\lambda} \hat{a}_{\lambda} e^{i\vec{k}_{\lambda}\vec{R}_{\alpha}} + \bar{g}_{n}^{\alpha\lambda} \hat{a}_{\lambda}^{\dagger} e^{-i\vec{k}_{\lambda}\vec{R}_{\alpha}} \right) . \tag{2.7}$$

The coupling strengths $g_{n}^{\alpha\lambda}$ have the dimensions of a frequency and are given below in gauss units and in the length gauge,

$$g_{n}^{\alpha\lambda} = -i\sqrt{\frac{2\pi\omega_{\lambda}}{\hbar V}}\, \vec{d}_{n}^{\alpha} \cdot \vec{e}_{\lambda} \,, \tag{2.8}$$

$$\bar{g}_{n}^{\alpha\lambda} = i\sqrt{\frac{2\pi\omega_{\lambda}}{\hbar V}}\, \vec{d}_{n}^{\alpha} \cdot (\vec{e}_{\lambda})^{*} \,, \tag{2.9}$$

with $\vec{d}_n^{\alpha}$ the dipole moment of the transition, which is the matrix element of the dipole operator $\hat{\vec{d}}_\alpha$ and reads $\vec{d}_n^{\alpha} = {}_\alpha\langle n_1|\hat{\vec{d}}_\alpha|n_2\rangle_\alpha$. We remark that this description applies the long-wave approximation, and thus it is valid when the size of the electronic wave packet is smaller than the optical wavelength. Moreover, in our model, we did not include the self-energy which appears in the length gauge (see Refs. [72, 73] for an insightful discussion).

For later convenience, we introduce the frequency ω_n,

$$\omega_n = (E_{n_1} - E_{n_2})/\hbar\,. \tag{2.10}$$

By definition, it can also take negative values.

2.3.2 *Master equation for an ensemble of multilevel emitters*

We now proceed to derive the Born-Markov master equation using the coarse-grained formalism. The procedure repeats, in the essential steps, the one of Ref. [15], with some notable differences due to the many-body nature of the problem.

We first introduce the density matrix $\hat{\rho}(t)$ describing the state of the emitters at time t. Operator $\hat{\rho}(t)$ is defined in the Hilbert space $\mathcal{H}_\mathrm{A}$ and is related to the density matrix $\hat{\chi}(t)$ by the equation $\hat{\rho}(t) = \mathrm{Tr}_R\{\hat{\chi}(t)\}$, where Tr_R denotes the partial trace over the degrees of freedom of the EMF.

We now consider the von Neumann equation, given by Eq. (2.1), and move to the interaction picture with respect to Hamiltonian $\hat{H}_0 = \hat{H}_\mathrm{A} + \hat{H}_\mathrm{R}$. We denote the system's density matrix in the interaction picture by

$$\tilde{\chi}(t) = \hat{U}_0(t)^\dagger \hat{\chi}(t)\hat{U}_0(t)\,, \tag{2.11}$$

where we have introduced the unitary operator $\hat{U}_0(t) = \exp(\hat{H}_0 t/(\mathrm{i}\hbar))$. In this representation, the reduced density matrix of the system is related to the reduced density matrix in the Schrödinger picture by the relation:

$$\tilde{\rho}(t) = \mathrm{Tr}_R\{\tilde{\chi}(t)\} = \mathrm{e}^{-\hat{H}_\mathrm{A}t/(\mathrm{i}\hbar)}\hat{\rho}(t)\mathrm{e}^{\hat{H}_\mathrm{A}t/(\mathrm{i}\hbar)}\,.$$

In the interaction picture the unitary operator determining the time evolution reads

$$\tilde{U}(t,t') = \mathcal{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_t^{t'} dt_1 \tilde{V}(t_1)\right)\,, \tag{2.12}$$

where $\tilde{V}(t) = \hat{U}_0(t)^\dagger \hat{V}\hat{U}_0(t)$ and $\mathcal{T}$ denotes the time ordering, such that

$$\mathcal{T}\tilde{V}(t_1)\tilde{V}(t_2) = \tilde{V}(t_1)\tilde{V}(t_2)\theta(t_1 - t_2) + \tilde{V}(t_2)\tilde{V}(t_1)\theta(t_2 - t_1)\,,$$

with $\theta(t)$ the Heaviside function. Using this formalism, at $t' > t$ the state $\hat{\tilde{\chi}}(t)$ evolves into state

$$\tilde{\chi}(t') = \tilde{U}(t,t')\tilde{\chi}(t)\tilde{U}(t,t')^\dagger\,. \tag{2.13}$$

2.3.2.1 *Dyson equation and Born-Markov approximation*

Let now $\Delta t = t' - t > 0$ denote a finite and sufficiently small time step, which we quantify later. We write the Dyson series of the right-hand side of Eq. (2.13) until the second order in the interaction, but keep the exact form. After tracing out the EMF degrees of freedom, we obtain the expression

$$\tilde{\rho}(t+\Delta t) = \tilde{\rho}(t) + \Delta t \sum_{\alpha} \Lambda_1^{\alpha} \tilde{\rho}(t) + \Delta t \sum_{\alpha,\beta} \frac{1}{\Delta t} \int_{t-\Delta t}^{t+\Delta t} \mathrm{d}T \int_{-\Delta t}^{\Delta t} \mathrm{d}\tau \theta(\tau) \Lambda_2^{\alpha,\beta}(T,\tau) \tilde{\rho}(T-\tau) \,. \quad (2.14)$$

The terms Λ_1^{α}, Λ_2^{α} on the RHS are linear maps, and the subscript indicates the order in the Dyson expansion. In deriving Eq. (2.14), we have made the Born approximation at the initial time t, namely, we have assumed that there are no quantum correlations at time t between EMF and emitter. This corresponds to writing $\tilde{\chi}(t) = \hat{R} \otimes \tilde{\rho}(t)$ where $\hat{R}$ is the thermal state of the EMF, given by Eq. (2.5).

The map Λ_1^{α} acts over the Hilbert space of the emitter α and is given by

$$\begin{aligned} \Lambda_1^{\alpha} \tilde{\rho}(t) &= \frac{1}{\mathrm{i}\hbar \Delta t} \int_t^{t+\Delta t} dt_1 \mathrm{Tr}_{\mathrm{R}} \left\{ \left[\tilde{V}_{\alpha}(t_1), \tilde{\chi}(t) \right] \right\} \\ &= \frac{1}{\mathrm{i}\hbar} \left[\langle \tilde{V}_{\alpha}(t) \rangle_{\mathrm{R}}, \tilde{\rho}(t) \right] , \end{aligned} \quad (2.15)$$

where, between the first and the second line, we have applied the Born approximation and introduced the time-averaged operator (here in interaction picture):

$$\langle \tilde{V}_{\alpha}(t) \rangle_{\mathrm{R}} = \frac{1}{\Delta t} \int_t^{t+\Delta t} \mathrm{Tr}_{\mathrm{R}} \left\{ \tilde{V}_{\alpha}(t_1) \hat{R} \right\} . \quad (2.16)$$

Note that operator $\hat{V}_{\alpha}$, given by Eq. (2.6), vanishes over the thermal state of the EMF, given by Eq. (2.5). The second integrand of Eq. (2.14) contains the Heaviside function $\theta(\tau)$ and also includes the coupling between different emitters. Its detailed form is reported in Appendix 2.7.1.

Equation (2.14) is generally valid for sufficiently short time intervals Δt, over which one can assume that the Born approximation holds. After some time, in fact, the interactions establish quantum correlations between system and reservoir. These correlations can be neglected when the interactions can be treated perturbatively.

The master equation becomes local in time when the Markov approximation holds. The Markov approximation consists in approximating $\tilde{\rho}(T-\tau) \approx \tilde{\rho}(t)$ in Eq. (2.38). It is equivalent to the Wigner-Weisskopf approximation for the propagator [72] and is justified when the characteristic time scale τ_R of the correlation function $C_{\alpha\beta}(\tau)$, given by

Eq. (2.40), is orders of magnitude smaller than the system's relaxation time. In a thermal bath, the correlation function is composed of a term which decays exponentially with the correlation time, $\tau_R = \hbar/k_B T$, and by power-law tails that can be discarded for typical evolution times [47, 72]. At room temperatures, $T \sim 300$ K, this time is of the order of $\tau_R \sim 10^{-13}$ sec. This time shall be compared with the relaxation time of the system. For optical transitions, the natural linewidth of a single atom, $\gamma \sim 2\pi \times 10^6 - 10^8$ Hz, fulfills $\gamma\tau_R \ll 1$. In this limit, we can choose the time scale Δt such that $\tau_R \ll \Delta t \ll 1/\gamma$ and ignore memory effects in the integral.

In the presence of dipole-dipole interactions, there are some issues to be considered: in first place, superradiance gives rise to an N-fold enhancement of the single atom decay rate, and thus when $N\gamma$ becomes comparable with $1/\tau_R$, the approximation becomes invalid. This is the regime where one can observe the Dicke phase transition in an ensemble of two-level systems [74], and where the assumptions at the basis of this treatment break down. At the same time, subradiant states can be characterized by extremely small linewidths. Observing their decay requires one to analyze the system's dynamics over long time scales, over which the power-law tails of the correlation function can become important. These considerations suggest that the formalism shall be revisited for media with very high optical dense media.

2.3.2.2 *Coarse-grained master equation*

In what follows, we assume an optically dense medium for which the Born-Markov approximation is valid. Then, from Eq. (2.14), we derive the Born-Markov master equation (now back in the Schrödinger picture):

$$\partial_t \hat{\rho} = \frac{1}{\mathrm{i}\hbar}[\hat{H}_A + \hat{H}_S, \hat{\rho}(t)] + \mathcal{L}_D \hat{\rho}(t)\,, \tag{2.17}$$

where Hamiltonian $\hat{H}_S$ and superoperator (dissipator) $\mathcal{L}_D$ contain both the single-atom as well as the interatomic interference terms between parallel dipoles. The details of the derivation are standard and are reported in Appendix 2.7.1. The master equation is valid for any time $t > 0$ within a grid whose resolution is determined by the coarse-grained timescale Δt. As a consequence, the coefficients multiplying the terms of the operator $\hat{H}_S$ and the superoperator $\mathcal{L}_D$ are scaled by the function

$$\Theta_{ij}^{(\Delta t)} = \frac{\sin((\omega_i + \omega_j)\Delta t/2)}{(\omega_i + \omega_j)\Delta t/2}\,. \tag{2.18}$$

This term selects transitions which are resonant within the resolution set by the coarse-graining time Δt. For optical transitions, this factor selects a pair of frequencies ω_i and ω_j with opposite signs. Correspondingly, it selects terms in the Hamiltonian and dissipator

where the pairs of operators $\hat{\sigma}_i^{\alpha}\hat{\sigma}_j^{\beta}$ describe an excitation and a deexcitation along two (quasi)resonant transitions. For convenience, we introduce the operator $\hat{\zeta}_i^{\alpha\dagger} \equiv \hat{\sigma}_i^{\alpha}$, which describes a transition $i_2 \to i_1$ with $\bar{\omega}_i = \omega_i > 0$ and dipole moment $\vec{D}_i^{\alpha *} = \vec{d}_i^{\alpha}$. Then, the operators appearing in the master equation are of the form $\hat{\zeta}_i^{\alpha\dagger}\hat{\zeta}_j^{\beta}$ or $\hat{\zeta}_i^{\alpha}\hat{\zeta}_j^{\beta\dagger}$, and the factor (2.19) now reads

$$\Theta_{ij}^{(\Delta t)} = \frac{\sin((\bar{\omega}_i \pm \bar{\omega}_j)\Delta t/2)}{(\bar{\omega}_i \pm \bar{\omega}_j)\Delta t/2}\,. \tag{2.19}$$

In what follows, we discard the processes where two transitions are simultaneously excited or deexcited, corresponding to the $+$ sign in the argument of Eq. (2.19).

Hamilton operator. The Hamiltonian term due to the interaction with the EMF is given by the expression

$$\hat{H}_S = \sum_{\alpha}\langle \hat{V}_{\alpha}\rangle_R + \frac{1}{2}\sum_{\alpha,\beta}\hat{H}_{\alpha\beta}^S\,,$$

where $\langle \hat{V}_{\alpha}\rangle_R$ is given in Eq. (2.16) and is now reported in the Schrödinger picture. This latter term vanishes since we assume that the EMF is in the thermal state. The Hamilton operator $\hat{H}_{\alpha\beta}^S$ contains the frequency shifts and couplings due to the multilevel interference, and is derived from the expression (here given in the interaction picture)

$$\begin{aligned}\tilde{H}_{\alpha\beta}^S \;=\; & -\frac{\mathrm{i}}{2\hbar\Delta t}\int_t^{t+\Delta t}\mathrm{d}t_1\int_t^{t+\Delta t}\mathrm{d}t_2 \\ & \times\theta(t_1-t_2)\mathrm{Tr}_R\left\{[\tilde{V}_{\alpha}(t_1),\tilde{V}_{\beta}(t_2)]R(t)\right\} + \mathrm{H.c.}\end{aligned} \tag{2.20}$$

For $\alpha = \beta$, it is the Hamilton operator for a single atom and it coincides with the operator derived in Ref. [15]. For $\alpha \neq \beta$, it describes the Hamiltonian terms due to the dipole-dipole interactions, including the interference between all parallel transitions of different atoms. We report it in the form which includes both cases,

$$\begin{aligned}\hat{H}_{\alpha\beta}^S = -\hbar\sum_{i,j} \quad & \Big[\left(\Delta_{ij}^{\alpha\beta-} + \Delta_{ij}^{\alpha\beta(T)}\right)\hat{\zeta}_i^{\alpha\dagger}\hat{\zeta}_j^{\beta} \\ & + \left(\Delta_{ij}^{\alpha\beta+} - \Delta_{ij}^{\alpha\beta(T)}\right)^*\hat{\zeta}_i^{\alpha}\hat{\zeta}_j^{\beta\dagger}\Big] + \mathrm{H.c.},\end{aligned} \tag{2.21}$$

where $\Delta_{ij}^{\alpha\beta(T)} = \Delta_{ij}^{\alpha\beta-}(T) - \Delta_{ij}^{\alpha\beta+}(T)$ and the individual coefficients read (below in gauss units)

$$\Delta_{ij}^{\alpha\beta\pm} = \Theta_{ij}^{(\Delta t)}\frac{\vec{D}_i^{\alpha *}\cdot\vec{D}_j^{\beta}}{(2\pi)^2\hbar c^3}\mathcal{P}\int_0^{\omega_{\mathrm{cut}}}\frac{d\omega\,\omega^3}{\omega\pm\omega_{ij}}F_{\alpha\beta}^{ij}(\vec{R}_{\alpha\beta}), \tag{2.22}$$

$$\Delta_{ij}^{\alpha\beta\pm}(T) = \Theta_{ij}^{(\Delta t)}\frac{\vec{D}_i^{\alpha *}\cdot\vec{D}_j^{\beta}}{(2\pi)^2\hbar c^3}\mathcal{P}\int_0^{\omega_{\mathrm{cut}}}\frac{d\omega\,\omega^3 n(\omega,T)}{\omega\pm\omega_{ij}}F_{\alpha\beta}^{ij}(\vec{R}_{\alpha\beta})\,. \tag{2.23}$$

Here, $\mathcal{P}$ denotes the Cauchy principal value and ω_{cut} is the cutoff frequency. The frequency

$$\omega_{ij} = \frac{\bar{\omega}_i + \bar{\omega}_j}{2}$$

is the average between the two transition frequencies, and the coefficient $F^{ij}_{\alpha\beta}(\vec{R}_{\alpha\beta})$ depends also on the distance $\vec{R}_{\alpha\beta} = \vec{R}_\alpha - \vec{R}_\beta$ between the atoms and on the wave number $k = \omega/c$. It takes the form[1]

$$F^{ij}_{\alpha\beta}(\vec{R}_{\alpha\beta}) = 4\pi \left(j_0(kR_{\alpha\beta}) \left[1 - \frac{(\vec{D}^\alpha_i \cdot \vec{R}_{\alpha\beta})^* (\vec{D}^\beta_j \cdot \vec{R}_{\alpha\beta})}{D^\alpha_i D^\beta_j R^2_{\alpha\beta}} \right] - \frac{j_1(kR_{\alpha\beta})}{kR_{\alpha\beta}} \left[1 - \frac{3(\vec{D}^\alpha_i \cdot \vec{R}_{\alpha\beta})^* (\vec{D}^\beta_j \cdot \vec{R}_{\alpha\beta})}{D^\alpha_i D^\beta_j R^2_{\alpha\beta}} \right] \right) , \tag{2.24}$$

where we used the notation $D^\alpha_i = |\vec{D}^\alpha_i|$ and $R_{\alpha\beta} = |R_{\alpha\beta}|$. Here, $j_0(x)$ and $j_1(x)$ are spherical Bessel functions of the first type [75]. The dependence on the vector joining the two atoms breaks the spherical symmetry and is at the origin of the anisotropic light emission of superradiance [2]. For the case of one atom, $N = 1$, one has $F^{ij}_{\alpha\alpha}(0) = 8\pi/3$ [20], and Hamiltonian of Eq. (2.21) takes the form of the single-atom Hamiltonian of Ref. [15].

Dissipator. The Lindblad term $\mathcal{L}_D$ describes the incoherent processes. It can be decomposed into the sum

$$\mathcal{L}^D \hat{\rho}(t) = \sum_{\alpha,\beta} \mathcal{L}^{\alpha\beta}_D \hat{\rho}(t) , \tag{2.25}$$

where the terms with $\alpha = \beta$ describe the dissipation of N non-interacting atoms, while the terms with $\alpha \neq \beta$ originate from multiple scattering of resonant photons and vanish when the distance between the atoms exceeds several wavelengths. The individual terms are obtained from the expression in the interaction picture,

$$\tilde{\mathcal{L}}^{\alpha\beta}_D \tilde{\rho}(t) = \frac{1}{2\hbar^2 \Delta t} \int_t^{t+\Delta t} \mathrm{d}t_1 \int_t^{t+\Delta t} \mathrm{d}t_2 \mathrm{Tr}_R \left\{ \mathcal{A}(t_1, t_2) \right\} ,$$

where

$$\begin{aligned} \mathcal{A}(t_1, t_2) \;=\; & 2\tilde{V}_\beta(t_1)[\tilde{\rho}(t) \otimes \tilde{R}(t)]\tilde{V}_\alpha(t_2) \\ & -[\tilde{V}_\alpha(t_1)\tilde{V}_\beta(t_2), \tilde{\rho}(t) \otimes \tilde{R}(t)]_+ \end{aligned}$$

1 Here it is written specifically for the non-orthogobal dipoles

and $[,]_+$ denotes the anticommutator. After performing the integration and going back to the Schrödinger picture, the individual terms take the form

$$\begin{aligned}\mathcal{L}_D^{\alpha\beta}\hat{\rho}(t) &= \sum_{i,j}(1+n(\omega_{ij},T)) \\ &\quad\times\left(\frac{\Gamma_{\alpha\beta}^{ij}}{2}\left[\hat{\zeta}_j^{\beta}\hat{\rho}(t),\hat{\zeta}_i^{\alpha\dagger}\right]+\frac{\Gamma_{\alpha\beta}^{ij}}{2}\left[\hat{\zeta}_j^{\beta},\hat{\rho}(t)\hat{\zeta}_i^{\alpha\dagger}\right]\right) \\ &+ \sum_{i,j} n(\omega_{ij},T) \\ &\quad\times\left(\frac{\Gamma_{\alpha\beta}^{ij*}}{2}\left[\hat{\zeta}_j^{\beta\dagger}\hat{\rho}(t),\hat{\zeta}_i^{\alpha}\right]+\frac{\Gamma_{\alpha\beta}^{ij*}}{2}\left[\hat{\zeta}_j^{\beta\dagger},\hat{\rho}(t)\hat{\zeta}_i^{\alpha}\right]\right), \quad (2.26)\end{aligned}$$

with the damping coefficients

$$\Gamma_{\alpha\beta}^{ij}=\Theta_{ij}^{(\Delta t)}\frac{\vec{D}_i^{\alpha*}\cdot\vec{D}_j^{\beta}}{2\pi\hbar c^3}\omega_{ij}^3F_{\alpha\beta}^{ij}(k_{ij}), \quad (2.27)$$

and $k_{ij}=\frac{\omega_{ij}}{c}$. We note that for $i\neq j$, the damping coefficients are different from zero if the scalar product $\vec{D}_i^{\alpha*}\cdot\vec{D}_j^{\beta}\neq 0$. Master equation (2.17) fulfills the Lindblad form and take into account the multilevel structure of the quantum emitters.

2.3.2.3 *Discussion*

We first review the dynamics that the master equation (2.17) predicts for a very dilute ensemble of emitters ($R_{\alpha\beta}\to\infty$), when it is well approximated by N independent experiments with a single atom. In this case, the damping coefficients $\Gamma_{\alpha\alpha}^{ii}$ are the Einstein coefficients of spontaneous emission. For $i\neq j$, instead, the coefficients $\Gamma_{\alpha\alpha}^{ij}$ describe processes where two different transitions with parallel dipoles are simultaneously deexcited. These transitions shall be resonant within the frequency resolution of the coarse graining $1/\Delta t$. This process, even though incoherent, is a quantum interference between spectral lines [15, 21, 68, 70]. The corresponding terms have been denoted by cross-damping terms in the literature [10, 71]. These dynamics have a corresponding Hermitian component in the Hamiltonian term $\hat{H}_S^{\alpha\alpha}$. The coefficients include an energy shift of the electronic states due to the vacuum fluctuations, which for the ground state is the non-relativistic Lamb shift, as well as a shift due to thermal fluctuations of the EMF. Vacuum and thermal fluctuations also give rise to an effective coupling between electronic levels with parallel dipoles and quasiresonant frequencies; the coupling coefficients are given by Eqs. (2.22)-(2.23) after setting $\alpha=\beta$. They can be estimated by using the approximate relation [15]

$$\Delta_{ij}^{\alpha\alpha\pm}\approx\frac{1}{2}(\vec{D}_i^{\alpha*}\cdot\vec{D}_j^{\alpha})\Theta_{ij}^{(\Delta t)}\left(\frac{1}{|\vec{D}_i^{\alpha}|^2}\Delta_{ii}^{\alpha\alpha\pm}+\frac{1}{|\vec{D}_j^{\alpha}|^2}\Delta_{jj}^{\alpha\alpha\pm}\right). \quad (2.28)$$

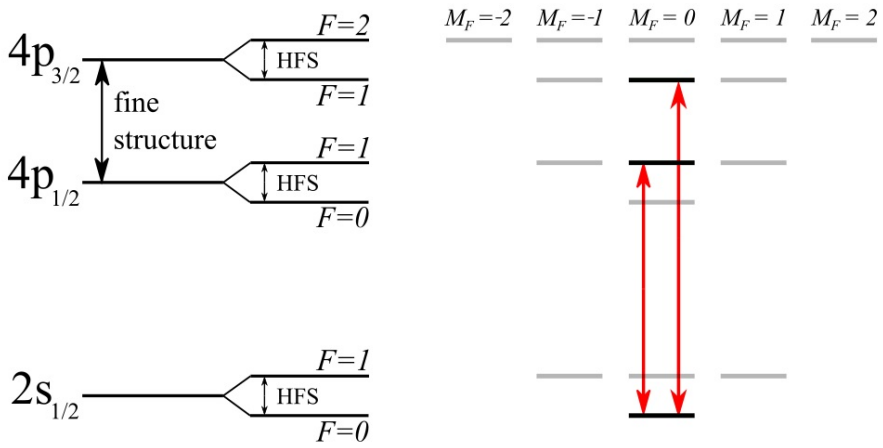

Figure 2.2: The structure of electronic states 2S and 4P of the hydrogen atom (left panel) and the transitions we consider in the numerical simulations of this work (right panel): The three states which we consider in this work are marked with the black colour, the scattering transitions are indicated by the red (gray) arrows.

When the interparticle distances are comparable with the wavelength, namely, for $\alpha \neq \beta$, Eq. (2.17) is the master equation for optically dense media which now includes quantum interference between transitions with parallel dipoles. Keeping only the terms with $i = j$, one obtains the master equation discussed in the literature [2, 3, 5, 24], where the dissipator gives rise to phenomena such as superradiance and subradiance, while the coherent part describes coherent dipole-dipole interaction, including frequency shifts such as the so-called collective Lamb shift [3, 59, 76, 77]. Our derivation highlights, in addition, the existence of interference terms between quasi-resonant transitions of different atoms with parallel dipoles both in the incoherent as well as in the coherent parts of the master equation.

We finally remark that by taking the limit $\Delta t \to 0$, then for an infinitesimally small coarse-grained timescale, the function (2.19) becomes a Dirac delta function. Then, the coarse-grained master equation reduces to the Born-Markov master equation, discussed, for instance, in Refs. [20, 72, 78]. In this limit, however, one discards effects due to the finite timescale of the reservoir dynamics, and thus interference phenomena between parallel transitions which are close in frequency but not exactly resonant. The coarse-graining master equation allows one to include these dynamics in a systematic way. We refer the interested reader to Refs. [15, 17, 35, 79] for discussions on the coarse-grained master equation and to the next section for a discussion of the choice of Δt.

2.4 EXCITATION SPECTRUM OF TWO EMITTERS

We now determine the excitation spectrum of two emitters, which are pinned at the positions $\vec{R}_1 = 0$ and $\vec{R}_2 = \vec{R}$ and are uniformly driven by a linearly polarized laser. Their electronic configuration is composed of three electronic levels of hydrogen, which consists of the ground state $|1\rangle$ and the two excited states $|2\rangle$ and $|3\rangle$. The transitions $|1\rangle \to |2\rangle$ and $|1\rangle \to |3\rangle$ are parallel optical dipoles with moments $\vec{D}^{\alpha}_{12}$ and $\vec{D}^{\alpha}_{13}$, respectively, and the transition frequencies are denoted by ω_{12} and ω_{13} (from now on, $\bar{\omega}_{1e} = \omega_{1e} > 0$ with $e = 2, 3$). The reduced level structure allows us to highlight the effects of multilevel interference. Despite the fact we consider the parameters of two transitions of the hydrogen atoms, however, the choice we perform breaks the rotational symmetry of the atoms. This shall be kept in mind when discussing the single-emitter properties.

The dynamics induced by the laser is described by a Hamiltonian term, which is added to the Hamilton operator of Eq. (2.17). This procedure corresponds to assuming that the laser field is described by a coherent state and to moving to the reference frame where the quantum state of the laser field is in the vacuum [80]. We denote by ω_L the laser frequency, and assume that the laser polarization is linear and that the spatial dependence of the laser field wave vector $\vec{k}_L$ is orthogonal to the vector $\vec{R}$ joining the two emitters. The laser-atom Hamiltonian has the form

$$\hat{H}_L = -\hbar \sum_{\alpha=1,2} \sum_{e=2,3} g^{\alpha}_{1e} e^{-i\omega_L t} \hat{\zeta}^{\alpha\dagger}_{1e} + \text{H.c.}\,, \tag{2.29}$$

where we have introduced the Rabi frequency $g^{\alpha}_{1e} = -\vec{d}^{\alpha}_{1e} \cdot \vec{E}_L/2\hbar$, which depends on the electric field amplitude $\vec{E}_L$. The master equation takes the form

$$\partial_t \hat{\rho} = \frac{1}{i\hbar}[\hat{H}_A + \hat{H}_S, \hat{\rho}(t)] + \mathcal{L}_D \hat{\rho}(t) + \frac{1}{i\hbar}[\hat{H}_L, \hat{\rho}]\,, \tag{2.30}$$

where now the sums over the atoms run to $N = 2$ and the sums over the internal transitions include just the two transitions with parallel dipolar moments. For simplicity, thus, we can now replace the sum over the transitions $i = i_1, i_2$ with the sum over the excited state $e = 2, 3$. Using the simplified level structure, we simplify the Hamiltonian term $\hat{H}^S_{12}$, given by Eq. (2.21), as follows:

$$\hat{H}^S_{12} = -\sum_{e,e'=2}^{3} \mathcal{F}_c(\omega_{1e} + \omega_{1e'}) \Xi^F_{e\,e'}(\vec{R}) \hat{\zeta}^{1\dagger}_{1e} \hat{\zeta}^{2}_{1e'} + \text{H.c.}\,, \tag{2.31}$$

where $\mathcal{F}_c(\omega_{1e} + \omega_{1e'})$ is obtained by means of a smoothening of the fast-oscillating function $\Theta^{(\Delta t)}_{ij}$ (see Ref. [15] and Sec. 2.4.3), and

$$\Xi^F_{e\,e'}(\vec{R}) = \vec{D}_{1e} \cdot \vec{D}_{1e'} \left(\frac{\omega_{e\,e'}}{c}\right)^3 \left(y_0(kR) - \frac{y_1(kR)}{kR}\right). \tag{2.32}$$

Here we used that the atomic dipole moments are real vectors and introduced the notation $\omega_{e\,e'} = (\omega_{1e} + \omega_{1e'})/2$. Moreover, we have used that the dipole moments are orthogonal to the vector connecting the two atoms. When the interference between different transitions is discarded, $\mathcal{F}_c(\omega_{1e} + \omega_{1e'}) = \delta_{e,e'}$ and this term takes the form of the collective Lamb shift of Ref. [5] for the corresponding laser excitation.

In the dissipator's coefficient, we also use the smoothening procedure by replacing $\Theta_{ij}^{(\Delta t)}$ with $\mathcal{F}_c(\omega_i + \omega_j)$. Moreover, we discard the temperature-dependent terms since they give negligibly small contribution at $T = 300$ K and optical frequencies.

2.4.1 *Photon-count signal*

In order to study the effect of multilevel interference, we determine the excitation spectrum $S(\delta_L)$ over the whole solid angle and as a function of the laser detuning $\delta_L = \omega_L - \omega_{12}$. The excitation spectrum (or photon-count signal) is defined as:

$$S(\delta_L) = \sum_{\alpha,\beta} \sum_{e,e'} \Gamma_{\alpha\beta}^{e\,e'\,F} \mathrm{Tr}[\hat{\zeta}_{1e'}^{\beta} \hat{\rho}_{\mathrm{st}} \hat{\zeta}_{1e}^{\alpha\,\dagger}] \,, \tag{2.33}$$

and it is calculated for the steady-state density matrix $\hat{\rho}_{\mathrm{st}}$, which is the solution of Eq. (2.17) at eigenvalue zero, $\partial_t \hat{\rho}_{\mathrm{st}} = 0$. In our simulations, we take the parameters of the transition 2S→4P of hydrogen. Specifically, the ground state is $|1\rangle = |2s_{\frac{1}{2}}, F = 0, M_F = 0\rangle$, and the excited states are $|2\rangle = |4p_{\frac{1}{2}}, F = 1, M_F = 0\rangle$ and $|3\rangle = |4p_{\frac{3}{2}}, F = 1, M_F = 0\rangle$, as illustrated in Fig. 2.2. Further details of the parameters are given in Appendix 2.7.2. The coefficients are calculated taking a coarse-grained timescale $\Delta t = 10^{-11}$ sec (see Sec. 2.4.3 for the analysis of the dependence of the results on the choice of the coarse-graining timescale). For further details, we refer the reader to the discussion at the end of this section. We note that for the level scheme which breaks rotational symmetry, the excitation spectrum of a single emitter exhibits nonvanishing shifts even after integration over the whole solid angle [15].

Figure 2.3 displays the photon-count signal (cyan line) for a given value of the laser intensity and as a function of the laser detuning δ_L for two interatomic distances: (a) $R = 0.01\,\mu$m and (b) $R = 0.1\,\mu$m. These shall be compared with the wavelength $\lambda_{12} = 2\pi c/\omega_{12} = 0.468\,\mu m$ such that (a) corresponds to $kR \simeq 0.13$ and (b) to $kR \simeq 1.3$. The blue line gives the signal obtained when one artificially sets the multilevel interference effects to zero (corresponding to setting $\Theta_{ij}^{(\Delta t)} \to \delta(\bar{\omega}_i - \bar{\omega}_j)$, namely $\Delta t \to 0$). The mismatch between the cyan and the blue superradiant peaks is caused by the cross-interference terms.

We start with discussing the case $R = 0.1\,\mu$m, when the interatomic distance is of the order of the wavelength. In this case, the photon-

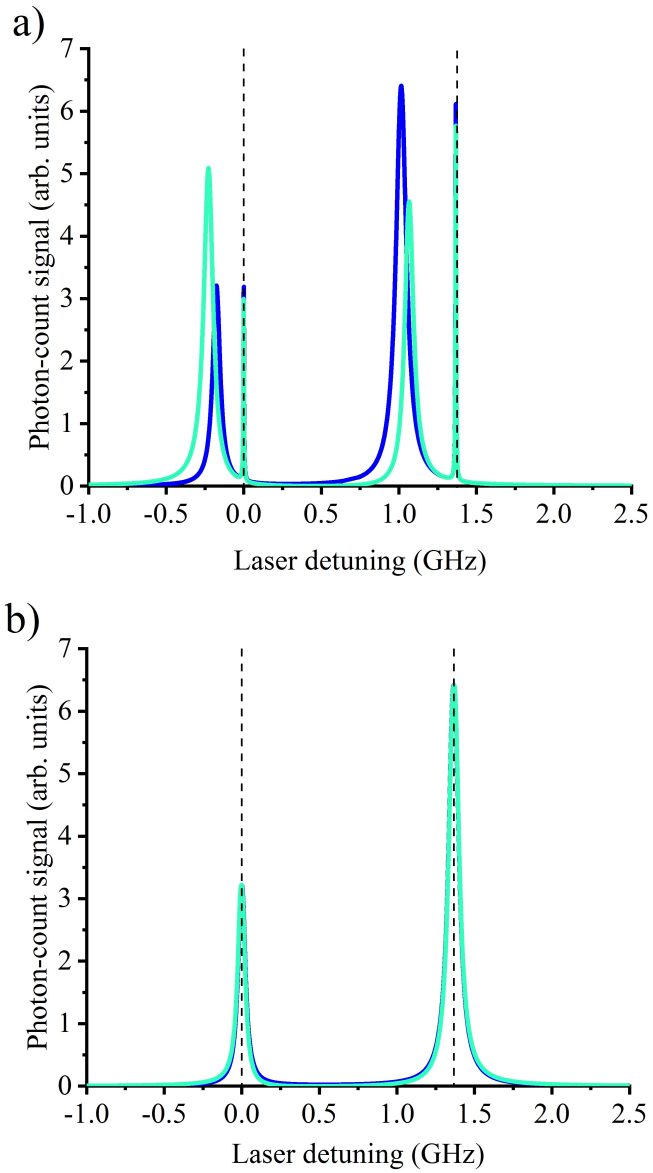

Figure 2.3: Photon-count signal, given by Eq. (2.33), for two emitters as a function of the laser detuning δ_L and at interatomic distance (a) $R = 0.01\,\mu$m and (b) $R = 0.1\,\mu$m. The cyan (light-gray) curve is calculated with the full master equation (2.17). The blue (dark-gray) curve is calculated by setting all cross-interference terms to zero in Eq. (2.17). The Rabi frequency for the $|1\rangle \to |3\rangle$ transition is $g_{13} = 20\,\gamma_3$, where γ_3 is the decay rate from the state $4P_{3/2}^{F=1}$ to the state $2S_{1/2}^{F=0}$. The coarse-graining time is taken to be $\Delta t = 10^{-11}$ sec. The vertical dashed lines indicate the frequency ω_{12} and ω_{13} of the individual atomic resonances. The parameters of the atomic transitions are reported in the text and in Appendix 2.7.2.

count signal is dominated by the photon-count signal of the individual atoms, the peak maxima are at the frequency of the atomic levels, and there are no evident features which could be attributed to superradiance and/or subradiance. Here, the inclusion of cross-interference terms gives rise to a slightly visible discrepancy between the two curves in the frequency interval between the two peaks. When decreasing the interatomic distance to $R = 0.01\,\mu$m, the spectroscopic lines are split into the sub- and superradiant components. The frequency gap between the peaks of the sub- and superradiant components is given by the corresponding diagonal frequency shifts of Eq. (2.20). In the next section, we determine the line shifts one extracts by analyzing these spectra.

2.4.2 *Line shifts due to cross interference*

In order to quantify the effect of the cross-interference terms, we determine the line shifts $\delta\omega_j$ due to the multilevel interference. We focus on the lines of the superradiant states and extract the shift

$$\delta\omega_j = \frac{1}{2\pi}\left(x'_j - x_j\right), \tag{2.34}$$

where the quantity x'_j (with $j = 2, 3$ for $|1\rangle \to |j\rangle$) is extracted from the photon-count signal calculated using the master equation (2.17). The frequency x_j, instead, is obtained by artificially setting all multilevel interference terms to zero, namely, by setting $\Theta_{ij}^{(\Delta t)} \to \delta(\bar{\omega}_i - \bar{\omega}_j)$ in the coefficients of Eq. (2.17). Thus, the frequency x_j also includes the collective Lamb shift. The line shifts we report are determined from the photon count signal as a function of the interatomic distance by taking the limit of vanishing Rabi frequencies, and are extracted by fitting the photon-count signal using the following function, which is the sum of two Lorentzian curves:

$$S^{LL}(x) = \frac{a_2}{\pi}\frac{b_2/2}{(x - x_2)^2 + (b_2/2)^2} + \\ + \frac{a_3}{\pi}\frac{b_3/2}{(x - \omega_0 - x_3)^2 + (b_3/2)^2}, \tag{2.35}$$

and $\omega_0 = 2\pi\nu_0$ is the frequency gap between states $|2\rangle$ and $|3\rangle$ and is given in Appendix 2.7.2. It discards the presence of the subradiant peaks, whose magnitude becomes very small at low Rabi frequencies (for instance, for Rabi frequencies that are 1% of the natural linewidth, the magnitude is approximately $10^{-3}, 10^{-4}$ smaller than the superradiant ones). Nevertheless, these signals are generally different from zero and give rise to a systematic error in determining the line shift of the superradiant resonance. We remark that the choice of the fitting function is not optimal: In fact, Eq. (2.35) corresponds to the spectroscopic signal due to the sum of two independent decay processes, and does

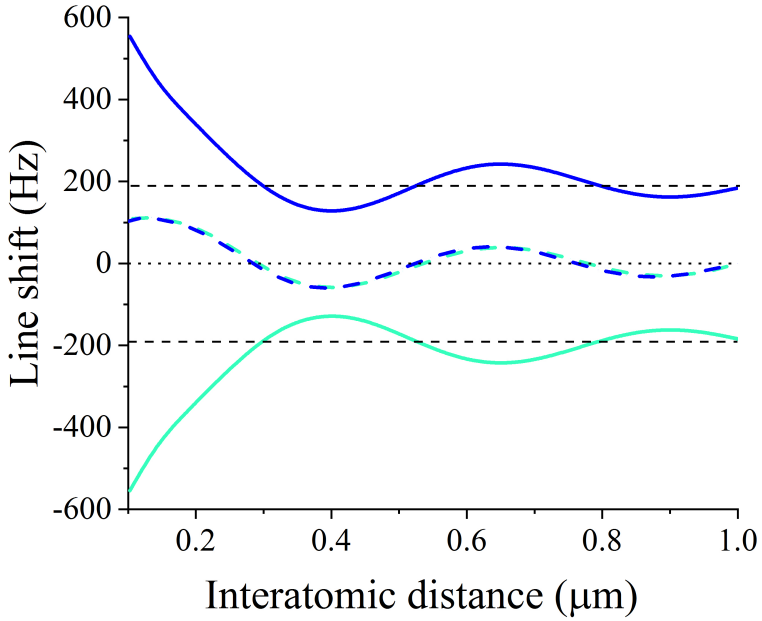

Figure 2.4: Line shifts versus the interatomic distance for two emitters transversally driven by linearly-polarized light. The cyan (light-gray) curve corresponds to the line of transition $|1\rangle \rightarrow |2\rangle$ and the blue (dark-gray) ones to the transition $|1\rangle \rightarrow |3\rangle$. The solid lines are extracted from the photon count signal using the fit of Eq. (2.35); the dashed lines are the curves in the absence of multilevel interference, where ideally $\delta\omega_j = 0$. The deviation from zero is here due to the fact that we have discarded the presence of the subradiant peaks in applying the fitting function (2.35). The horizontal dotted lines indicate the shift due to multilevel interference in a single three-level emitter ("atom").

not properly catch the features due to interference. Indeed, the data in Fig. 2.3 show that the curves are more similar to Fano-like profiles. Previous studies showed that the excitation spectra of optically dense (homogeneously broadened) media differ from Lorentz resonances [5, 24, 81]. Our choice is thus not going to be a reliable estimate of the shifts induced by multilevel interference. We expect, nevertheless, that it allows us to gain insight into their order of magnitude.

Figure 2.4 shows the line shifts as a function of the interatomic distance: at sufficiently short distances, the shifts are significantly larger than the ones predicted for a single emitter and above the systematic error, due to discarding the subradiant peaks and illustrated by the dashed lines. The line shifts tend to increase the frequency gap between the two excited states as $R \rightarrow 0$, while for $R \rightarrow \infty$ they converge to the values indicated by the dashed lines, which are the shifts that we calculate for the case of a single artificial emitter composed by three levels.

We now argue that the observed shifts are due to quantum interference between the processes illustrated in Fig. 2.1. For this purpose we analyze the shifts by considering two artificial cases: (i) The *single-atom cross interference*, in which we only consider the scattering processes displayed in Figs. 2.1(a) and 2.1(b). This corresponds to set $\Delta_{ij}^{12} = 0$ in (2.21) and $\Gamma_{12}^{ij} = 0$ in (2.26) for $i \neq j$. (ii) The *interatomic cross interference*, in which we discard scattering processes displayed in Fig. 2.1(a) and we keep the others. In this case, we set $\Delta_{ij}^{\alpha\alpha} = 0$ and $\Gamma_{\alpha\alpha}^{ij} = 0$ for $i \neq j$. We further separately analyze the effect of the cross-damping terms (namely, the terms of the master equations where multilevel interference appears in the dissipator) and of the cross-shift terms (where multilevel interference appears in the Hamiltonian (2.21)).

We first study the impact of the cross-damping terms versus R and artificially set all terms $\Delta_{ij}^{\alpha\beta} = 0$ with $i \neq j$ in Hamiltonian (2.20). Figure 2.5(a) represents the results when we include the cross-damping terms (i) only in the single-atom dissipator (intra-atomic, $\alpha = \beta$), (ii) only in the interatomic dissipator (interatomic, $\alpha \neq \beta$) and (iii) when we consider both intratomic and interatomic cross-damping terms. In the case (i), the shifts due to the *single-atom* cross-damping terms at large distance oscillate around a magnitude of ~ 100 Hz. In the case (ii) the line shifts vanish for $R \to \infty$. For vanishing distances, the line shifts (i) and (ii) converge to a similar value. The total contribution of the intra- and interatomic cross-damping terms is not additive, as visible when comparing these curves with the ones obtained including both kinds of cross-damping terms. Figure 2.5(b) displays the impact of the cross-shift terms on the line shifts after artificially setting all terms $\Gamma_{ij}^{12} = 0$ in the dissipator (2.25). Over the interval of distances, $R = [0.1, 1]\mu$m. The total line shift has some oscillatory behaviour which tends to the single-atom result as R increases. At small R, the cross-shift terms become dominant and tend to increase the frequency gap between the spectroscopic lines.

The behaviour at short distances is diplayed in Fig. 2.6. Here it is evident that the cross-shift terms are responsible for large shifts of the lines. Below $R = 48$ nm (which corresponds to $R \sim \lambda/10$), the shift of the line $|1\rangle \to |3\rangle$ increase rapidly to the magnitude of 0.6 MHz, which starts to be comparable with the natural linewidth for optical transitions.

2.4.3 *About the coarse graining time scale*

The use of the coarse graining master equation allows one to derive, *ab initio*, a master equation fulfilling the Lindlad form and yet systematically including the cross-interference terms. The drawback is the explicit dependence on the coarse-graining time, which becomes visible in the functional form of $\Theta_{ij}^{(\Delta t)}$, given by Eq. (2.19), and which

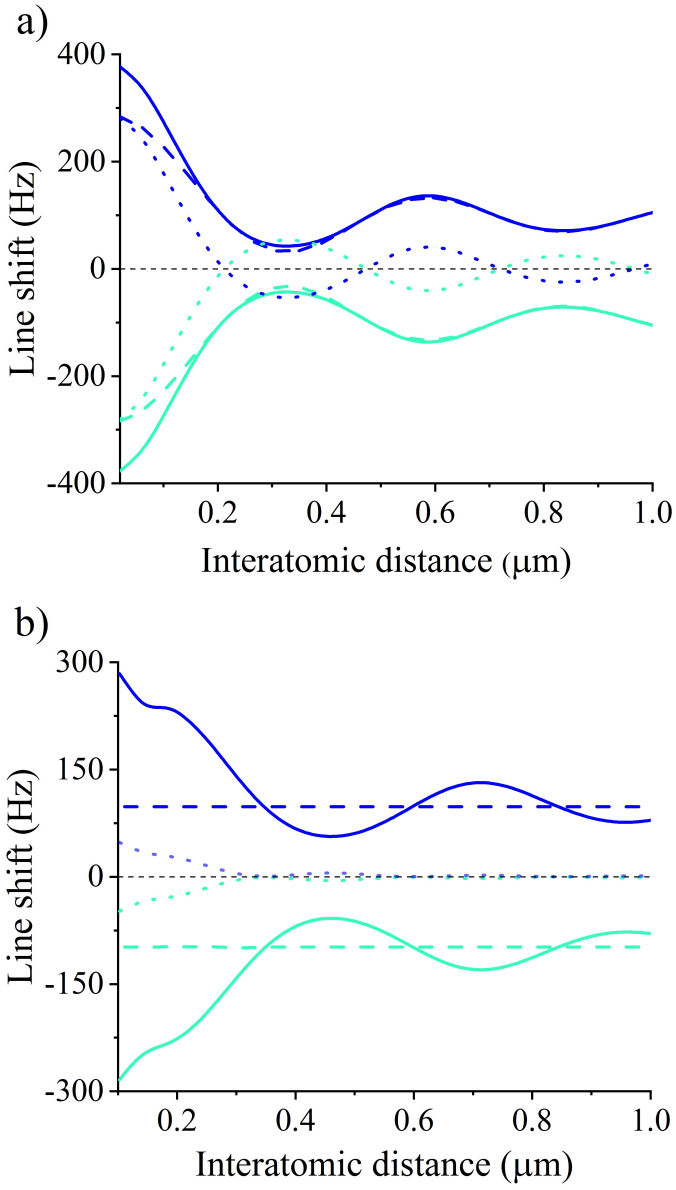

Figure 2.5: Line shifts vs the interatomic distance for two atoms transversally driven by a linearly polarized laser due to (a) the cross-damping terms (after setting all cross-shift terms $\Delta_{ij}^{\alpha\beta} = 0$ for all $i \neq j$ in Hamiltonian (2.20)) and (b) the cross shift terms (after setting all cross-damping terms $\Gamma_{ij}^{\alpha\beta} = 0$ for all $i \neq j$ in the dissipator (2.25)). The cyan (light-gray) curves correspond to the line of transition $|1\rangle \rightarrow |2\rangle$ and the blue (dark-gray) ones to the transition $|1\rangle \rightarrow |3\rangle$. The dashed curves correspond to case (i), the dotted lines correspond to case (ii), and the solid lines include both intra-atomic and interatomic (a) cross damping and (b) cross-shift terms.

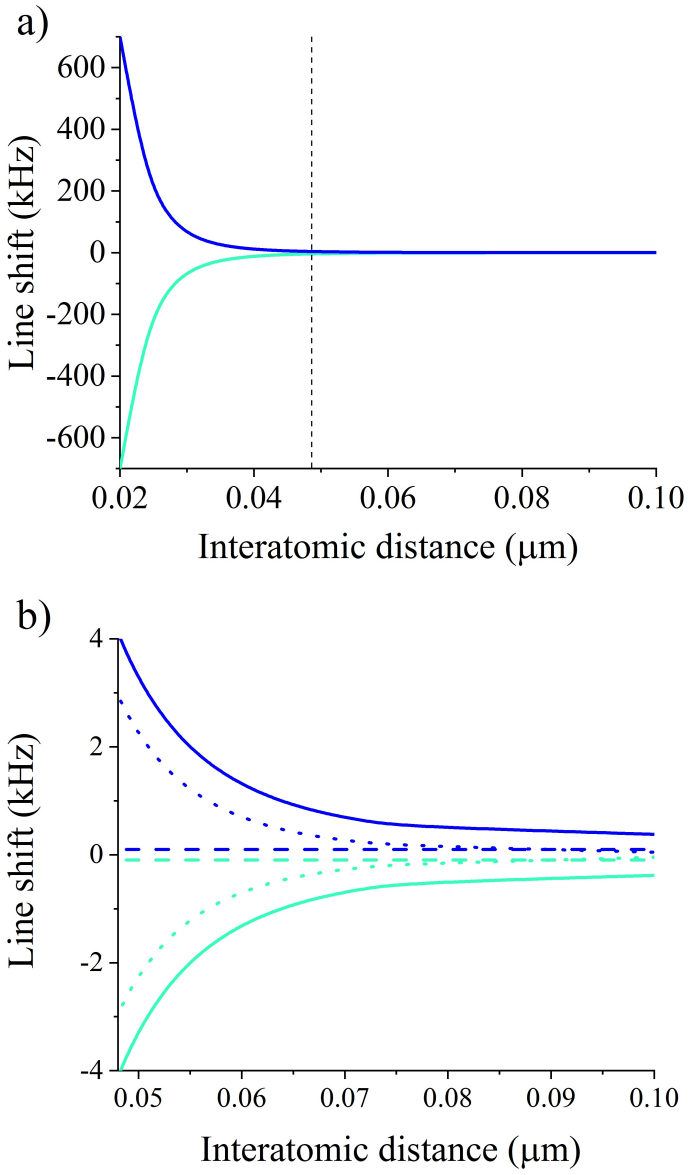

Figure 2.6: Same as Fig. 2.5(b), but for interatomic distances below $\lambda/5$; the vertical dotted line indicates the value $\lambda/10$. (b) Zoom of the behaviour in the interval $[\lambda/10, \lambda/5]$.

multiplies all coefficients for $i \neq j$. We note that this function determines the frequency window, for which the interference of two parallel dipolar transitions gives rise to relevant contributions to the dynamics.

One striking property is that $\Theta_{ij}^{(\Delta t)}$ gives rise to strong oscillations of the coefficients with Δt. The oscillations are majorly due to the sharp time intervals over which the dynamics has been divided and could be eliminated by introducing a smoothening, for instance by taking a Gaussian function of width Δt and calculating the convolution [15]

$$\Theta_{ij}^{(\Delta t)} \to \mathcal{F}_c(\omega_i + \omega_j) = \int_0^\infty dx \Theta_{ij}(x) \frac{\mathrm{e}^{-x^2/\Delta t^2}}{\sqrt{\pi \Delta t/2}}\,. \tag{2.36}$$

This smoothening procedure delivers the new damping coefficients,

$$\Gamma_{\alpha\beta}^{ij\,(F)} = \mathcal{F}_c(\omega_i + \omega_j) \frac{\vec{D}_i^{\alpha *} \cdot \vec{D}_j^{\beta}}{2\pi\hbar c^3} \omega_{ij}^3 F_{\alpha\beta}^{ij}(k_{ij})\,, \tag{2.37}$$

which preserve the Lindblad form of the density matrix. Similarly, we obtain the cross-coupling Hermitian terms after the smoothening.

Even after this smoothening, the coefficients of the master equation still depend on the choice of Δt. For the master equation to be valid, their value shall be independent of the specific choice of Δt over an interval of value. A rigorous lower bound for Δt can be found by imposing the positivity of the Lindblad equation, as discussed in Ref. [79]. A heuristic approach is based on identifying the coarse-grained time for which the scattering properties are stable over several orders of magnitude, such that $\tau_R \ll \Delta t$ and Δt is smaller than the smallest rate of the system dynamics. Figure 2.7 shows the line shifts for different values of the coarse-graining time. The results do not vary over the interval of values of Δt, over which we expect that the timescale separation ansatz holds. They start to appreciably vary for $\Delta t > 10^{-10}$ sec, and thus when Δt becomes comparable with the natural lifetime of the excited states, which is here of the order of 10^{-8} sec.

2.5 CONCLUSIONS

In this work, we have presented the systematic derivation of a master equation for an optically dense medium, which is composed of multilevel emitters. The master equation fulfills the Lindblad theorem [35] and includes the effect of interference between transitions which have parallel dipoles. This interference is induced by vacuum effects and gives rise to additional terms in the dissipator and Hamiltonian which can mutually interfere and whose strengths depend on the mean interparticle distance.

We have provided a numerical example where we have applied our master equation to two identical emitters, each consisting of two parallel dipoles with a common ground state. We have shown that

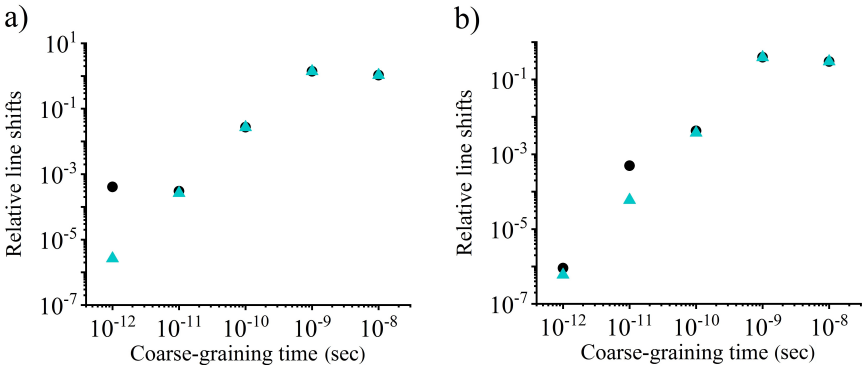

Figure 2.7: Dependence of the relative line shifts on the coarse-graining parameters. The relative line shifts are defined as $|(x(\Delta t_i) - x(\Delta t_{i+1}))/x(\Delta t_i)|$. Here, $\Delta t_i = 10^{-i}$ sec is the coarse-graining time and the index i takes integer values from 8 to 12. Cyan (black) triangles correspond to a relative shift of the first (second) line. The interatomic distance (a) $R = 0.1\,\mu$m and (b) to $R = 1\,\mu$m.

even if the dipoles are not resonant, vacuum-induced interference gives rise to measurable effects in the excitation spectrum. We have verified that the magnitude of the shifts depends on the ratio between the frequency gap between the interfering dipoles and their average linewidth and increases as this ratio decreases [21], they become more evident when the interparticle distance decreases and emerge from the interplay of the interference between parallel dipoles of a single emitter and of the two emitters. Moreover, for realistic configurations the photodetection signal depends on the angle of emission and can be larger for certain directions [15].

Future work shall focus on alkali-metal or alkali-earth metal atoms, consider the full sublevel structure and analyze the spectrum at different detection angles. A more accurate choice of the fitting functions shall provide a better estimate of the line shift due to multi-level interference [81, 82]. This model, moreover, can be extended to Rydberg transitions [83], where the multilevel interference is expected to be more prominent [67], and to molecules [84].

The master equation here derived can be extended and applied to studying propagation of quantum light in superradiant media and confined geometries [85–87]. By means of the input-output formalism [20, 88], one can extract from our model the coherence properties of the scattered light and analyze the effect of vacuum induced interference on field- and intensity-intensity correlation functions. Future studies will analyze its prediction on light transport in a disordered medium [24, 89, 90] and in an ordered array of emitters [91, 92] for level configurations where vacuum-induced interference is expected to be relevant.

2.6 ACKNOWLEDGEMENTS

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2.7 APPENDIX

2.7.1 *Derivation of the Born-Markov master equation in the coarse graining formalism*

The second integrand on the right-hand side of Eq. (2.14) is reported here after applying the Born approximation:

$$\begin{aligned}\Lambda_2^{\alpha,\beta}(T,\tau)\tilde{\rho}(\tau_-) &= \sum_{i,j}\bar{C}_{ij}^{\alpha\beta}(\tau)\Big(\Big[\tilde{\sigma}_j^{\beta}(\tau_-)\tilde{\rho}(\tau_-),\tilde{\sigma}_i^{\alpha}(\tau_+)\Big] \\ &\quad+\Big[\tilde{\sigma}_i^{\alpha}(\tau_+),\tilde{\rho}(\tau_-)\tilde{\sigma}_j^{\beta}(\tau_-)\Big]\Big)+\text{H.c.}\,, \qquad (2.38)\end{aligned}$$

where $\tau_\pm = T \pm \tau$. Subscript i labels a pair of levels coupled by a nonvanishing dipole moment: $i \equiv i_1, i_2$ with dipole moment $\vec{d}_i^{\alpha} = {}_\alpha\langle i_1|\vec{d}|i_2\rangle_\alpha$. The function $\bar{C}_{ij}^{\alpha\beta}(\tau)$ specifically reads

$$\begin{aligned}\bar{C}_{ij}^{\alpha\beta}(\tau) &= \sum_{\lambda}\Big(g_i^{\lambda}\bar{g}_j^{\lambda}(n(\omega_\lambda,T)+1)\mathrm{e}^{-\mathrm{i}\omega_\lambda\tau}\mathrm{e}^{\mathrm{i}\vec{k}_\lambda\cdot(\vec{R}_\alpha-\vec{R}_\beta)} \\ &\quad+\bar{g}_i^{\lambda}g_j^{\lambda}n(\omega_\lambda,T)\mathrm{e}^{\mathrm{i}\omega_\lambda\tau}\mathrm{e}^{-\mathrm{i}\vec{k}_\lambda\cdot(\vec{R}_\alpha-\vec{R}_\beta)}\Big)\,, \qquad (2.39)\end{aligned}$$

where $n(\omega,T) = 1/[\exp(\hbar\omega/k_BT)-1]$ is the mean photon number at frequency ω and temperature T, and the sum over the modes is bounded by the cutoff frequency ω_{cut}. In the continuum limit it is given by the expression

$$\begin{aligned}\bar{C}_{ij}^{\alpha\beta}(\tau) &\to \int_0^{\omega_{\text{cut}}}\frac{d\omega}{(2\pi)^2\hbar c^3}\,\omega^3\Big([1+n(\omega,T)]e^{-i\omega\tau} \\ &\quad+n(\omega,T)e^{i\omega\tau}\Big)\,\bar{F}^{ij}(k,\vec{R}_{\alpha\beta})\,. \qquad (2.40)\end{aligned}$$

Assuming the Born-Markov approximation, we can write $\tilde{\rho}(T-\tau)\approx\tilde{\rho}(T)$ in Eq. (2.38) [17, 35]. We also note that consistently with the Markov approximation, $\tilde{\rho}(T)$ is essentially constant over the interval

of integration $[t, t+\Delta t]$ of the variable T. We then set $\tilde{\rho}(T) = \tilde{\rho}(\bar{t})$, with $\bar{t} = t + \Delta t/2$. Using that $\tilde{\sigma}_j^\beta(t_1) = e^{i\omega_j(t_1-\bar{t})}\tilde{\sigma}_j^\beta(\bar{t})$, we first rewrite Eq. (2.38) as

$$\begin{aligned}\Lambda_2^{\alpha,\beta}(T,\tau)\tilde{\rho}(\tau_-) \;\approx\; & \sum_{i,j} C_{ij}^{\alpha\beta}(T,\tau)\Big(\Big[\tilde{\sigma}_j^\beta(\bar{t})\tilde{\rho}(\bar{t}),\tilde{\sigma}_i^\alpha(\bar{t})\Big] \\ & + \Big[\tilde{\sigma}_i^\alpha(\bar{t}),\tilde{\rho}(\bar{t})\tilde{\sigma}_j^\beta(\bar{t})\Big]\Big) + \text{H.c.}\,, \end{aligned} \tag{2.41}$$

where

$$C_{ij}^{\alpha\beta}(T,\tau) = \tilde{C}_{ij}^{\alpha\beta}(\tau)e^{i(\omega_i+\omega_j)T}e^{i(\omega_i-\omega_j)\tau}. \tag{2.42}$$

Using now that $\tilde{\sigma}_j^\alpha(t) = \exp(i\omega_j t)\sigma_j^\alpha$ in Eq. (2.38), the time integrals take the form:

$$\begin{aligned}&\frac{1}{2\Delta t}\int_{-\Delta t}^{\Delta t} dT e^{\pm i(\omega_i-\omega_j)T/2}\int_{-\Delta t}^{\Delta t} d\tau\,\theta(\tau)C_{\alpha\beta}(\tau)e^{\pm i(\omega_i+\omega_j)\tau/2} \\ &= \Theta_{ij}^{(\Delta t)}\int_{-\Delta t}^{\Delta t} d\tau\,\theta(\tau)C_{\alpha\beta}(\tau)e^{\pm i(\omega_i-\omega_j)\tau/2}\,,\end{aligned} \tag{2.43}$$

where

$$\Theta_{ij}^{(\Delta t)} = \frac{\sin((\omega_i+\omega_j)\Delta t/2)}{(\omega_i+\omega_j)\Delta t/2}\,. \tag{2.44}$$

When the transitions are in the optical range, this function selects secular terms. For this reason, in the following we restrict the sum to all pairs such that $\omega_i > 0$. The second integral is evaluated after approximating the extrema of integration by $[-\Delta t, \Delta t] \to [-\infty, \infty]$, which is consistent with the assumption that $C(\tau)$ decays to zero over time scales much shorter than Δt.

2.7.2 *Parameters of the simulation*

The magnitude of the fine structure splitting for the 4p state is taken to be $\nu_0 \approx$1.367 GHz [71, 93] and also includes the hyperfine structure splitting and QED corrections. We neglect thermal effects: we set $n(\omega_{1e}) = 0$, which is a good approximation at room temperature, $T =$ 300 K. Moreover, we take the following values for the radiative shifts: $\Delta_{22}^S = -2\pi \times 1401.52$ kHz for the state $4p_{\frac{1}{2}}$ and $\Delta_{33}^S = 2\pi \times 1767.30$ kHz for the state $4p_{\frac{3}{2}}$ [82]. We then construct the atomic cross-shift term between the excited states using relation (2.28): $\Delta_{23}^S = \Delta_{32}^S = 2\pi \times 366.2$ kHz using the relation between dipole moments of the corresponding transitions: $d_{12} = (1/3)d_R$, $d_{13} = -(\sqrt{2}/3)d_R$, where d_R is the radial integral $d_R = \langle 2s|r|4p\rangle = 1.28$ [a.u.]. The values for the natural line width are $\gamma_2 = \Gamma_{22} = 2\pi \times 511$ kHz for the state $4p_{\frac{1}{2}}$ and $\gamma_3 \equiv \Gamma_{33} = 2\pi \times 1022$ kHz for the state $4p_{\frac{3}{2}}$. All the cross-interference terms both for the dissipator and the Lamb shift were computed with the coarse-graining time $\Delta t = 10^{-11}$ sec. The computational checks showed that the solutions of the master equation for the chosen system remain stable in this coarse-graining time region; see Fig. 2.7 in Sec. 2.4.3.

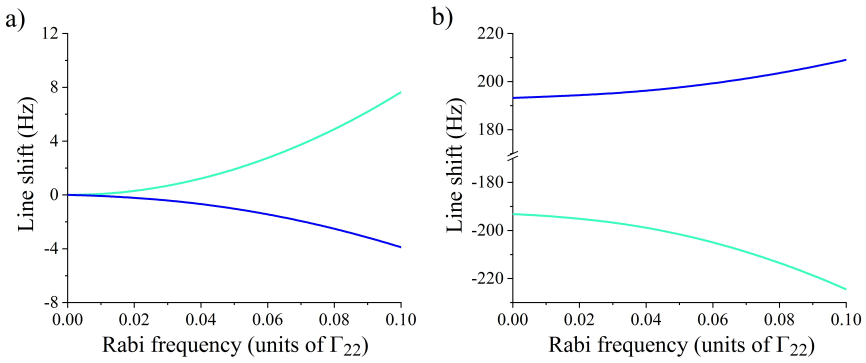

Figure 2.8: Line shift $\Delta_j(g)$ of a single emitter as a function of the Rabi frequency g_{13}. The cyan (light-gray) curves correspond to the line of transition $|1\rangle \rightarrow |2\rangle$ and the blue (dark-gray) ones to the transition $|1\rangle \rightarrow |3\rangle$. The line shift is extracted from the photon-count signal by using the fitting functions of Eq. (2.35). (a) The line shifts without any cross-interference terms. (b) The line shifts are obtained for the full master equation (2.17) for a single emitter. The levels are illustrated in Fig. 2.2, and the parameters are detailed in the text.

2.7.3 *Determination of the line shifts*

Line shifts due to cross-interference for a single emitter. In this Appendix, we illustrate the procedure that we apply in order to determine the line shifts due to the multilevel quantum interference terms. We provide the example of a single emitter, and we refer to it as a "single atom". However, due to the special structure, we assume the emitter is not rotationally invariant, which changes the spectroscopic properties and gives rise to a global line shift when integrating the photon count signal over the whole solid angle.

The line shifts for a single atom are defined as

$$\Delta_j(g) = \frac{1}{2\pi}\left(x_j^g - x_j^{\text{eigen}}\right), \tag{2.45}$$

where x_j^{eigen} is the eigenfrequency of the j^{th} transition ($j = 1$ for $|1\rangle \rightarrow |2\rangle$ and $j = 2$ for $|1\rangle \rightarrow |3\rangle$) which we extract from the master equation when we set all multilevel interference terms to zero, and x_j^g is the line position obtained by fitting the photon-count signal using the fitting function (2.35). The line shifts $\Delta_j(g)$ depend on the laser intensity and thus on the Rabi frequency g. The line shift we identify corresponds to the limit

$$\Delta_j = \lim_{g\rightarrow 0} \Delta_j(g). \tag{2.46}$$

The limit is extracted from our numerical analysis: We evaluate it for decreasing values of g. We report the behaviour in Fig. 2.8(a), when we set to zero the multilevel interference terms and 2.8(b), for the full

master equation. The presence of the interference terms shifts both peaks to the magnitudes $\pm$ 195 Hz for vanishing laser intensity.

OUTLOOK

In the presented thesis we theoretically investigated the excitation spectrum of superradiant ensemble of multilevel quantum emitters. As a theoretical tool we used the derived coarse-grained master equation, which includes the cross-interference terms formed by non-degenerate dipoles while preserving the Lindblad form. The relevance of these cross-interference terms was shown for ensembles with strong dipole-dipole interaction, such as atomic pairs with ultra small interatomic distances. We found out that the cross-interference terms give rise to an off-resonant contribution to the dipole-dipole interaction.

The developed coarse-grained master equation is difficult to implement for description of systems with many atoms. The Hilbert space of the system grows exponentially with the number of particles. A further direction of our research might be a derivation of the model of coherent dipoles (MCD) [24, 25], taking the derived coarse-grained master equation as a basement. The MCD is shown to be a powerful tool for simulation of coherent light scattering on ultra-dense disordered atomic ensembles. We expect that incorporation of the cross-interference terms would be relevant for spectroscopy of ultracold atomic gases and potentially explain some recent experimental results, as for example [94], where the positions of spectral lines deviate from predictions of MCD based on a model with a single energy gap.

The presented theoretical framework includes only the transitions between atomic states allowed in the electric dipole approximation. It might be useful to incorporate higher-order multipole transitions such as electric quadrupoles. The resulting master equation would probably include cross-interference terms formed by different multipoles, such as dipole-quadrupole interaction terms. This could be relevant for transitions between highly-excited atomic Rydberg states and spectroscopy of forbidden transitions.

Another basic concept of the presented research is an atomic system as an open system. The coupling of atoms with the photon reservoir leads to the spontaneous emission rate, Lamb shift, interatomic dipole-dipole interaction and the cross-interference terms. It would be interesting to investigate what would happen if an atomic system was coupled with more than one reservoir. This might be, for example, a phonon reservoir, which would be relevant for quantum emitters placed on the surface of a crystal.

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