

On the theory and simulation of photonic condensates

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Declarations

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Some of the work presented in this thesis has been published in these papers [1, 2, 3, 4, 5].

Abstract

Photons in a dye filled microcavity have been proven to form Bose-Einstein condensates both theoretically and experimentally. The system may also be placed in a fundamentally non-equilibrium state where multiple modes are condensed. This thesis theoretically examines some of the deviations from traditional Bose-Einstein condensate models which have been observed and which may be expected in future experiments. Unusual and potentially unseen condensed states are predicted, along with the unexpected non-critical slowing down of system evolution when in these states.

A rigorous derivation of a master equation from a microscopic Hamiltonian is given in chapter two. This is used to study the multimode phases of the condensate in chapter three along with transitions between them. The temporal evolution of the condensate in various phases and close to phase boundaries is presented in chapter four. Dramatic improvements in the simulation of photonic condensates are also discussed in chapter four. These improvements also offer a conceptual shift in the theoretical description of photonic condensates which allows new insights to be made. The fifth chapter establishes a foundation of coupled rate equations which may be used to model the higher order coherences of photons and molecules in future work. Finally the transport of photons across non-standard cavities is modelled, providing guidance for future experiments and possible applications of photonic condensates.

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As I'm sure many people know by now, PhDs are quite difficult and require a great deal of support to complete. I would like to thank my supervisors Florian Mintert and Rob Nyman for their advice during my research, which was always freely given, well presented, and exceptionally useful. I would especially like to commend Rob on his guidance and pastoral care during the writing phase of this thesis, which was superb and given despite his reduced working hours.

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Default Parameters / Glossary

Symbol	Name	Description
$a / a^\dagger$	Raising / lowering operator	Creates / destroys a photon
σ	Pauli operator	Raises, lowers, or gives the energy of a molecule
$\Lambda_\uparrow / \Lambda_\downarrow$	Absorption / emission	Rate of molecular absorption / emission of photons
$\Gamma_\uparrow, P$	Pump rate	Rate at which molecules are pumped by external photons
$\Gamma_\downarrow$	Molecular loss	Rate of molecular decay via un-modelled channels
$f(r)$	Molecular excitation fraction	The fraction of molecules at a given position which are excited
f_m	Molecular overlap	Average molecular excitation fraction, weighted by the mode intensity as a function of position
f_m^{crit}	Critical overlap	The molecular overlap required to make a mode condense
n	Mode Population	The number of photons in a mode
$ \gamma_m\rangle$	Mode vector	The vector representing mode m
$g_{m,j}$	Mode-molecule coupling	The spatial coupling between mode m and molecules at position j
M_j	Molecule number	The number of molecules at position j
ρ	Density matrix	
$\bar{\rho}$	2D molecular density	
α	Alpha	Ratio of the mode population to pump power at infinite pump power
ψ	Mode wavefunction	The wavefunction / square root of intensity of a photon
Li	Polylogarithm	
ω	Mode frequency	
δ	Mode detuning	mode frequency relative to the frequency of the lowest mode
Ω	Vibrational splitting	Energy gap between adjacent molecular vibrational states
ξ	Molecular splitting	Energy gap between the ground and excited molecular electronic states
L	Characteristic mode width	The standard deviation of the ground state intensity
γ	Thermalisation Coefficient	A measure of whether photons thermalise before leaving the cavity
$\bar{\gamma}$	Transport thermalisation	A measure of thermalisation between different cavity regions
κ	Cavity decay rate	Exponential rate of loss of photons from the cavity

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Chapter 1

Introduction

1.1 Overview

Quantum mechanics and thermodynamics are both important and well established pillars of physics. Individually both have received a thorough investigation, however the study of their intersection is far more recent. For example, work in a macroscopic system is well understood, however there is disagreement about meaning of work at a quantum level [6, 7]. The disagreement is understandable as many postulates of thermodynamics assume thermalised, macroscopic systems. The introduction of quantum systems leads to the study of how thermodynamics changes when applied to small particles in discrete states, for example it is possible to construct a thermodynamic cycle from a single particle where quantum effects are relevant [8]. It is also possible to add particles to a system in a highly controlled manner [9], inserting them at a particular position [10], or with a specific energy [11, 12]. Not only does this break thermal equilibrium, but it does so in a targeted fashion, offering greater flexibility than classical methods of altering a thermodynamic system.

On the quantum side, the addition of thermodynamics provides easy methods of controlling the quantum system. There have been innumerable experiments on quantum information and control [13], in attempts both to create a quantum computer and simply to further our understanding of quantum mechanics. Many of these involve complex apparatus which must be precisely tuned for the experiment to succeed. Additionally these experiments are prone to decoherence due to interaction with the environment [14]. This is not the case for thermodynamic systems where the random actions of the environment lead directly to the observed behaviour. Engineering the thermodynamic properties of a quantum system can therefore help to protect against decoherence and can even create desired quantum states [15]. Quantum properties such as coherence have interesting behaviours in the presence of thermodynamic forces and may be exploited to improve the efficiency of processes, e.g. photosynthesis [16, 17].

1.2 Bose-Einstein Distribution

Bose Einstein condensates were one of the first predictions of quantum mechanics. Initially studied in atomic systems at thermal equilibrium, Bose Einstein condensates exhibit a thermal distribution of particles in higher energy states, along with a macroscopic occupation of a discrete lowest-energy state, which is a highly quantum phenomena. These systems are difficult to create experimentally, resulting in 70 years between the theoretical proposal and experimental demonstration. Never-the-less the equilibrium system gives useful insight into the non-equilibrium systems presented in this thesis. The principles of the macroscopic occupation of the ground state, and the saturation of population in the higher states for a conservative system may be generalised to dissipative systems. The starting point for the study of Bose-Einstein condensation is the Bose-Einstein distribution, which gives the expected number of particles in a state. This distribution is derived from the partition function [18] of a single state

$$Z = \sum_{n=0}^{\infty} e^{-\beta n(E-\mu)} \propto \sum_{n=0}^{\infty} P(n) , \quad (1.1)$$

where n is the number of particles in the state, $P(n)$ is the probability of finding n particles in the state, E is the energy of the state, μ is the chemical potential of the state, and β is the inverse temperature $1/k_B T$. As the particles are bosons, the sum over n ranges from zero to infinity. The summation in Eq. (1.1) may be simplified [19] to

$$Z = \frac{1}{1 - e^{-\beta(E-\mu)}} . \quad (1.2)$$

The expected number of photons

$$\langle n \rangle = \sum_{n=0}^{\infty} P(n) n \propto \sum_{n=0}^{\infty} n e^{-\beta n(E-\mu)} , \quad (1.3)$$

may be derived from the partition function, Eq. (1.1), by exploiting the similarity of their forms. Taking the derivative of the partition function with respect to β gives an expression proportional to the expected number of photons, which allows the expected number of photons to be written as

$$\langle n \rangle = \frac{1}{\beta Z} \frac{\partial Z}{\partial \mu} , \quad (1.4)$$

where the factor $1/Z$ accounts for the constant of proportionality. The expectation (1.4) may be evaluated using the summed form of the partition function Eq. (1.2) as

$$\langle n \rangle = \frac{1}{e^{\beta(E-\mu)} - 1} . \quad (1.5)$$

Eq. (1.5) is called the Bose-Einstein distribution and is shown in Fig. 1.1 and gives the expected number of particles in a state with energy E . The Bose-Einstein distribution matches the Boltzmann distribution for a classical thermal system [20] at high energies, low chemical potentials, or high temperatures. In the other limit, where the energy of the state relative to the chemical potential is less than the thermal energy $k_B T$, the Bose-Einstein distribution departs from the Boltzmann distribution. As the chemical potential tends towards the energy of the state, the population of the state tends to infinity.

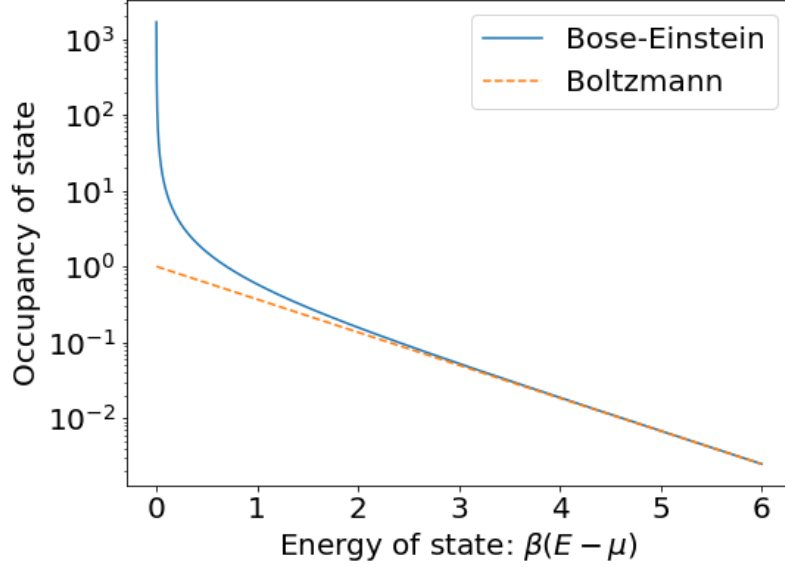


Figure 1.1: The Bose-Einstein distribution.

1.2.1 Bose Einstein Condensation

As the chemical potential of the system tends towards the energy of the ground state the population of the ground state becomes macroscopic¹, forming a condensate. At thermal equilibrium, the population in higher energy states is not macroscopic and continues to follow the thermal distribution given by Eq. (1.5). The method used to achieve condensation varies depending on the system. Increasing the number of particles in the system or reducing the temperature of the system can both cause Bose-Einstein condensation. Increasing the number of particles is the more intuitive way to study the system, despite not being the method used in the original BEC experiments [21].

In thermal equilibrium the chemical potential of all states is identical. The number of particles in each state is therefore given by the energy of the state E_i and the global chemical potential as

$$\langle n_i \rangle = \frac{1}{e^{\beta(E_i - \mu)} - 1} . \quad (1.6)$$

Given the total number of particles in the system N_{tot} , the chemical potential may be found by requiring that the sum of the occupation of each state equals the total number of particles

$$N_{tot} = \sum_i \langle n_i \rangle = \sum_i \frac{1}{e^{\beta(E_i - \mu)} - 1} . \quad (1.7)$$

This summation is impossible to solve exactly, and in some systems it may be approximated as an integral over a continuum of energies if $k_B T$ is larger than the splitting of energy levels. The occupation in the energy range E to $E + dE$ is given by the product of the Bose-Einstein distribution (1.5) $\langle n(E, \mu) \rangle$, the density of states $\bar{g}(E)$ Box. 1.1, and the energy range dE

$$N_H = \int \bar{g}(E) \langle n(E, \mu) \rangle dE . \quad (1.8)$$

¹Here macroscopic occupation means that a significant fraction of the total number of particles are in the macroscopically occupied state.

Box 1.1: Density of States

The density of states is the number of quantum states per unit change in energy, i.e. there are $\bar{g}(E) dE$ states between energies E and $E+dE$. The density of states changes depending on the dimensions of the system and the shape of the potential creating the quantum states. For example the density of states of a uniform potential is proportional to $\sqrt{E}$ in 3D, and constant with respect to energy in 2D. For a harmonic potential the density of states is proportional to E^2 in 3D, and E in 2D.

This integral fails to account for the population in the ground state for two reasons, firstly the Bose-Einstein distribution diverges close to the ground state energy, making the conversion from a sum to an integral inappropriate. Secondly the density of states $\bar{g}(E)$ may equal zero at the ground state energy. Eq. (1.8) is therefore equal to the sum over the populations in the higher modes, and is given the symbol N_H . The occupancy of the ground state N_0 may be added to the occupancy of higher states to give the total number of particles

$$N_{tot} = N_0 + N_H . \quad (1.9)$$

Given the total number of particles, the chemical potential may be found from Eq. (1.9), using the Bose-Einstein distribution for the occupation of the ground state N_0 , and Eq. (1.8) for the occupation of higher states N_H . There is a single solution to this equation which is identical to the solution to Eq. (1.7) and may be found by varying the chemical potential. As Eq. (1.9) is generally difficult to solve exactly the solution may be approximated in the condensed and uncondensed cases. The form of N_H with respect to the chemical potential depends on the geometry of the system via the density of states $\bar{g}(E)$, Box 1.1, and in some systems the integral (1.8) has a finite value when the chemical potential equals the energy of the lowest state

$$\lim_{\mu \rightarrow E_0} N_H = N_H^{max} . \quad (1.10)$$

As the chemical potential of the system cannot exceed the energy of the lowest state², the occupation of the higher modes has a finite maximum value N_H^{max} . If the total number of particles in the system exceeds this maximum value then the additional particles must be in the ground state, which has population $N_0 = N_{tot} - N_H^{max}$. The ground state is therefore macroscopically occupied, and has condensed.

To calculate the chemical potential for a condensed system, recognise that the chemical potential must be close to its maximum value, and the occupancy of the ground state may therefore be calculated from the total number of particles and the maximum number of particles allowed in the higher states. The Bose-Einstein distribution Eq. (1.6) then gives the chemical potential required to produce this ground state occupation. If the total number of particles is less than the maximum occupancy of

²This would cause the Bose-Einstein distribution to predict a negative population in the ground state, which is un-physical

higher states, then the chemical potential is far from the energy of the lowest energy state. In this case the occupancy of the lowest energy state may be approximated as zero, and $N_H = N_{tot}$. The chemical potential may then be calculated from Eq. (1.8). The calculations for the condensed and uncondensed chemical potentials are approximations; the chemical potential never reaches the energy of the lowest state, therefore the occupation of higher states never reaches the exact maximum value.

For a uniform (box) trapping potential in three dimensions the density of states is proportional to $\sqrt{E}$. In this case N_H Eq. (1.8) integrates to the polylogarithm function of the $3/2$ order

$$N_H \propto \text{Li}_{3/2}\left(e^{\beta(\mu-E_0)}\right) . \quad (1.11)$$

The polylogarithm function is defined as

$$\text{Li}_s(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^s} , \quad (1.12)$$

and various polylogarithm functions are plotted in Fig. 1.2. The $3/2$ polylog has a finite value of 2.61 at $\mu = E_0$. The density of states for particles trapped in a 2D harmonic potential is $\bar{g}(E) = E$ and N_H Eq. (1.8) integrates to the polylogarithm function of the second order. This polylogarithm has a value of $\pi^2/6$ at $\mu = E_0$. The population of higher states in a 3D box potential and a 2D harmonic potential are therefore bounded from above, and any additional population must form a BEC in the lowest energy state. It is important to check whether the occupation of higher states has a maximum value, as it does not in some systems. For example a 2D uniform trap has a density of states $\bar{g}(E) = 1$. In this case N_H integrates to the first order polylogarithm function which diverges as the chemical potential approaches the energy of the lowest energy state. A uniform 2D system only forms a BEC at zero temperature, however it can form a Berezinskii-Kosterlitz-Thouless phase [22, 23] when inter-particle interactions are present see Box 1.2, not a Bose-Einstein condensate. A harmonically trapped Bose gas in one dimension forms a BEC at low temperatures and high particle numbers, however it can also form a quasicondensate at higher temperatures, or a Tonks's gas at low particle numbers [24].

Fig. 1.3 shows the number of particles in the lowest energy states of a 2D harmonic system. As the chemical potential approaches zero the higher states saturate, whereas the ground state continues to gain population. This pattern is very similar to the non-equilibrium condensates discussed in Chapter 3. Driven-dissipative BECs, however, have inhomogeneous pumping and loss, which allows the chemical potential to vary in space. As different modes have different chemical potentials the state populations may deviate from Fig. 1.3, and multiple modes may condense at the same time.

1.3 Systems Exhibiting Condensation

The Bose-Einstein condensation described in the previous section (1.2.1) required only that the particles were identical bosons and at thermal equilibrium. It also assumed that the particles did not interact, however this is not a requirement for Bose-Einstein condensation. The theory may therefore be applied to a variety of particles in different environments. These environments fall into two categories: those which have a single chemical potential and temperature, both of which are constant in time, and those which do not. Systems with a single constant chemical potential and temperature

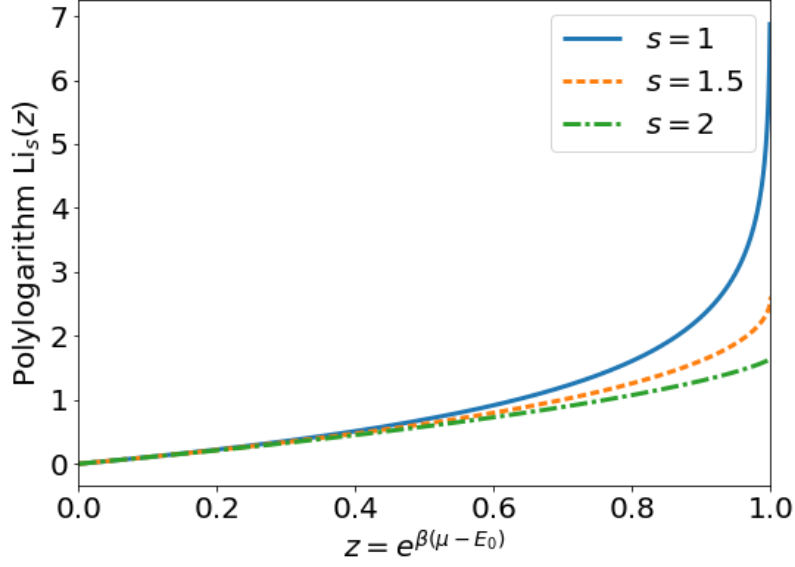


Figure 1.2: The polylogarithm functions for a 3D uniform potential $s = 3/2$, a 2D harmonic potential $s = 1$, and a 2D uniform potential $s = 2$.

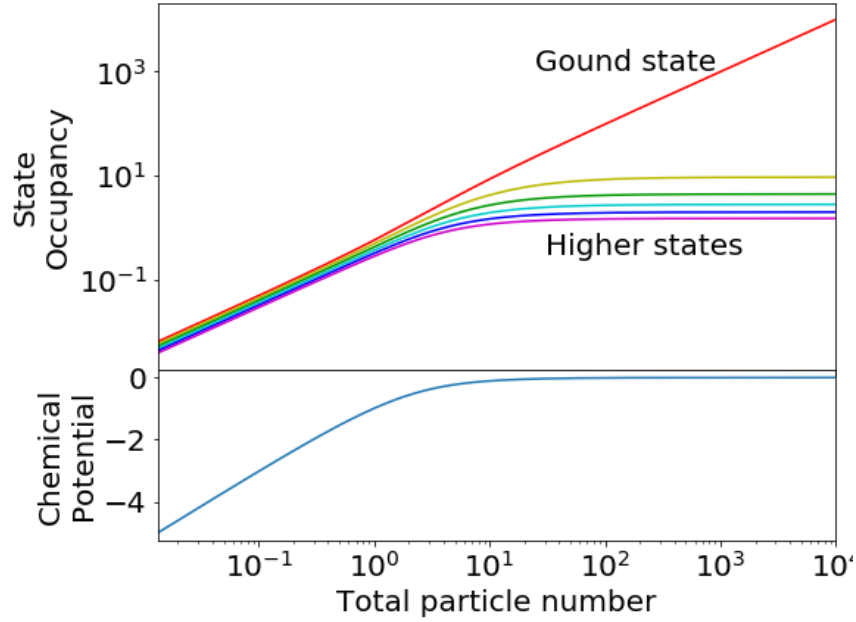


Figure 1.3: (TOP) The occupation of each state as the total number of particles is increased. The states are uniformly spaced with energy spacing $0.1k_B T$, the lowest energy state has energy zero. Colours from red to purple (top to bottom) give the state energy from low to high. (BOTTOM) The chemical potential in units of $k_B T$.

are described by the Bose-Einstein distribution given in section 1.2.1; as the derivation of this distribution uses thermal equilibrium these systems are called equilibrium Bose-Einstein condensates. An example of this type of system is liquid helium-4 which forms a superfluid as a result of Bose-Einstein condensation [25, 26]. Bose-Einstein condensation may also be used to explain superconductivity; two

electrons collectively form a boson, called a Cooper pair [27, 28, 29]. Despite their exceptional number and temperature, the immense density of neutrons inside a neutron star allows pairs of them to form a BEC [30]. The first BEC to be intentionally created was a collection of alkali atoms in a magnetic trap [21, 31]. The number of atoms in the trap is fixed, and the trapping potential is constant³ in time, therefore the system exhibits an equilibrium Bose-Einstein condensate. Later experiments have made use of other systems which break thermal equilibrium (they do not have a single constant chemical potential and temperature), and are therefore called non-equilibrium condensates. The breaking of thermal equilibrium causes interesting deviations from the Bose-Einstein statistics which depend on the manner in which it was broken.

A sample of different BECs is given in this section, beginning with exciton polariton condensates. An exciton is formed by exciting an electron to produce a free electron and a hole where the electron used to be. The electron and hole orbits each other forming a single bosonic particle. The electron holes may be Excitons may be formed inside a cavity containing photons, may be created by the annihilation of a photon, and may emit a photon when destroyed, therefore the photons and excitons are coupled. The Hamiltonian for a system containing a single excitation may be written as

$$H = \begin{pmatrix} E_{\text{photon}}(k) & \tilde{g} \\ \tilde{g} & E_{\text{exciton}}(k) \end{pmatrix}, \quad (1.13)$$

where the basis states are the existence of a photon, and the existence of an exciton

$$\begin{aligned} \begin{pmatrix} 1 \\ 0 \end{pmatrix} &= |\text{single photon}\rangle \\ \begin{pmatrix} 0 \\ 1 \end{pmatrix} &= |\text{single exciton}\rangle, \end{aligned} \quad (1.14)$$

and $E_x(k)$ is the energy of x at wavevector or momentum k . If the difference in energies of the photon and exciton is large compared to the coupling $\tilde{g}$, then the eigenstates of the Hamiltonian are a single photon and a single exciton. If, however, the energies are comparable, then the eigenstates of the Hamiltonian undergo an avoided crossing, shown in Fig. 1.4. The system is tuned so that the excitons and photons have equal energies at zero wavevector. The coupling between excitons and photons causes the eigenstates of the Hamiltonian to split into superpositions of excitons and photons with different energies. These superposition particles are called polaritons, and the ratio of photon to exciton within the polariton is given by the Hopfield coefficients [33]. The photonic components of polaritons do not interact, however the exciton components may collide, providing interactions between polaritons and allowing them to thermalise with each other. As polaritons are bosons they may condense into the ground state and form a BEC. This may occur at a higher temperature than an exciton or atomic condensate as polaritons have comparatively low mass due to their photonic component. These BECs have been observed in semiconductors [34, 35, 36], and organic molecules [37, 38]

A similar particle suitable for creating a BEC is a plasmon, which, in this case, is a quantum of charge oscillation in a nanoparticle [39, 40, 41]. The plasmons may form quasi-particles by mixing

³The experimental method used to create the trapping potential uses a magnetic field which oscillates faster than the trapped atoms can respond, and may therefore be approximated as constant [32].

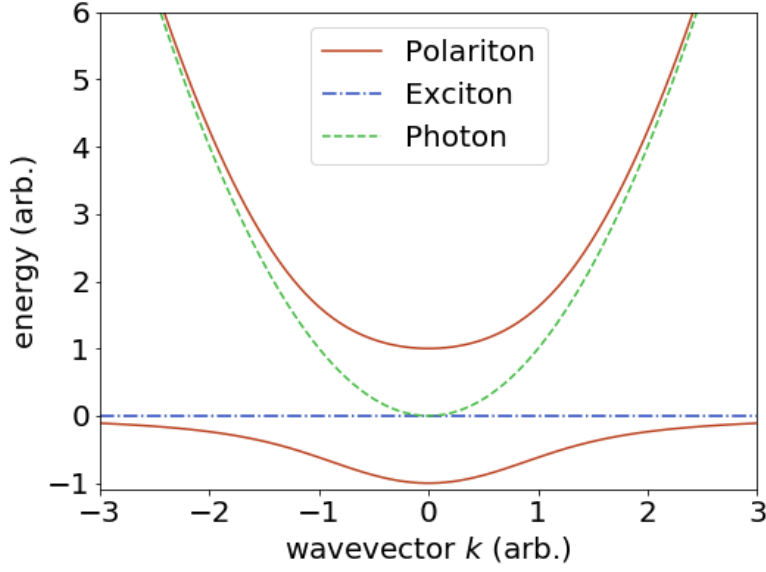


Figure 1.4: An example dispersion of a photon, exciton and polariton. The units are arbitrary.

the plasmons with the photonic modes close to the nanoparticles, in a process similar to that used to create exciton-polaritons. These quasi-particles may then condense. Unlike polaritons, the plasmons interact via a dye [42] which absorbs and emits the photonic part of the plasmons. This mechanism is identical to that used by photonic condensates and is discussed further in Chapter 2. Unlike most other condensates a plasmonic condensate is not trapped in all directions, instead the condensate travels along one dimension of the surface coated in the nano-particles. This allows the temporal properties of the condensate to be easily imaged, as the time dimension is mapped onto position. These and other plasmonic results are presented in Sec. 2.6, after discussions of the microscopic model used to explain them.

Photon BEC has also been created in Erbium doped fibres [43, 44]. These are 1D systems with a constant potential. In the thermodynamic limit of infinite system size and a continuum of states this system would not form a BEC as the population of the higher modes is not bound from above. For a finite system, however, the lower bound of the integral in Eq. (1.8) is not zero, but the finite energy of the first excited state. This small change creates an upper bound for the population of excited states and therefore allows them to saturate, and the ground state to condense.

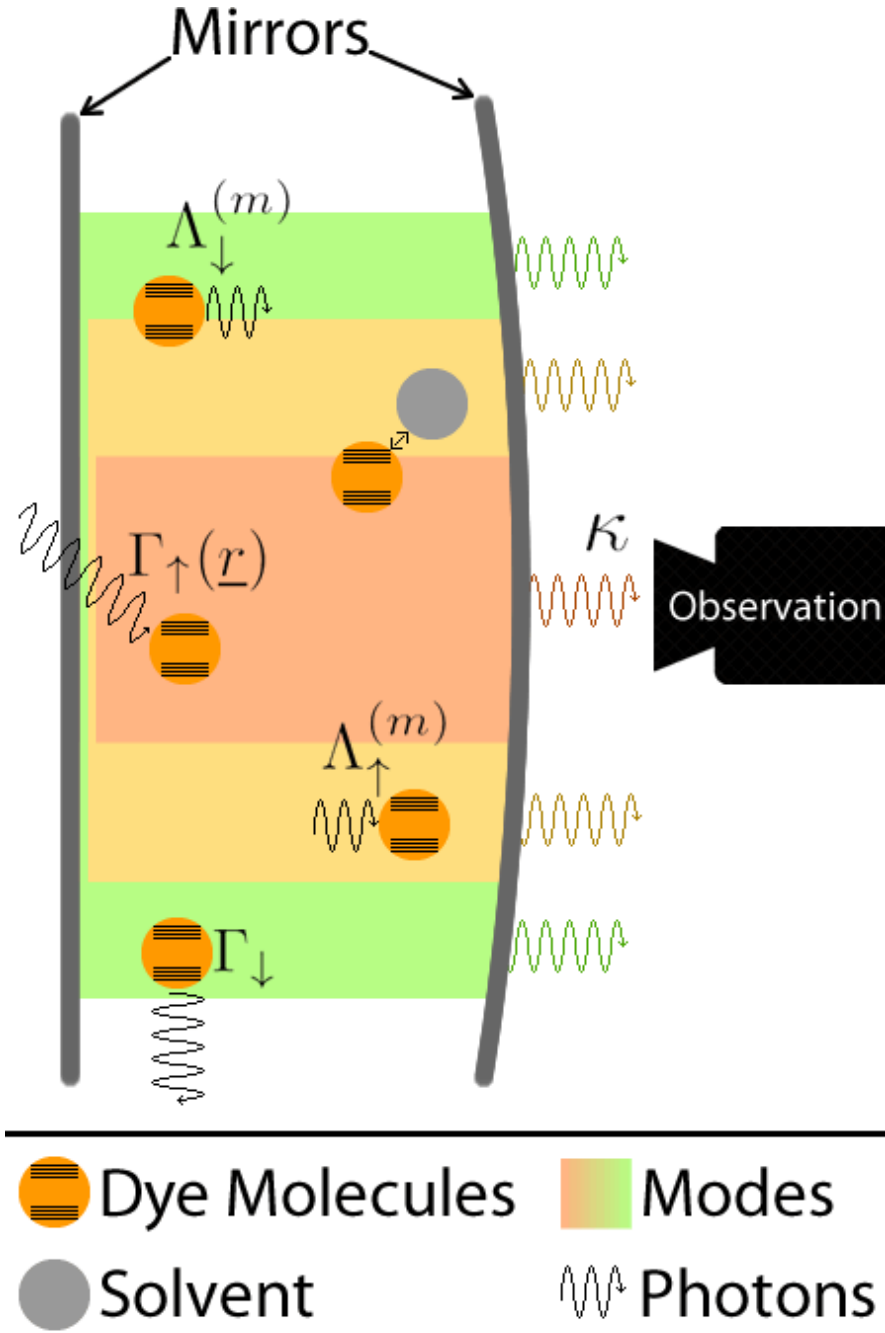


Figure 1.5: This figure shows the experimental setup required to create a photonic condensate. From top to bottom the processes shown are: emission of photons into the cavity by dye molecules, thermalisation of the molecular vibrational state via collisions with the solvent and other molecules, excitation of molecules by a pumping laser, absorption of cavity photons by molecules, and emission of photons out of the cavity. Photons are lost through the right mirror and detected by a variety of optical instruments. The symbols in this diagram are defined in Secs. 2 and 1.7. The coloured sections represent different transverse modes, with narrow modes in the centre of the cavity having lower frequencies than modes at the edge of the cavity. The modes are represented discretely to aid visualisation, in reality the modes overlap and have continuous profiles.

1.4 Photonic Condensate Apparatus

This section shall outline the experimental apparatus required to create a photon BEC and review relevant experimental results. A theorist's representation of the experimental setup is shown in Fig. 1.5. The cavity consists of two mirrors, one is usually flat, and the other is curved. The shape of the second mirror determines the frequency and profiles of the cavity modes, as derived in Sec. 1.7. In principle the mirror can have any shape, however in the majority of the literature, and this thesis, a spherical mirror with a small curvature is used. This may be approximated as a parabola which leads to cavity modes identical to a harmonic oscillator. A dye (e.g. Rhodamine 6G [45, 46]) dissolved in a solvent is placed between these mirrors. The dye has two electronic levels of interest, each of which is vibrationally broadened, indicated by horizontal lines in the orange circles in Fig. 1.5. The dye is pumped by a laser which adds excitations to the system. These excitations are transferred between different modes and molecules via molecular absorption and emission. Photons escape the cavity through one of the mirrors and are measured by a variety of optical instruments. As the properties of the escaped photons are strongly correlated with the cavity photons (e.g. the escaped population is proportional to the cavity population) this allows the state of the cavity photons to be measured. The ease of measurement is a great advantage which photonic condensates have over other forms of BEC, e.g. atomic [21].

The Bose-Einstein condensation described in Sec. 1.2.1 requires thermalisation (implicit in the use of the partition function), and a ground state. Both of these properties do not usually apply to photons, which, in vacuum, do not interact with each other, and have arbitrarily low frequencies [47]. The combination of the cavity and dye creates both thermalisation and a ground mode as follows. When a molecule absorbs a photon it is excited to a particular vibrational state determined by the energy of the photon and the previous vibrational state of the molecule. This disturbs the distribution of population in the vibrational molecular states away from thermal equilibrium. Collisions with the surrounding solvent and molecules will redistribute the vibrational population back to the Boltzmann distribution. This redistribution occurs at rates faster than the emission of photons [48], therefore the frequency of the emitted photon is uncorrelated with the frequency of the absorbed photon. The normalised absorption and emission spectra of the molecules are shown in Fig. 1.6. The plots are generated from fits to the real data published in [49]. The fit to the absorption is the equation

$$\log(A(\lambda)) = c_0 + B + \Theta + G(\lambda, b_2, c_2, s_2) + G(\lambda, b_3, c_3, s_3) + G(\lambda, b_4, c_4, s_4) + G(\lambda, b_5, c_5, s_5) \\ + G(\lambda, b_6, c_6, s_6) + G(\lambda, b_7, c_7, s_7) \quad (1.15)$$

$$B = (m_1 + dm_1/2)\lambda + \sqrt{s_1^2 + (\lambda - c_1)^2} dm_1/2 - (m_1 + dm_1/2)c_1 - s_1 dm_1/2$$

$$\Theta = b_a / (1 + e^{(\lambda - c_a)/s_a})$$

$$G(\lambda, b, c, s) = b e^{-\left(\frac{\lambda - c}{s}\right)^2},$$

with the constants: $c_0 = 0.0498$, $m_1 = 0.0243$, $dm_1 = -0.0833$, $c_1 = 537$, $s_1 = 6.11$, $b_a = 0.348$, $c_a = 502$, $s_a = 5.01$, $b_2 = -0.188$, $c_2 = 586$, $s_2 = 14.5$, $b_3 = 0.195$, $c_3 = 555$, $s_3 = 15.1$, $b_4 = -0.111$, $c_4 = 536$, $s_4 = 7.97$, $b_5 = 0.0137$, $c_5 = 519$, $s_5 = 5.49$, $b_6 = -0.052$, $c_6 = 474$, $s_6 = 9.46$, $b_7 = -0.0479$, $c_7 = 446$, $s_7 = 7.11$. The lengths c , s , dm^{-1} , and m^{-1} have units of nanometers, and the output absorption is dimensionless. The fit to the emission spectrum is the absorption function reflected

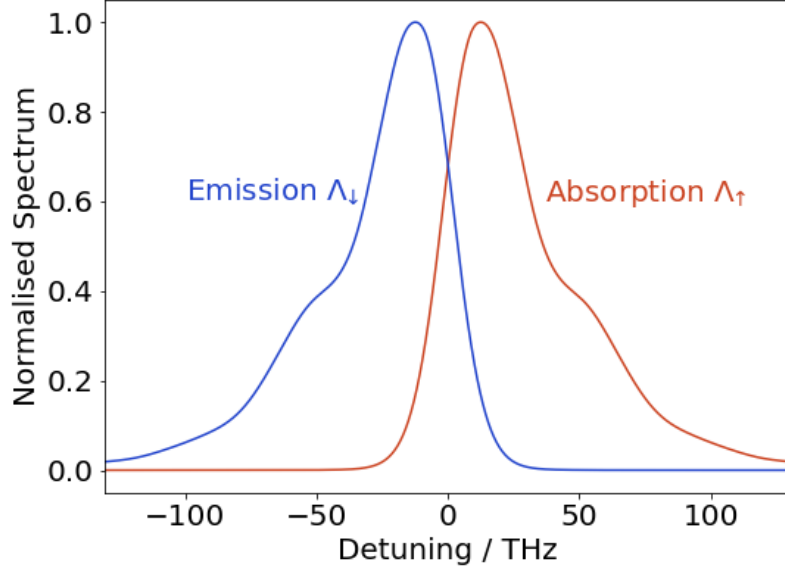


Figure 1.6: The absorption and emission spectra of Rhodamine 6G dye molecules as functions of detuning from molecular resonance (the frequency at which an absorption or emission does not result in a change in vibrational state).

in the zero-phonon line 545nm . The fit was *not* generated from a physical model and any physical significance offered by the terms or parameters is entirely coincidental.

Due to the rapid collisions of molecules and solvent the absorption and emission spectra are related by a Boltzmann factor

$$\Lambda_{\downarrow} = \Lambda_{\uparrow} e^{-\frac{\hbar\delta}{k_B T}}, \quad (1.16)$$

where δ is detuning from molecular resonance⁴, k_B is the Boltzmann constant, $\hbar$ is Plank's constant, and T is the temperature of the dye. This relationship is called the Kennard-Stepanov relation and is discussed in Sec. 2.5. If only absorption and emission events are considered, then the Kennard-Stepanov relation ensures that the steady state distribution of photons is a Bose-Einstein distribution, where the chemical potential is determined by the excitation level of the molecules (this may be proven using the rate equation (2.78) derived in Sec 2.3). The only requirement for a thermalising process is that it drives the system towards a thermal steady state [18], therefore molecular absorption and emission is thermalising. At thermodynamic equilibrium⁵ the photons are therefore in equilibrium with the molecules, solvent and other photons.

The second requirement for Bose-Einstein condensation is a ground state for the photons to condense into. To achieve this the cavity mirrors are separated by a very small distance, e.g. 3.5 wavelengths in [45]. The narrow separation results in a large frequency gap between longitudinal modes. The cavity is configured so that one longitudinal mode has a small negative detuning and therefore has large rates of absorption and emission. The other longitudinal modes are widely spaced and therefore receive far less absorption and emission. The inability of the molecules to emit into the other longitudinal modes is

⁴The frequency at which an absorption or emission does not result in a change in vibrational state.

⁵this is never actually achieved due to pumping and loss

equivalent to the other longitudinal modes not existing. The system may therefore be approximated as having only one longitudinal mode, and any emission into other longitudinal modes may be considered a loss from the system and does not create a new ground state. In addition to the single longitudinal mode there are many closely spaced transverse modes, the profiles of which are discussed in Sec. 1.7. The transverse mode with the lowest frequency is the ground mode, and all other transverse modes are higher modes. To summarise, the molecules absorb and emit photons according to a thermal, Kennard-Stepanov relation which redistributes photons between modes so that they form a Bose-Einstein distribution with the lowest frequency transverse mode as the ground mode. Absorption and emission are not the only processes affecting the system. The degree to which thermalisation is achieved will depend on the strength of absorption and emission compared to other processes.

The experimental apparatus used to create a dye laser is very similar to that used to create a photon BEC, both require a cavity and a pumped dye. As discussed in Chapter 3, the distinction between a laser and a BEC is not discrete, and the similarity between lasers and BECs has caused disagreements about whether the label “BEC” is required, as the label “laser” describes many of the same features. A key feature of a BEC is the thermodynamic distribution of mode populations resulting in condensation of the lowest frequency mode. A laser, in contrast, condenses into the single mode permitted by the cavity, or into the mode which happens to have the largest gain. It is therefore the thermodynamic nature of the BEC which differentiates its study from existing theory on lasers and permits novel insights to be made [45, 50].

1.5 Experimental Results

This section shall review some of the experimental results in photonic condensates. The goal is to establish the experimental foundation for photonic condensates and support the specific investigations detailed in this thesis, not to provide a comprehensive review. The first experimental results showing a photon BEC were published in 2010 [45, 48] using the setup described in Sec. 1.4. Fig. 1.7 shows that increasing the pump power causes macroscopic occupation of the ground mode, *i.e.* condensation. As the spectrum fits a Bose-Einstein distribution this confirms that the molecules thermalise the photons, and that the existence of other longitudinal modes does not affect the viability of the ground mode. The images on the right show the condensation of the light into the ground mode at the centre of the cavity.

The papers [45, 48] also show the effects of varying the spacing between cavity mirrors. Varying the spacing shifts the frequencies of each modes by a constant (see Sec. 1.7). Fig. 1.8 (left) shows that as the frequencies of the cavity modes are decreased the cavity spectrum departs from the Bose-Einstein distribution. The right plot shows that decreasing the frequencies also causes the photon distribution to centre on the pump profile, rather than the ground mode in the centre of the cavity. These effects are explained by the break down of thermalisation as follows. Fig. 1.6 shows that if a mode frequency is below -15THz then decreasing the frequency of the mode will decrease the strength of absorption and emission. As absorption and emission lead to thermalisation decreasing the mode frequencies will also reduce the thermalisation and the mode populations will assume a distribution determined by

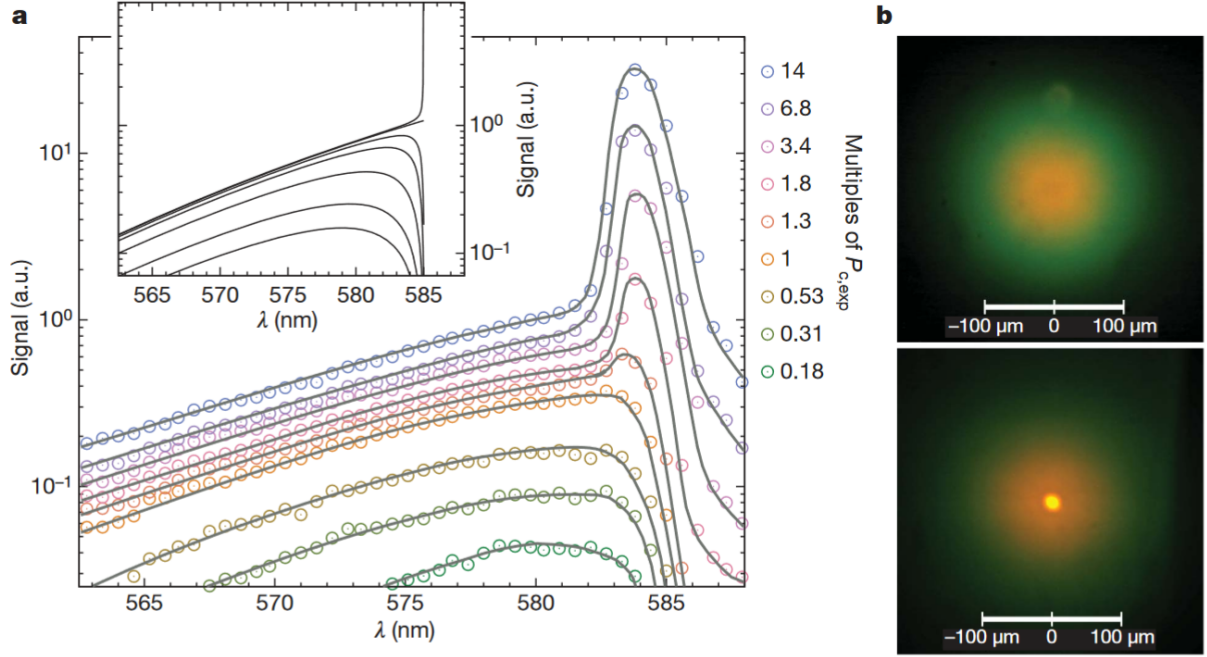


Figure 1.7: Figure taken from [45] showing (a) the spectrum of light inside the cavity for a variety of pump powers (indicated by circle colour). As the pump power is increased a peak appears at the longest wavelength indicating the condensation of the ground mode. The width of this peak is limited by the spectrometer resolution. The inset shows the theoretical spectrum given by the Bose-Einstein distribution at room temperature and various chemical potentials. (b) shows images of the light escaping the cavity below (top) and above (bottom) the BEC threshold.

pumping and loss, rather than the Bose-Einstein distribution [46, 51].

1.5.1 Correlation Functions

When characterising a light source, it is instructive to go beyond the phase⁶ and intensity of the light. The intensity gives the number of photons escaping the cavity per unit area averaged over time, but *when* the photons escape the cavity may vary dramatically whilst maintaining a constant intensity. Fig. 1.9 shows three different patterns of photons leaving the cavity. The left diagram shows photons leaving the cavity at random, uncorrelated times; the distribution of the number of photons leaving over a fixed period of time is Poissonian. The middle diagram shows the photons leaving in pairs. This represents a high degree of correlation between photons as observing the first photon guarantees the immediate observation of the second photon. As the photons leave the cavity in groups this distribution and similar distributions of photons are called “bunched”. The right diagram shows evenly spaced photons which represents anti-correlation, as the observation of one photon guarantees the absence of any observation of another photon for a period of time. This, and similar distributions are called “anti-bunched”.

These three different categories of photon correlation may be mathematically quantified by considering

⁶Angular, or complex phase, not thermodynamic

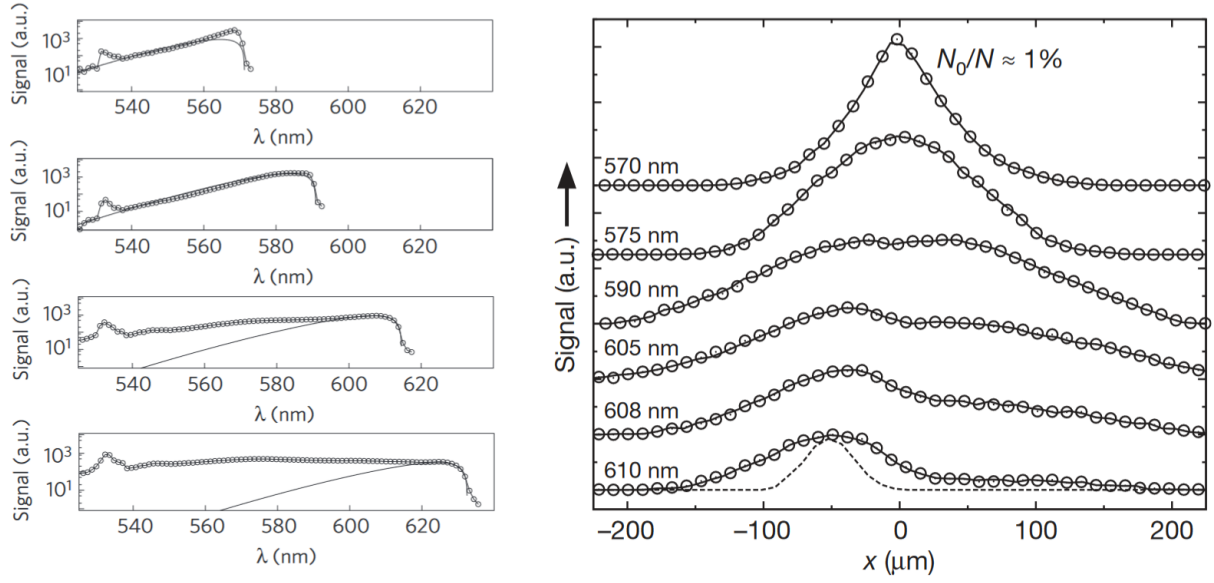


Figure 1.8: Figure taken from [45] and [48]. The effects of reducing the frequency of the ground mode. (LEFT) The spectrum of light escaping the cavity, is shown as connected dots, and the Bose-Einstein distribution shown as solid lines. Higher plots have higher frequencies, as shown by the wavelengths of the distributions. The bumps at approximately 535nm is the pump laser. (RIGHT) Cross-sections of the light escaping the cavity as a function of position shown as connected dots. The dashed line is the pump profile. Numbers on the left of the figure indicate the wavelength of the ground mode.

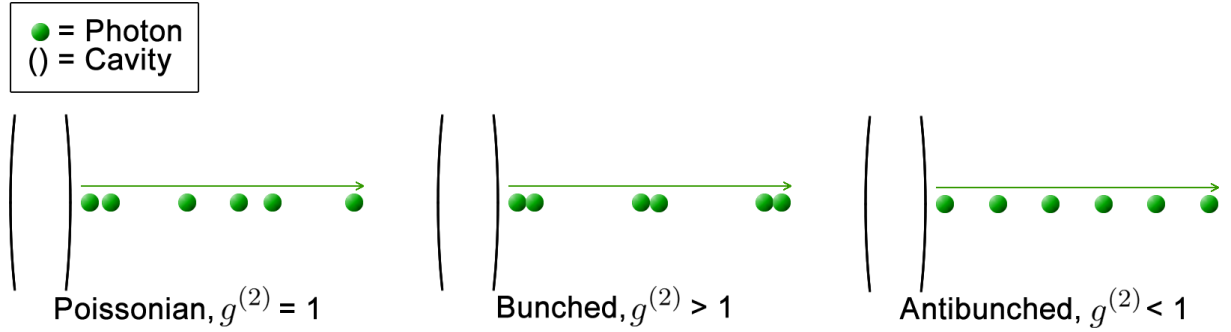


Figure 1.9: Idealised diagram depicting light leaving a cavity with poissonian, bunched, and anti-bunched statistics.

the expectation of the second order correlation operator $G^{(2)} = a^\dagger a^\dagger a a$, where a is the annihilation operator. As the annihilation operator appears twice, ideal anti-bunched light will have a $G^{(2)}$ of zero as there is only ever one photon at a particular time. This is not a problem for bunched light which therefore has a large $G^{(2)}$. This is an illustrative example which does not hold for intense light with higher photon numbers. It is possible for a beam of light to have millions of overlapping photons, and for those photons to be either bunched or anti-bunched by how they are distributed in time. To quantify this the second order correlation function is normalised to

$$g^{(2)} = \frac{\langle a_b^\dagger a_c^\dagger a_b a_c \rangle}{\langle a_b^\dagger a_b \rangle \langle a_c^\dagger a_c \rangle}, \quad (1.17)$$

which ensures that the correlation is independent of the intensity of the light. The subscripts b and c have been added to the operators to indicate that these can correspond to different modes, or to different times. If the operators are entirely unrelated then they commute and separate, i.e. $\langle a_b^\dagger a_c^\dagger a_b a_c \rangle = \langle n_b \rangle \langle n_c \rangle$, and $g^{(2)} = 1$, indicating that there is no correlation between the photons described by b and c . If b and c correspond to the same mode at the same time, then $[a_c^\dagger, a_b] = -1$ and $g^{(2)}$ simplifies to

$$g^{(2)} = \frac{\langle n^2 \rangle - \langle n \rangle^2}{\langle n \rangle^2} = \frac{v - \mu^2}{\mu^2} + 1, \quad (1.18)$$

where v is the variance of the photon number, and μ is the mean. For uncorrelated, Poissonianally distributed light the mean is equal to the variance and $g^{(2)}$ again equals one. Bunched light has a large variance in photon number and the photon number oscillates between high when there is a bunch, and low when there is not. Bunched light therefore has a $g^{(2)}$ greater than one. Similarly anti-bunched light has a low variance and a $g^{(2)}$ less than one.

Correlating a mode with itself at a later time gives information about the temporal coherence of the mode. This is shown in Fig. 1.10 (left) [52], where the ground mode is correlated with itself delayed by the time τ to give the intensity coherence. The decay of coherence from the maximum at delay time zero shows that the ground mode maintains its coherence for approximately two nano seconds. This is the duration of the intensity fluctuations of the mode. The phase coherence of photon BEC has also been measured [53]. Long intensity and phase coherence times of are interesting in and of themselves and are also required in many quantum computation experiments to ensure that the qubits do not decohere.

The value of $g^{(2)}$ at zero delay time may be used to calculate the variance of the ground mode population using Eq. (1.18) (assuming that the mean has already been calculated from the intensity). Fig. 1.10 (left) therefore also shows that increasing the fraction of photons in the ground mode reduces the variance of the ground mode. This can be explicitly seen in Fig. 1.10 (middle), which shows smaller fluctuations in the ground mode population for larger mean population in the ground mode. The reduction in the fluctuations occurs due to the finite number of molecules which transfer photons into and out of the ground mode. If the number of molecules is far larger than the ground mode occupation then the number of available photons is approximately infinite and the system is in the grand canonical ensemble. If the number of molecules is less than the ground mode population then the number of photons which may be absorbed or emitted is limited, and the system is better described by the canonical ensemble. The fluctuations observed in each ensemble match those predicted in other BEC systems [54] and match the theory produced by Weitz's group [55]. By sampling the population in the ground state over time, the probability of each mode population may be obtained. This is plotted in Fig. 1.10 (right). When the number of molecules is large compared to the number of photons, the distribution is exponential, when it is small the distribution is approximately Poissonian.

1.5.2 Spatial Correlations

The coherence length of the light escaping the cavity may be measured using an interferometer [56]. The light is split with a beam splitter, sent along two similar paths, recombined using a beam splitter and

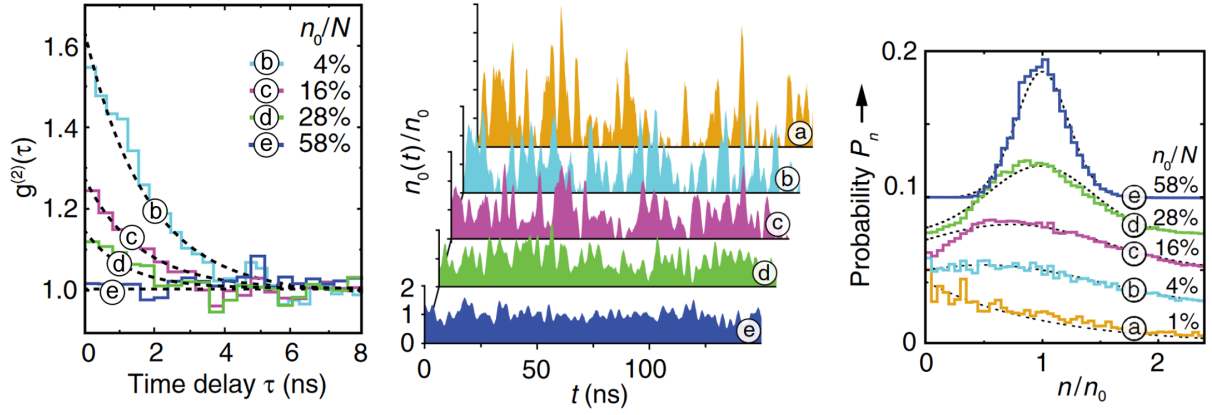


Figure 1.10: Figure taken from [52]. (LEFT) The second order correlation function between the condensate and the condensate delayed by time τ . Lines from (a) to (d) show increasing population in the ground mode n_0 as a fraction of the total photon number N . (MIDDLE) Plots of mode populations fluctuating over time, fluctuations are suppressed with increasing population in the ground mode. (RIGHT) Probability distribution for finding n photons in the ground mode given a time averaged population in the ground mode of n_0 . Distributions are shifted vertically for clarity.

then imaged with a camera. Each camera pixel provides intensity data, shown in Fig. 1.11 (left). If one of the paths of the interferometer is made progressively longer, on the order of the wavelength of light, then the recombined light will exhibit oscillations between constructive and destructive interference. These oscillations may be measured to calculate the visibility, defined as

$$V = \frac{I_{max} - I_{min}}{2\bar{I}}, \quad (1.19)$$

where $I_{max/min}$ are the maximum and minimum intensities and $\bar{I}$ is the average intensity. If the light from one path is completely coherent with light from the other path then I_{max} is twice the average intensity and I_{min} is zero; the visibility would therefore be one. If the light is completely incoherent then there are no interference fringes and the visibility is zero. The visibility is therefore a measure of the degree of coherence between two beams of light. One of the interferometer paths may be lengthened by a large distance relative to the frequency of light, this allows the visibility of the light to be measured as a function of time⁷. The visibility decays as the time delay between the two paths is increased, and the decay constant is the coherence time, also shown in Fig. 1.11 (left). The coherence time at the centre of the cavity is found to be 0.2ps below threshold and 2ps above threshold. The change of phase of a beam of light due to the absorption or emission of a photon is inversely proportional to the number of photons in the beam⁸. As the coherence is destroyed by random changes of phase, the large population in a condensate results in a long coherence time.

Similarly to the coherence time, the coherence length may be calculated by altering one path of the interferometer so that the light is shifted on the focal plane of the camera and measuring the change

⁷because it takes time for the light to travel the extra distance.

⁸Each event involving a single photon may shift the Wigner distribution of light by a unit length. The closer the distribution is to the origin the larger the change of phase generated by this shift.

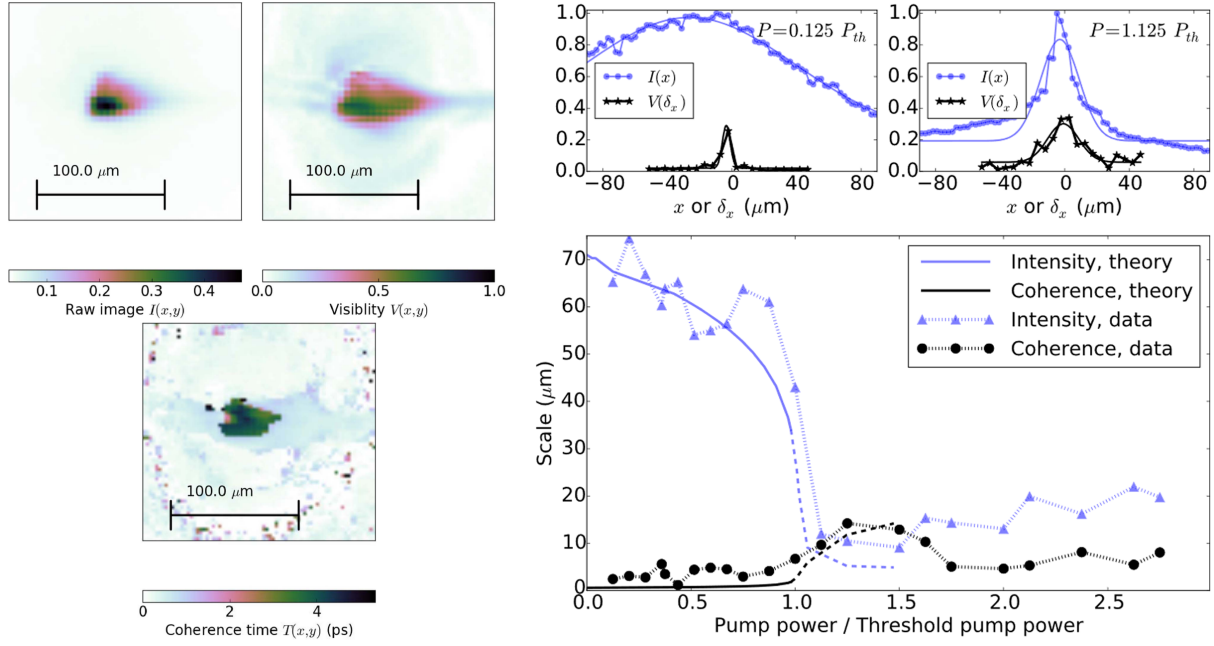


Figure 1.11: Fig taken from [4]. (LEFT) The intensity of the light escaping the cavity as a function of position. The visibility of interference fringes observed by adding a small variable delay to one path of the interferometer. The coherence time of the condensate calculated from the decay rate of the visibility over time. (RIGHT TOP) The intensity at position x and the visibility of light escaping the cavity when one interferometer path is shifted by length δ_x , both taken at zero delay time and fitted with Gaussians. The left plot is generated from data taken below threshold and the right plot above threshold. (RIGHT BOTTOM) The intensity and coherence widths of the light escaping the cavity as functions of pump power, calculated from the widths of the fitted Gaussians similar to those plotted in the top figures. The solid lines are theoretical fits from a conservative equilibrium Bose gas theory.

in visibility. This interferes light from one position on the condensate with light from another position on the condensate. Fig. 1.11 (right, top) shows the normalised intensity of the light below (left) and above (right) threshold in blue. The black lines show the visibility as a function of shift in position. Gaussian fits to these plots allow the intensity and coherence widths to be extracted and plotted in Fig. 1.11 (right, bottom). This shows that the intensity width drops at threshold but that the coherence width increases. Far above threshold the coherence is suppressed due to multiple modes exhibiting macroscopic occupation.

1.5.3 Streak Camera

Imaging the light escaping the cavity with a streak camera allows for picosecond resolution of the mode populations [57]. This permits the observation of oscillations in photon density after an off centre pump pulse. The evolution of the system is the quantum equivalent of a ball rolling up and down a harmonically shaped bowl. Fig. 1.12 (right) shows the spatial intensity of the light over time, instead of continuously moving across the cavity it vanishes from one side of the cavity and appears at the other. If the thermalisation is increased (by decreasing the wavelength), this oscillation is damped

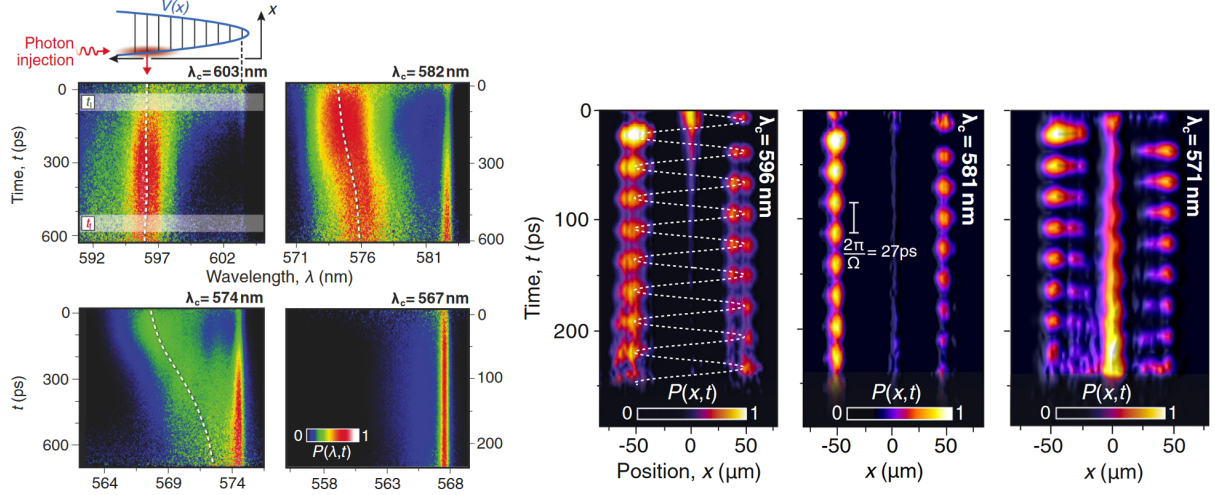


Figure 1.12: Figure taken from [57]. (LEFT) The frequency distribution of light in the cavity over time. The cavity is pumped off centre which injects photons into the cavity at the wavelength indicated by the red arrow. Plot with decreasing wavelength show increasing thermalisation. (RIGHT) The spacial distribution of light over time when pumped off centre.

as the photons are transferred from the higher, oscillating modes into the ground mode. This can also be seen in Fig. 1.12 (left), at high thermalisation rate the photon density is transferred from high frequencies to the ground mode. In both the frequency and spatial domain the transfer into the ground state is a discrete jump, not a smooth transfer through all intermediate modes.

1.6 Theoretical Models of Photon BEC

The majority of this thesis uses the Kirton and Keeling model presented in chapter 2. This section presents alternative models which lead up to the Kirton and Keeling model, and models which provide different perspectives and areas of validity.

1.6.1 Derivation of the Bose-Einstein Distribution

The Kirton and Keeling model is capable of predicting a Bose-Einstein distribution of light within a cavity, however it is instructive to derive this distribution from a simpler model, as shown in [58], using the Einstein A-B coefficients [59]. This provides a strong foundation for the treatment of light as a Bose-Einstein condensate, and also provides insight into the chemical potential of light [60]. Consider a set of molecules with a single ro-vibrationally broadened electronic transition, as shown in Fig. 1.5. The rates of spontaneous emission, stimulated emission, and absorption are respectively:

$$\begin{aligned}
 R_{sp}(\omega) &= \int dE_{\uparrow} N(E_{\uparrow}) A(E_{\uparrow}, \omega) \\
 R_{st}(\omega) &= \int dE_{\uparrow} N(E_{\uparrow}) B_{\downarrow}(E_{\uparrow}, \omega) u(\omega) \\
 R_a(\omega) &= \int dE_{\downarrow} N(E_{\downarrow}) B_{\uparrow}(E_{\downarrow}, \omega) u(\omega)
 \end{aligned} \tag{1.20}$$

where $N(E_{\uparrow})$ are the number of molecules with rovibrational energy $E_{\uparrow}$ for the excited state and $E_{\downarrow}$ for the ground state, A and B are the Einstein A-B coefficients, and u is the spectral energy density per unit volume of light. The number of molecules with rovibrational energy may be expressed as the product of density of rovibrational states $\Upsilon(E_{\uparrow})$, the total number of excited and ground state molecules $N_{\uparrow\downarrow}$, and the relative probability of being in a state with energy $E_{\uparrow}$ of $p_{\uparrow} = e^{-\beta E_{\uparrow}}$.⁹ This gives:

$$N(E_{\uparrow}) = \frac{N_{\uparrow\downarrow} p_{\uparrow} \Upsilon(E_{\uparrow})}{W_{\uparrow}} \quad (1.21)$$

$$W_{\uparrow} = \int E_{\uparrow} \Upsilon(E_{\uparrow}) p_{\uparrow} .$$

The relationships between the Einstein A-B coefficients

$$A(E_{\uparrow}, \omega) dE_{\uparrow} = \hbar \omega D(\omega) B_{\uparrow}(E_{\uparrow}, \omega) \quad (1.22)$$

$$\Upsilon(E_{\uparrow}) B_{\uparrow}(E_{\uparrow}, \omega) dE_{\uparrow} = \Upsilon(E_{\downarrow}) B_{\downarrow}(E_{\downarrow}, \omega) dE_{\downarrow} ,$$

where $D(\omega)$ is the spectral mode density per unit volume, may be also be substituted into Eqs. (1.20), which will allow the common Einstein coefficient to be cancelled at a later point. The rates of spontaneous emission, stimulated emission, and absorption with these substitutions are

$$R_{sp}(\omega) = \frac{N_{\uparrow}}{W_{\uparrow}} \int dE_{\uparrow} \Upsilon(E_{\uparrow}) p_{\uparrow} \hbar \omega D(\omega) B_{\uparrow}(E_{\uparrow}, \omega)$$

$$R_{st}(\omega) = \frac{N_{\uparrow}}{W_{\uparrow}} \int dE_{\uparrow} \Upsilon(E_{\uparrow}) p_{\uparrow} B_{\uparrow}(E_{\uparrow}, \omega) u(\omega) \quad (1.23)$$

$$R_a(\omega) = \frac{N_{\downarrow}}{W_{\downarrow}} \int dE_{\uparrow} \Upsilon(E_{\uparrow}) p_{\downarrow} B_{\downarrow}(E_{\uparrow}, \omega) u(\omega)$$

In the limit of no photon loss, which is achieved in a high fidelity cavity, the rate of change of photon number is the sum of the individual rates

$$\frac{dn}{dt} = R_{sp}(\omega) + R_{st}(\omega) - R_a(\omega) , \quad (1.24)$$

and at steady state is equal to zero. Substitution of Eqs. (1.23) into Eq. (1.24) gives, at steady state,

$$0 = \int dE_{\uparrow} \Upsilon(E_{\uparrow}) B_{\uparrow}(E_{\uparrow}, \omega) \left[\frac{N_{\uparrow}}{W_{\uparrow}} p_{\uparrow} \hbar \omega D(\omega) + \frac{N_{\uparrow}}{W_{\uparrow}} u(\omega) p_{\uparrow} - \frac{N_{\downarrow}}{W_{\downarrow}} u(\omega) p_{\downarrow} \right] . \quad (1.25)$$

which, as $\Upsilon(E_{\uparrow}) B_{\uparrow}(E_{\uparrow}, \omega) > 0$, is true only if the term in the square brackets is zero. This permits the calculation of the steady state spectral density

$$u^{(s)}(\omega) = \frac{\hbar \omega D(\omega)}{\frac{N_{\downarrow} W_{\uparrow} p_{\downarrow}}{N_{\uparrow} W_{\downarrow} p_{\uparrow}} - 1} . \quad (1.26)$$

The ratio of the probabilities of being in the ground and excited states may be calculated using the conservation of energy $\hbar(\omega - \omega_0) = E_{\uparrow} - E_{\downarrow}$ to give

$$u^{(s)}(\omega) = \frac{\hbar \omega D(\omega)}{\frac{N_{\downarrow} W_{\uparrow}}{N_{\uparrow} W_{\downarrow}} e^{\beta \hbar(\omega - \omega_0)} - 1} . \quad (1.27)$$

⁹where $\beta = 1/k_B T$, k_B being the Boltzmann constant, and T being the temperature.

As both the energy density u and the mode density D are per unit volume the photon number distribution may be obtained by integrating over volume, and dividing by the energy of a photon $\hbar\omega$

$$n^{(s)} = \frac{g(\omega)}{\frac{N_{\downarrow}W_{\uparrow}}{N_{\uparrow}W_{\downarrow}} e^{\beta\hbar(\omega-\omega_0)} - 1} . \quad (1.28)$$

where $g(\omega)$ is the spectral mode density. The photon number distribution in Eq. (1.28) has the form of the Bose-Einstein distribution, Eq. (1.6), multiplied by the density of states of frequency ω , provided that the chemical potential of the light is defined as

$$e^{-\beta\mu} = \frac{N_{\downarrow}W_{\uparrow}}{N_{\uparrow}W_{\downarrow}} e^{-\beta\hbar\omega_0} \quad (1.29)$$

or equivalently

$$\mu = \hbar\omega_0 + k_B T [\log(N_{\uparrow}W_{\downarrow}) - \log(N_{\downarrow}W_{\uparrow})] . \quad (1.30)$$

The chemical potential of light in a dye-filled cavity is therefore non-zero, unlike the chemical potential of photons in a black box following the Planck distribution [61]

$$n(\omega) = \frac{\hbar\omega^3}{4\pi^3 c^2} \frac{1}{e^{\beta\hbar\omega} - 1} . \quad (1.31)$$

A non-zero chemical potential is essential for the creation of a BEC, because particles are not conserved when the chemical potential is zero. As the frequency of the light following the Plank distribution approaches the zero chemical potential, the denominator of Eq. (1.31) diverges in an identical fashion to the denominator of a Bose-Einstein distribution. The Plank distribution, however, also exhibits a vanishing density of states as the photon frequency approaches zero, caused by the ω^3 in Eq. (1.31). The vanishing density of states prevents the plank distribution from diverging in the same way as a Bose-Einstein distribution. This problem is overcome in a dye-filled cavity by shifting the chemical potential to a frequency where the density of states is finite, which permits the creation of a condensate. The second interesting property of Eq. (1.30) is its dependence on the molecular excitation $N_{\uparrow}$. As the molecular excitation is easily varied by a pump laser, this allows easy control of the photonic chemical potential during experiments.

1.6.2 Schwinger-Keldysh Model

The Schwinger-Keldysh formalism [62, 63] is a powerful tool capable of calculating future operator expectations in non-equilibrium or chaotic systems. Readers unfamiliar with path integrals may find the online lectures [64] useful to fulfil the general prerequisites of this topic. The Schwinger-Keldysh formalism has been applied to a broad variety of topics, of which [65, 66, 67] are similar to the photonic condensate case. A derivation of the model used in photonic condensates is given in [68] and begins

with the action

$$\begin{aligned}
S[\{a_{\mathbf{k}}\}, \{a_{\mathbf{k}}^*\}, \{b_{\mathbf{p}}\}, \{b_{\mathbf{p}}^*\}] = & \sum_{\mathbf{k}} \int_{G^\infty} dt a_{\mathbf{k}}^*(t) \left(i\hbar \frac{\partial}{\partial t} - \epsilon_\gamma + \mu_\gamma \right) a_{\mathbf{k}}(t) \\
& + \sum_{\mathbf{p}} \int_{G^\infty} dt b_{\mathbf{p}\uparrow}^*(t) \left(i\hbar \frac{\partial}{\partial t} - \epsilon(\mathbf{p}) + \mu_\uparrow - K_\uparrow \right) b_{\mathbf{p}\uparrow}(t) \\
& - \frac{i}{\sqrt{2V}} \sum_{\mathbf{k}, \mathbf{p}} \int_{G^\infty} dt g a_{\mathbf{k}}(t) b_{\mathbf{p}\downarrow} b_{\mathbf{p}+\mathbf{k}_+, \uparrow}^*(t) + \text{h.c.} \\
& + \frac{i}{\sqrt{2V}} \sum_{\mathbf{k}, \mathbf{p}} \int_{G^\infty} dt g a_{\mathbf{k}}(t) b_{\mathbf{p}\downarrow} b_{\mathbf{p}+\mathbf{k}_-, \uparrow}^*(t) + \text{h.c.}
\end{aligned} \tag{1.32}$$

where $a_{\mathbf{k}}$ is the photonic field with momentum $\hbar\mathbf{k}$, $b_{\mathbf{p}}$ are the molecular fields in either the excited or ground state. $\uparrow$ indicates an sum over the excited $\uparrow$ and ground $\downarrow$ fields. Integration is performed along the Schwinger-Keldysh contour G^∞ which runs from time t_0 to infinity and then back to t_0 . μ_γ is the photon chemical potential, $\mu_\uparrow$ and $\mu_\downarrow$ are the chemical potentials of the excited and ground states, $\epsilon_\gamma(\mathbf{k})$ is the photon energy, g is the homogeneous coupling between photons and molecules, V is the cavity volume, and K describes the difference in molecular electronic state energy with $K_\uparrow = \Delta$ and $K_\downarrow = 0$. h.c. indicates the hermitian conjugate of the previous term. The third and fourth terms are identical expect for a change of sign and the exchange of the momentum of the photons travelling forward in the cavity $\mathbf{k}_+$ for the corresponding momentum of photons travelling backwards in the cavity $\mathbf{k}_-$. Explicit dependence on the molecular fields is eliminated from Eq. (1.32) by integrating over them and performing a perturbative expansion to second order in the photon-molecule coupling g . The remaining dependence of the action on the molecules is given by the population of molecules of momentum $\mathbf{p}$ in the ground and excited states, given by the Boltzmann factor

$$N_\uparrow = e^{-\beta(\epsilon(\mathbf{p}) - \mu_\uparrow + K_\uparrow)}, \tag{1.33}$$

where β equals the inverse temperature, $1/k_B T$.

The action given in Eq. (1.32) permits the calculation of the retarded self energy of the photons. An approximation to the absorption and emission spectra of the rhodamine dye used in photonic condensates may be calculated from this as follows. The imaginary part of the photon's self energy is Fourier transformed giving

$$\frac{1}{\hbar} R(\omega) = \frac{|g|^2 m_d^2 c}{2\omega \pi \beta \hbar^5} \sinh\left(\frac{\beta \hbar \omega}{2}\right) e^{\beta(\mu_\downarrow + \mu_\uparrow - \Delta)/2} e^{-\frac{\beta}{4} \left(\epsilon(\omega) + \frac{(\Delta - \hbar \omega)^2}{\epsilon(\omega)} \right)} \tag{1.34}$$

where ω is the photon angular frequency. m_d is the effective mass of the molecules and accounts for the vibrational structure of the dye. ϵ is the dispersion relation of the dye and is given by

$$\epsilon(\mathbf{p}) = \frac{\hbar^2 \mathbf{p}^2}{2m_d},$$

and $\omega = pc$. To calculate the steady state absorption of a beam of photons passing through the dye, the chemical potentials of the excited $\mu_\uparrow$ and ground $\mu_\downarrow$ states of the molecules must be equal, the

photon chemical potential may not be used in this case as most absorption experiments do not have a fixed average photon number. The absorption cross-section of the molecules is then given by

$$\sigma_{abs}(\omega) = \frac{2R(\omega)}{c\hbar n_{\downarrow}} , \quad (1.35)$$

where the density of ground state molecules $n_{\downarrow}$ is

$$n_{\downarrow} = \left(\frac{M}{2\pi\hbar^2\beta} \right)^{3/2} e^{\beta\mu_{\downarrow}} , \quad (1.36)$$

and M is the non-effective mass of the Rhodamine molecules.

The action given in Eq. (1.32) may also be used to prove the fluctuation-dissipation theorem [69, 70] which may be written using the Keldysh self-energy $\Sigma^K(\mathbf{k}, \omega)$ as

$$\hbar\Sigma^K(\mathbf{k}, \omega) = -2i(1 + 2N(\omega))R(\mathbf{k}, \omega) , \quad (1.37)$$

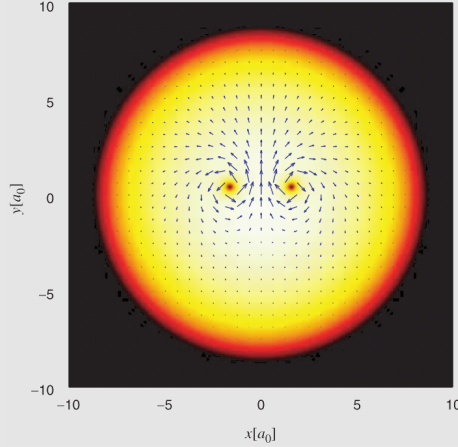
where $N(\omega)$ is the Bose-Einstein distribution. The action may be transformed into a Langevin field equation describing the photon field which, in the approximation of low energy photons, proves that the photons relax to the Bose-Einstein distribution over time. Finally in [68] the chemical potential and spectral functions of the photons at steady state are calculated.

A similar action may be used to calculate the first order correlation of a photon BEC [71]. The results predict that the correlation length of the condensate is larger than condensate size. This demonstrates that the condensate is in a BEC and not a BKT phase, see Box 1.2. This also helps justify treating the photon state as a superposition of modes which span the entire cavity, which the majority of this thesis uses. The model also predicts the temporal phase coherence of photon BECs [72] to be of the order of nano-seconds. It has also been used to study the superfluid-Mott-insulator transition in cavities whose refractive index fluctuates periodically [73]. It has also been used to model an extension of the original photon BEC setup to an array of nanofabricated semiconductor microcavities, which should be capable of demonstrating photon scissor modes [73], which would demonstrate the photon's behaviour as a superfluid [74, 75]

The Schwinger-Keldysh model has many advantages, it incorporates both coherent and incoherent effects and thereby provides an equation for the entire photon field at all positions and time. It includes Gaussian noise, which can model thermal and quantum fluctuations. It generates a closed set of equations containing many system parameters, which allows these parameters to be estimated from experimental data, and also reveals the effects the parameters have on the system. It is similar to other treatments of condensates, for photons [77], exciton polaritons [78], and cold atoms [79, 80], allowing an easy transfer of ideas and innovation between fields. The formalism focuses on modelling the single-mode condensates where the inhomogeneity in molecule excitation does not play a role, which effectively models the early experiments in photon BEC [45]. The homogeneous treatment of the molecules and their early elimination from the action prevents the Schwinger-Keldysh model from treating phenomena involving molecular clamping, e.g. multimode condensation. Additionally the focus on functional integrals provides an excellent mathematical framework, but is far harder to simulate than models employing finite states and operators, which may be represented as vectors and matrices.

Box 1.2: Berezinskii-Kousterlitz-Thouless

Some systems form a Berezinskii-Kousterlitz-Thouless (BKT) phase [22, 23] at finite temperatures instead of a BEC phase. This phase is often called a quasi-condensate and differs from the BEC phase by the presence of bound vortex, anti-vortex pairs. A vortex (anti-vortex) is defined as a $+(−)360$ degree change of phase when travelling along a closed contour. A vortex, anti-vortex pair is shown below [76].



The BKT transition occurs when the bound vortex, anti-vortex pairs separate into free vortices, which is then called the normal phase. This occurs when the free energy

$$\delta F = \delta E - T \delta S$$

is minimised by the separation. In a 2D uniform system both the entropy and energy of the vortices is logarithmic in the system size. This means that the phase boundary between the BKT and normal phases is independent of the system size and instead depends on other system parameters, like the density of vortices. When the vortices are bound the system coherence exhibits long range algebraic order. When the vortices separate this order is destroyed as the vortices no longer cancel out the anti-vortices. At zero temperature the system forms a BEC.

1.6.3 Other Models

[81] uses a quantum Boltzmann equation to show that phase coherence may spontaneously form through the incoherent interactions between photons and the molecules, which is necessary for a “true” BEC. Photonic condensates may also be studied using the a dissipative Gross-Pitaevskii, or Lugiato-Lefever equation [82]. This may be derived from Maxwell’s equations [83, 84] and has the form

$$-i\hbar \frac{\partial \psi}{\partial t} = \left[V(\mathbf{r}) - \frac{\hbar^2}{2m} \nabla_{\perp}^2 + g|\psi|^2 + i(\gamma_{net} - \Gamma|\psi|^2) \right] \psi \quad (1.38)$$

where g is the inter-photon interaction, m is the effective mass of the photons due to the cavity shape $m = \hbar n^2 / c \lambda_0$, V is the potential created by the cavity see Sec. 1.7, γ_{net} is the total rate of

photon gain comprising pumping and loss, and Γ ensures that the pumping is reduced as the photon population increases due to molecular saturation. This model also predicts a non-vanishing photon chemical potential and mass which gives rise to a Bogoliubov dispersion, and sound waves at low photon energies. This has been used to model photons in *flat* cavities, where the photons behave as a superfluid [85, 86], and can exhibit the BKT phase transition [87]. It also predicts oscillations in the position of the photon gas when a curved cavity is pumped off-centre [87]. Readers looking for additional models of photonic condensates may be interested in [88, 89, 90, 91, 92], however these models are not relevant to this thesis.

1.7 Cavity Mode Calculation

The interaction between light and dye is sufficiently weak¹⁰ that the photon state is best described by the modes of the cavity. These may be derived classically, quantised and used to construct a Hamiltonian. The derivation presented in this chapter is sufficient to show that the cavity modes are the 2D harmonic oscillator modes required for this thesis. A derivation including Kerr non-linearity, pumping, and loss may be found in [83]. The electric $\mathbf{E}$ and magnetic $\mathbf{B}$ fields within the cavity obey Maxwell's equations. As there is no free charge or current within the cavity, these have the form

$$\begin{aligned}\nabla \cdot \mathbf{E} &= 0 \\ \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{E} &= -\frac{d\mathbf{B}}{dt} \\ \nabla \times \mathbf{B} &= \frac{1}{\eta^2 c^2} \frac{d\mathbf{E}}{dt}\end{aligned}\tag{1.39}$$

Where η is the refractive index of the dye and solvent, and c is the speed of light. The two curl equations may be combined to eliminate the magnetic field

$$\nabla \times \nabla \times \mathbf{E} = \nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = -\frac{1}{n^2 c^2} \frac{d^2 \mathbf{E}}{dt^2},\tag{1.40}$$

which may be simplified using $\nabla \cdot \mathbf{E} = 0$ into a wave equation

$$\nabla^2 \mathbf{E} = \frac{1}{n^2 c^2} \frac{d^2 \mathbf{E}}{dt^2}.\tag{1.41}$$

The solutions to Eq. (1.41) have the general form $\mathbf{E} = \sum_j \underline{u}_j(\underline{r}) e^{i(\underline{k} \cdot \underline{r} - \omega t)}$, where $\underline{r}$ is the position in the cavity, and $\underline{u}_j$ is a vector indicating the polarisation and amplitude of solution j . If the cavity consisted of two flat parallel mirrors then the solutions to Eq. (1.41) would propagate along the longitudinal axis z , with frequency $\omega = nck$, where k is the z component of $\underline{k}$. A solution to a non-flat cavity may be split into the flat solution $E^{(0)} = e^{ik(z - \eta ct)}$ multiplied by the envelope $E(x, y, z) e^{-i\omega t}$

$$\mathbf{E}(x, z, y) = \hat{\underline{u}} E(x, y, z) e^{ik(z - \eta ct)} e^{-i\omega t}.\tag{1.42}$$

¹⁰The rate of absorption is approximately equal to the rate of loss from the cavity in the systems considered, see Sec. 3.2. A typical cavity lifetime is 4ns [46], and the length of the cavity is approximately 7 wavelengths of light, therefore a photon has a 10^{-6} probability of being absorbed when crossing the cavity.

The frequency of this mode is $\omega = \eta ck + v$. Substituting Eq. (1.42) into Eq. 1.41 gives

$$\frac{d^2 E}{dx^2} + \frac{d^2 E}{dy^2} + \frac{d^2 E}{dz^2} + 2 \frac{dE}{dz} ik = -\frac{v^2}{n^2 c^2} E - \frac{2vk}{\eta c} E \quad (1.43)$$

Where the time derivative of $e^{-ik\eta ct}$ cancels the z derivative of e^{ikz} . As the cavity is approximately flat the solutions to Eq. (1.41) are close to the flat cavity solutions. The envelope therefore varies slowly across the cavity, *i.e.* $\frac{d^2 E}{dz^2} \ll k \frac{dE}{dz}$ and the term $\frac{d^2 E}{dz^2}$ may be neglected. The frequency of the mode is approximately the flat cavity frequency $v \ll \eta ck$, therefore v^2 may be neglected. Eq. (1.43) simplifies to

$$\frac{dE}{dz} = \frac{i}{2k} \left(\frac{d^2 E}{dx^2} + \frac{d^2 E}{dy^2} + \frac{2vk}{\eta c} E \right), \quad (1.44)$$

which is a simplified wave equation of the envelope decoupled from the solution to the flat cavity.

The modes of the cavity are assumed to be constant over time, therefore the phase of the electric field before a round trip of the cavity must be equal to the phase after a round trip. This imposes restrictions on the allowed frequencies of light in the cavity, for a flat cavity the phase of the electric field at position $z = 0$ must be equal to the phase at $z = 2L$, where L is the length of the cavity. This leads to a restriction on k : $e^{i2kL} = 1$. A non-flat cavity introduces two phase shifts to the electric fields over a single round trip. The first is due to the non-zero evolution of the envelope $\frac{dE}{dz} \neq 0$. The second is due to the change in cavity length δL which causes the field to be reflected earlier than the solution to the flat cavity would be. The change in E due to the shape of the mode over a round trip of the cavity may be obtained by integrating Eq. (1.44)

$$\Delta E_{mode} = \frac{i}{2k} 2 \int_0^L \left(\frac{d^2 E}{dx^2} + \frac{d^2 E}{dy^2} + \frac{2vk}{\eta c} E \right) dz \quad (1.45)$$

Where the factor of 2 is included as a cavity round trip contains a forwards and backwards journey. As the cavity is almost flat the envelope E is approximately constant with respect to z , as is the derivative $\frac{dE}{dz}$. Eq. (1.45) therefore approximates to

$$\Delta E_{mode} = \frac{iL}{k} \left(\frac{d^2 E}{dx^2} + \frac{d^2 E}{dy^2} + \frac{2vk}{\eta c} E \right). \quad (1.46)$$

This is balanced by a small change in E over 1 round trip, due to the shape of the cavity. At the curved mirror the field picks up a phase

$$E_1 = E_0 e^{ik2\delta L(x,y)}, \quad (1.47)$$

where $\delta L(x, y)$ is the variation in the length of the cavity. As δL is small compared to the wavelength of light this may be approximated to

$$E_1 = E_0 (1 + ik2\delta L(x, y)). \quad (1.48)$$

Therefore the phase shift in one round trip due to the cavity is

$$\Delta E_{cavity} = ik2\delta L(x, y) E. \quad (1.49)$$

The sum of both phases must be 0 to get a steady state

$$\Delta E_{cavity} + \Delta E_{mode} = 0. \quad (1.50)$$

Substitution of the expressions for the phase shifts, and rearrangement of terms yields the equation

$$-\frac{\eta c}{2k}\nabla_{x,y}^2 E + \frac{\eta ck(-\delta L(x,y))}{L}E = vE, \quad (1.51)$$

where $\nabla_{x,y}^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2}$. This is equivalent to a time-independent Schrödinger equation with mass $\frac{\hbar k}{\eta c}$, potential $-\hbar\eta ck\delta L/L$, and energy $\hbar v$. The modes of the cavity may therefore be obtained by solving the Schrödinger equation with the usual methods.

As the majority of photonic condensates use a parabolic cavity the length change has the form $\delta L = Z(x^2 + y^2)/W^2$, where W is the characteristic width of the cavity and Z is the characteristic change in cavity length. The modes will be the solutions of a two dimensional (2D) harmonic oscillator. These solutions have relative frequencies $v = \omega_{HO}(n + \frac{1}{2})$, where $n \in \mathbb{N}$ and $\omega_{HO} = \eta c/W\sqrt{2Z/L}$ [93]. The frequency of the ground mode is the sum of the frequency obtained from the Schrödinger equation v and the frequency of the flat cavity ηck . As the frequency of the flat cavity varies with cavity length, the frequency of the ground mode may be freely chosen by varying the length of the cavity. The frequency spacing between modes may then be freely chosen by varying the width of the cavity W (or equivalently the depth of the parabola Z). The absorption and emission rates into and from each mode by molecules may therefore be experimentally varied by changing the width and length of the cavity, as they are dependent on the mode frequencies. This control allows the thermalisation of the photons to be varied, as discussed in Chapter 3, and provides a useful tool for studying the breakdown of thermalisation.

The modes of a 2D harmonic oscillator are the 2D Hermite-Gauss modes. The Electric field of a mode in 1D with quantum number m is

$$E_m(x) = H_m(x)e^{-\frac{x^2}{2}} \frac{1}{\sqrt{\sqrt{\pi} 2^m m!}}, \quad (1.52)$$

where the global phase has been discarded, and H_m is the Hermite polynomial of order m [93]. The modes in 2D may be labelled by the quantum number of each dimension of the harmonic oscillator $[p_x, p_y]$. The total electric field of this mode is the product of the fields for each dimension

$$E[p_x, p_y] = E_{p_x}(x)E_{p_y}(y) \quad (1.53)$$

Mode $[0, 0]$ is the ground mode, and has a Gaussian profile. Modes $[0, 1]$ and $[1, 0]$ are the 1st excited modes and the intensity profile of one is the 90 degree rotation of the other, etc. These modes are shown in Fig. 1.13.

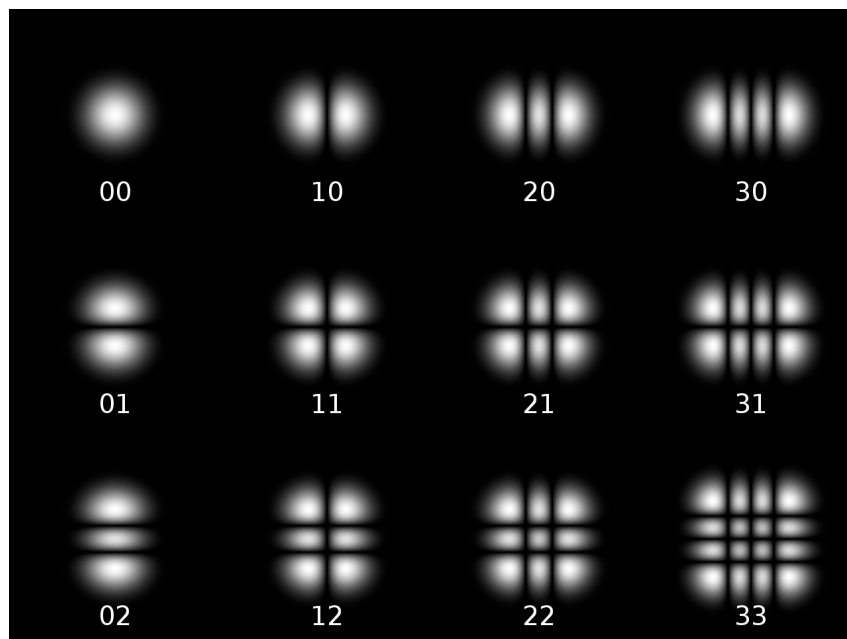


Figure 1.13: The intensity profiles of 12 Hermite-Gauss modes. The pairs of numbers under each profile indicate the level of excitation in each spatial dimension.
<https://en.wikipedia.org/wiki/File:Hermite-gaussian.png>

Chapter 2

A Microscopic Model

This chapter details the derivation of master and rate equations for a photonic condensate from a microscopic Hamiltonian. This work was done by Kirton and Keeling [94, 95, 96], which builds on work done on circuit quantum electro dynamics (QED) [97], quantum dot cavity QED [98], and the dynamics of exciton energy transfer [99]. The first section 2.1 of this chapter introduces a microscopic Hamiltonian which describes photonic condensates. The next section 2.2 transforms this Hamiltonian into a master equation which eliminates the vibrations of the molecules and allows the addition of incoherent pumping and loss. Section 2.2.2 shows how the probability distribution of the photon number may be calculated from the diagonal elements of the density matrix. This is an interesting level of analysis and aids in the understanding of the rate equations used in this thesis, however the diagonal approximation is not required for the derivation of the rate equations or the work presented in this thesis and may therefore be skipped. Section 2.3 uses the master equation to construct rate equations for the mode populations and molecular excitations. Finally some of the results obtained from this model by Kirton and Keeling, and others is presented in section 2.6.

2.1 Hamiltonian

The Hamiltonian constructed in this section will have units of frequency as this is more convenient than energy when considering light. To recover a typical Hamiltonian in units of energy, multiply by the Planck constant $\hbar$. The modes of the cavity derived in Sec. 1.7 may be converted into a Hamiltonian using the usual second quantisation [100]. This introduces the ladder operator $a_m(a_m^\dagger)$ which destroys(creates) a photon in mode m . The energy of the photons in mode m may be written as $\omega_m a_m^\dagger a_m$. The dye molecules are modelled as a two level system corresponding to a single electronic transition within the molecule. Molecule i is therefore in either state $|0_i\rangle$ or $|1_i\rangle$, and the electronic energy of the molecule may be expressed using the Pauli operator σ_z^i as $\frac{\xi}{2}\sigma_z^i$, where ξ is the frequency of the electronic transition. Each molecule also contains a ro-vibrational state modelled by a harmonic oscillator [101] with ladder operators b and $b^\dagger$, and frequency Ω . The vibrational energy of each molecule is therefore $\Omega b_i^\dagger b_i$. The photonic modes and molecules are coupled together using the usual Jaynes-Cummings Hamiltonian [100] $\sum_{m,i} g_{m,j}(a_m \sigma_i^+ + a_m^\dagger \sigma_i^-)$, where $g_{m,j}$ is the coupling strength

between mode m and molecule j . The sum of these terms gives the (incomplete) Hamiltonian

$$H = \sum_m \omega_m a_m^\dagger a_m + \sum_i \left[\frac{\xi}{2} \sigma_i^{(z)} + \Omega b_i^\dagger b_i \right] + \sum_{m,i} g_{m,i} (a_m \sigma_i^+ + a_m^\dagger \sigma_i^-) . \quad (2.1)$$

When a molecule is excited into a new electronic state the structure of the molecular bonds changes. This change causes a shift in the rest position of the molecule, about which the molecule is vibrating. The harmonic potential is therefore transformed from $k_v x^2$ to $k_v (x - x_0)^2$, where k_v gives the strength of the harmonic oscillator, x is the vibrational position, and x_0 the shift in rest position. Expanding the potential $k_v (x - x_0)^2$ gives the original potential $k_v x^2$, a constant term $k_v x_0^2$ which may be absorbed into the electronic transition energy, and a term linear in position, $2k_v x x_0$. This shift may be represented in the Hamiltonian by including an additional x term when the molecule is excited, this is accomplished by the operator $\sigma_i^{(z)} x$. The operator x is proportional to the sum of the ladder operators $b_i + b_i^\dagger$ [102]. The electronic and vibrational states of molecule i are therefore coupled by the term $\Omega \sqrt{S} \sigma_i^z (b_i + b_i^\dagger)$, where the Huang-Rhys parameter $\sqrt{S}$ [103] is the strength of the coupling. The total Hamiltonian for the system is therefore

$$H = \sum_m \omega_m a_m^\dagger a_m + \sum_i \left[\frac{\xi}{2} \sigma_i^{(z)} + \Omega b_i^\dagger b_i \right] + \sum_{m,i} g_{m,i} (a_m \sigma_i^+ + a_m^\dagger \sigma_i^-) + \sum_i \Omega \sqrt{S} \sigma_i^z (b_i + b_i^\dagger) . \quad (2.2)$$

The Hamiltonian contains two separate coupling terms which may be combined into a single coupling using a polaron transform [104], making subsequent analysis easier. The polaron transform may be written as $H \rightarrow U^\dagger H U$ with the unitary operator $U = \exp \left[\sum_i \sqrt{S} \sigma_i^z (b_i - b_i^\dagger) \right]$. To calculate the effect of this transform the following commutation relations are required: $[\sigma^z, \sigma^\pm] = \pm 2\sigma^\pm$ and $[b, b^\dagger] = 1$, as is the identity

$$e^z y e^{-z} = y + [z, y] + \frac{1}{2!} [z, [z, y]] + \frac{1}{3!} [z, [z, [z, y]]] \dots \quad (2.3)$$

with $z = -\sqrt{S} \sigma_i^z (b_i - b_i^\dagger)$. The polaron transformation is linear, therefore its effects on the Hamiltonian may be considered term by term. The mode and molecule energy terms $\sum_m \omega_m a_m^\dagger a_m$ and $\sum_i \frac{\xi}{2} \sigma_i^{(z)}$ are unaffected by the polaron transform as they commute with U . The transformation of the $\sigma_i^\pm$ in the Jaynes-Cummings term is

$$\begin{aligned} U^\dagger \sigma_i^\pm U &= \sigma_i^\pm \pm 2\sqrt{S} (b_i^\dagger - b_i) \sigma_i^\pm + \dots + \sum_n \frac{1}{n!} (\pm 1)^n (2\sqrt{S} (b_i^\dagger - b_i))^n \sigma_i^\pm \\ &= \sigma_i^\pm e^{\pm 2\sqrt{S} (b_i^\dagger - b_i)} . \end{aligned} \quad (2.4)$$

The transformation of $b_i^\dagger b_i$ terminates because $[b_i - b_i^\dagger, b_i^\dagger b_i] = b_i + b_i^\dagger$ and $[b_i - b_i^\dagger, b_i + b_i^\dagger] = 2$. Therefore

$$U^\dagger b_i^\dagger b_i U = b_i^\dagger b_i - \sqrt{S} \sigma_i^{(z)} (b_i + b_i^\dagger) + 2S \quad (2.5)$$

Similarly the transformation of $b_i + b_i^\dagger$ in the electronic and vibrational coupling is

$$U^\dagger \sqrt{S} \sigma_i^{(z)} (b_i + b_i^\dagger) U = \sqrt{S} \sigma_i^{(z)} (b_i + b_i^\dagger) - 2S \quad (2.6)$$

The transformed electronic and vibrational coupling Eq. (2.6) cancels the final two terms in the transformed vibrational energy Eq. (2.5), thereby eliminating the original vibrational-electronic coupling. The transformed Hamiltonian is therefore equal to

$$H = \sum_m \omega_m a_m^\dagger a_m + \sum_i \left[\frac{\xi}{2} \sigma_i^{(z)} + \Omega b_i^\dagger b_i \right] + \sum_{m,i} g_{m,i} (a_m \sigma_i^+ \hat{D}_i + a_m^\dagger \sigma_i^- \hat{D}_i^\dagger) , \quad (2.7)$$

where $\hat{D}_i = \exp[2\sqrt{S}(b_i^\dagger - b_i)]$. The polaron transform has made the coupling between the modes and electronic state explicitly dependent on the vibrational state. This allows the elimination of the vibrational state in the next section.

2.2 Master Equation

The goal of creating a master equation is to remove the vibrational state from the system, and to add incoherent pumping and loss. The vibrational relaxation of the molecules is faster than the other system processes, as discussed in Sec 1.4. This relaxation occurs due to thermal interactions with other molecules, and the dye solvent. The vibrational state of the dye can therefore be approximated as a constant thermal state. It therefore plays the role of the environment in the well established open systems framework [47], and the modes and electronic state of the molecules play the role of the system. The Hamiltonian derived in the previous section, Eq. (2.7), may be split into the system Hamiltonian H_0 , and an interaction Hamiltonian V , $H = H_0 + V$, where

$$\begin{aligned} H_0 &= \sum_m \omega_m a_m^\dagger a_m + \sum_i \left[\frac{\xi}{2} \sigma_i^{(z)} + \Omega b_i^\dagger b_i \right] \\ V &= \sum_{m,i} g_{m,i} (a_m \sigma_i^+ \hat{D}_i + a_m^\dagger \sigma_i^- \hat{D}_i^\dagger) . \end{aligned} \quad (2.8)$$

To create a master equation the system Hamiltonian is temporarily removed using the interaction picture. The interaction Hamiltonian is then treated perturbatively, up to second order. The vibrational part of the interaction Hamiltonian is eliminated by performing the trace over it with a thermal state. The system is then transformed out of the interaction picture so that the system Hamiltonian may be included. Finally the incoherent pumping and loss is added as Lindblad terms.

The evolution of the system may be explicitly included in the definition of the density matrix to eliminate it from the equation of motion. This transformation is called the interaction picture. The interaction density matrix is defined as $\tilde{\rho} = e^{iH_0 t} \rho e^{-iH_0 t}$. Taking the derivative with respect to time gives

$$\frac{d\tilde{\rho}}{dt} = e^{iH_0 t} \frac{d\rho}{dt} e^{-iH_0 t} + i e^{iH_0 t} H_0 \rho e^{-iH_0 t} - i e^{iH_0 t} \rho H_0 e^{-iH_0 t} . \quad (2.9)$$

The original density matrix is known to evolve under the full Hamiltonian as $\frac{d\rho}{dt} = -i[H_0 + V, \rho]$, therefore Eq. (2.9) simplifies to

$$\frac{d\tilde{\rho}}{dt} = -i e^{iH_0 t} [V, \rho] e^{-iH_0 t} . \quad (2.10)$$

Inserting the identity $e^{-iH_0 t} e^{iH_0 t}$ in between each product of V and ρ transforms these variables into the interaction picture, therefore Eq. (2.9) is equivalent to

$$\frac{d\tilde{\rho}}{dt} = -i[\tilde{V}, \tilde{\rho}] , \quad (2.11)$$

where $\tilde{V}$ is defined as $e^{iH_0t}V e^{-iH_0t}$. This transformation has removed the system Hamiltonian H_0 from the evolution. To proceed the transformed interaction Hamiltonian $\tilde{V}$ must be calculated. As all the terms in H_0 commute, the propagator e^{iH_0t} may be split into multiple exponentials giving this form for the transformed interaction Hamiltonian

$$\tilde{V} = e^{i\sum_m \omega_m a_m^\dagger a_m t} e^{i\sum_i \frac{\xi}{2} \sigma_i^{(z)} t} e^{i\sum_i \Omega b_i^\dagger b_i t} V e^{-i\sum_i \Omega b_i^\dagger b_i t} e^{-i\sum_i \frac{\xi}{2} \sigma_i^{(z)} t} e^{-i\sum_m \omega_m a_m^\dagger a_m t} . \quad (2.12)$$

The calculation of $\tilde{V}$ requires Eq. (2.3) and the following commutation relations

$$\begin{aligned} [a, a^\dagger] &= 1 \\ [a^\dagger a, a] &= -a \\ [a^\dagger a, a^\dagger] &= a^\dagger \\ [\frac{\sigma^z}{2}, \sigma^\pm] &= \pm \sigma^\pm . \end{aligned} \quad (2.13)$$

The first exponential is absorbed into the definition of D to give $D' = e^{i\sum_i \Omega b_i^\dagger b_i t} D e^{-i\sum_i \Omega b_i^\dagger b_i t}$. Note that D' contains no photonic or electronic terms and therefore has no direct effect on the system evolution. The second exponential commutes with everything except the electronic state operator $\sigma_i^\pm$, and the only transformation it induces is

$$\begin{aligned} e^{i\frac{\xi}{2} \sigma_i^{(z)} t} \sigma_i^\pm e^{-i\frac{\xi}{2} \sigma_i^{(z)} t} &= \sigma_i^\pm \pm i \xi t \sigma_i^\pm + \dots + \sum_n \frac{1}{n!} (\pm i)^n \xi^n t^n \sigma_i^\pm \\ &= \sigma_i^\pm e^{\pm i \xi t} . \end{aligned} \quad (2.14)$$

The photonic exponential commutes with everything except the mode ladder operators

$$\begin{aligned} e^{i\omega_m a_m^\dagger a_m t} a_m e^{-i\omega_m a_m^\dagger a_m t} &= a_m - i\omega_m a_m + \sum_n (-i)^n \omega_m^n a_m \\ &= a_m e^{-i\omega_m t} . \end{aligned} \quad (2.15)$$

The transformation of $a_m^\dagger$ is identical to a_m but with a negative frequency ω_m . The combination of the transformations induced by the exponentials in Eq. (2.12) is

$$\tilde{V} = \sum_{m,i} g_{m,i} \left[a_m \sigma_+^i e^{i(\xi - \omega_m)t} D_i'(t) + a_m^\dagger \sigma_-^i e^{-i(\xi - \omega_m)t} D_i'(t)^\dagger \right] . \quad (2.16)$$

It is hard to directly solve Eq. (2.11) using this value of interaction Hamiltonian $\tilde{V}$, so an iterative procedure is used. First Eq. (2.11) is integrated with respect to time

$$\tilde{\rho}(t) = \tilde{\rho}(0) - i \int_0^t [\tilde{V}(t'), \tilde{\rho}(t')] dt' . \quad (2.17)$$

This solution for $\tilde{\rho}(t)$ is substituted into the right hand side of equation Eq. (2.11) leading to

$$\frac{d\tilde{\rho}(t)}{dt} = -i [\tilde{V}, \tilde{\rho}(0)] - \int_0^t [\tilde{V}(t), [\tilde{V}(t'), \tilde{\rho}(t')]] dt' . \quad (2.18)$$

The first order term $-i [\tilde{V}, \tilde{\rho}(0)]$ shall be approximated as zero in this section, and discussed further in Sec. 2.2.1. Repeating the substitution would produce terms with higher powers of $\tilde{V}$. After the

approximations in this section have been applied these terms would lead to a more accurate result, however, as the coupling between modes and molecules is weak, higher powers of $\tilde{V}$ are negligible. To simplify this expression the system s (modes and electronic transition) and environment e (vibrations) are split. The system state starts out uncorrelated, in a product state $\tilde{\rho}_{s,e}(0) = \tilde{\rho}_s(0) \otimes \tilde{\rho}_e(0)$. As the vibrational relaxation time is fast, any correlations between the system and environment are quickly destroyed. The system therefore remains in a product state for all time, this is called the Born approximation. In addition to this, the environment state is a constant due to the rapid thermal interactions $\tilde{\rho}_e(t') = \tilde{\rho}_e(0)$. This allows the time dependent coupling between the system and vibrations to be replaced by a constant, which shall influence the rates of photon absorption and emission.

To evaluate the commutators in Eq. (2.18) and derive a master equation it is useful to split the interaction Hamiltonian $\tilde{V}$ into system terms $A_{m,j} = g_{m,j}a_m\sigma_j^+$ and environment (vibrational) terms $B_{m,j} = e^{-i(\xi-\omega_m)t}D'_j(t)$,

$$\tilde{V}(t) = \sum_{r,i} A_{r,i}B_{r,i}(t) + A_{r,i}^\dagger B_{r,i}(t)^\dagger . \quad (2.19)$$

Substitution into Eq. (2.18) gives

$$\frac{d\tilde{\rho}(t)}{dt} = - \sum_{r,m,i,j,conj} \int_0^t [A_{r,i}B_{r,i}(t), [A_{m,j}B_{m,j}(t'), \tilde{\rho}_{s,e}(t')]] dt' , \quad (2.20)$$

where *conj* indicates every combination of individually conjugating $A_{r,i}B_{r,i}$ and $A_{m,j}B_{m,j}$. As the system and environment variables in Eq. (2.20) commute they may be grouped together

$$\frac{d\tilde{\rho}(t)}{dt} = - \sum_{r,m,i,j,conj} \int_0^t [A_{r,i}B_{r,i}(t) , \{ A_{m,j}\tilde{\rho}_s(t') \} \{ B_{m,j}(t')\tilde{\rho}_e(0) \} - \{ \tilde{\rho}_s(t')A_{m,j} \} \{ \tilde{\rho}_e(0)B_{m,j}(t') \}] dt' . \quad (2.21)$$

The state of the environment is not required and can be removed by performing the trace over the environment.

$$\begin{aligned} \frac{d\tilde{\rho}_s(t)}{dt} &= \text{Tr}_e \left\{ \frac{d\tilde{\rho}(t)}{dt} \right\} \\ &= - \sum_{r,m,i,j,conj} \int_0^t \text{Tr}_e [A_{r,i}B_{r,i}(t) , (A_{m,j}\tilde{\rho}_s(t'))(B_{m,j}(t')\tilde{\rho}_e(0)) - (\tilde{\rho}_s(t')A_{m,j})(\tilde{\rho}_e(0)B_{m,j}(t'))] dt' . \end{aligned} \quad (2.22)$$

The commutator may be expanded using the identity

$$[ab, cd] = ac[b, d] + a[b, c]d + c[a, d]b + [a, c]db . \quad (2.23)$$

Due to the cyclicity of the trace the term $\text{Tr}_e[B_{r,i}, B_{m,j}\tilde{\rho}_e]$ is zero. The terms $A_{r,i}$ and $B_{r,i}$ only contain system and environment variables respectively, therefore they commute. The only remaining terms after performing the commutator expansion Eq. (2.23) are

$$\begin{aligned} \frac{d\tilde{\rho}_s(t)}{dt} &= - \sum_{r,m,i,j,conj} \int_0^t [A_{r,i}, A_{m,j}\tilde{\rho}_s(t')] \text{Tr}_e \{ B_{m,j}(t')\tilde{\rho}_e(0)B_{r,i}(t) \} \\ &\quad - [A_{r,i}, \tilde{\rho}_s(t')A_{m,j}] \text{Tr}_e \{ \tilde{\rho}_e(0)B_{m,j}(t')B_{r,i}(t) \} dt' . \end{aligned} \quad (2.24)$$

As discussed in Sec. 2.2.1, the environment terms $B_{r,i}$ oscillate rapidly compared to the evolution of the system. The term $\text{Tr}_e\{\tilde{\rho}_e(0)B_{m,j}(t')B_{r,i}(t)\}$ therefore averages to zero unless the frequencies of $B_{m,j}$ and $B_{r,i}$ cancel. As the anisotropy¹ of the cavity ensures that all modes have a different frequency, the term $\text{Tr}_e\{\tilde{\rho}_e(0)B_{m,j}(t')B_{r,i}(t)\}$ is proportional to a delta function in i, j and m, r . Eq. (2.24) therefore simplifies to

$$\begin{aligned} \frac{d\tilde{\rho}_s(t)}{dt} = & - \sum_{r,i,conj} \int_0^t [A_{r,i}, A_{r,i}^\dagger \tilde{\rho}_s(t')] \text{Tr}_e\{B_{r,i}(t')^\dagger \tilde{\rho}_e(0)B_{r,i}(t)\} \\ & + [\tilde{\rho}_s(t')A_{r,i}^\dagger, A_{r,i}] \text{Tr}_e\{\tilde{\rho}_e(0)B_{r,i}(t')^\dagger B_{r,i}(t)\} dt' . \end{aligned} \quad (2.25)$$

The molecules are being rapidly thermalised, therefore the displacement operators are uncorrelated in time and $\text{Tr}_e\{B_{r,i}(t')^\dagger \tilde{\rho}_e(0)B_{r,i}(t)\}$ is zero unless $t' \approx t$. Therefore the t' argument of $\tilde{\rho}_s(t')$ may be replaced with t , and the sum over the conjugates of $A_{r,i}$ and $B_{m,j}$ may be performed

$$\begin{aligned} \frac{d\tilde{\rho}_s(t)}{dt} = & - \sum_{r,i} \int_0^t [A_{r,i}, A_{r,i}^\dagger \tilde{\rho}_s(t)] \text{Tr}_e\{B_{r,i}(t)B_{r,i}(t')^\dagger \tilde{\rho}_e(0)\} + [\tilde{\rho}_s(t)A_{r,i}^\dagger, A_{r,i}] \text{Tr}_e\{B_{r,i}(t')^\dagger B_{r,i}(t)\tilde{\rho}_e(0)\} \\ & [A_{r,i}^\dagger, A_{r,i}\tilde{\rho}_s(t)] \text{Tr}_e\{B_{r,i}(t)^\dagger B_{r,i}(t')\tilde{\rho}_e(0)\} + [\tilde{\rho}_s(t)A_{r,i}, A_{r,i}^\dagger] \text{Tr}_e\{B_{r,i}(t')B_{r,i}(t)^\dagger \tilde{\rho}_e(0)\} dt' . \end{aligned} \quad (2.26)$$

The traces over the environment may be replaced with the constants

$$\begin{aligned} J_r^{(1)} &= \int_{-\infty}^t \text{Tr}_e\{B_{r,i}(t)B_{r,i}(t')^\dagger \tilde{\rho}_e(0)\} dt' \\ J_r^{(2)} &= \int_{-\infty}^t \text{Tr}_e\{B_{r,i}(t)^\dagger B_{r,i}(t')\tilde{\rho}_e(0)\} dt' , \end{aligned} \quad (2.27)$$

where the extension of the lower limit to $-\infty$ is permitted because $\text{Tr}_e\{B_{r,i}(t)B_{r,i}(t')^\dagger \tilde{\rho}_e(0)\}$ is zero unless $t' \approx t$. The thermal environment state $\tilde{\rho}_e$ is identical for all molecules, and the operators $B_{r,i}$ are invariant under change of molecule, therefore the constants $J_r^{(1)}$ and $J_r^{(2)}$ do not depend on the molecule index i . Conjugating $J_r^{(1)}$ and $J_r^{(2)}$ exchanges the time variables t and t' . To show this use the identity $\text{Tr}_e\{C\}^* = \text{Tr}_e\{C^\dagger\}$

$$J_r^{(1)*} = \int_0^t \text{Tr}_e\{(B_{r,i}(t)B_{r,i}(t')^\dagger \tilde{\rho}_e(0))^\dagger\} dt' . \quad (2.28)$$

Using the identity $(CD)^\dagger = D^\dagger C^\dagger$ and the cyclicity of the trace gives

$$J_r^{(1)*} = \int_0^t \text{Tr}_e\{B_{r,i}(t')B_{r,i}(t)^\dagger \tilde{\rho}_e(0)\} dt' . \quad (2.29)$$

The constants $J_r^{(1)}$ and $J_r^{(2)}$ may be substituted into Eq. (2.26) and split into real and imaginary parts

$$\begin{aligned} \frac{d\tilde{\rho}_s(t)}{dt} = & - \sum_{r,i} \int_0^t [A_{r,i}, A_{r,i}^\dagger \tilde{\rho}_s(t)] \left\{ \Re[J_r^{(1)}] + i\Im[J_r^{(1)}] \right\} + [\tilde{\rho}_s(t)A_{r,i}^\dagger, A_{r,i}] \left\{ \Re[J_r^{(2)}] - i\Im[J_r^{(2)}] \right\} \\ & [A_{r,i}^\dagger, A_{r,i}\tilde{\rho}_s(t)] \left\{ \Re[J_r^{(2)}] + i\Im[J_r^{(2)}] \right\} + [\tilde{\rho}_s(t)A_{r,i}, A_{r,i}^\dagger] \left\{ \Re[J_r^{(1)}] - i\Im[J_r^{(1)}] \right\} . \end{aligned} \quad (2.30)$$

¹A 2D harmonic oscillator is used with slightly different frequencies in each dimension which ensures that the term $\text{Tr}_e\{\tilde{\rho}_e(0)B_{m,j}(t')B_{r,i}(t)\}$ oscillates fast enough to destroy inter-mode coherence without greatly changing the mode frequencies.

The real terms combine to give Lindblad operators

$$\mathcal{L}[\hat{X}](\rho) = \hat{X}^\dagger \hat{X} \rho + \rho \hat{X}^\dagger \hat{X} - 2\hat{X} \rho \hat{X}^\dagger, \quad (2.31)$$

and the imaginary terms form commutators. Eq. (2.30) therefore becomes

$$\begin{aligned} \frac{d\tilde{\rho}_s(t)}{dt} = & - \sum_{r,i} \left\{ \Re[J_r^{(1)}] \mathcal{L}[A_{r,i}^\dagger] \tilde{\rho}_s(t) + \Re[J_r^{(2)}] \mathcal{L}[A_{r,i}] \tilde{\rho}_s(t) + \right. \\ & \left. + i \Im[J_r^{(1)}] (A_{r,i} A_{r,i}^\dagger \tilde{\rho}_s(t) - \tilde{\rho}_s(t) A_{r,i} A_{r,i}^\dagger) + i \Im[J_r^{(2)}] (A_{r,i}^\dagger A_{r,i} \tilde{\rho}_s(t) - \tilde{\rho}_s(t) A_{r,i}^\dagger A_{r,i}) \right\}. \end{aligned} \quad (2.32)$$

Substituting the system operators $A_{r,i} = g_{r,i} a_r \sigma_i^+$ back into Eq. (2.32) gives

$$\begin{aligned} \frac{d\tilde{\rho}_s(t)}{dt} = & - \sum_{r,i} g_{r,i}^2 \left\{ \Re[J_r^{(1)}] \mathcal{L}[a_r^\dagger \sigma_i^-] \tilde{\rho}_s(t) + \Re[J_r^{(2)}] \mathcal{L}[a_r \sigma_i^+] \tilde{\rho}_s(t) + \right. \\ & \left. + i \Im[J_r^{(1)}] [a_r \sigma_i^+ a_r^\dagger \sigma_i^-, \tilde{\rho}_s(t)] + i \Im[J_r^{(2)}] [a_r^\dagger \sigma_i^- a_r \sigma_i^+, \tilde{\rho}_s(t)] \right\}. \end{aligned} \quad (2.33)$$

Eq. (2.33) may be transformed out of the interaction picture into the original Schrödinger picture using the inverse transformation $\rho = e^{-iH_0 t} \tilde{\rho} e^{iH_0 t}$. The identity $\mathcal{I} = e^{iH_0 t} e^{-iH_0 t}$ may be inserted between all products of operators, so that each operator is transformed individually. In Eqs. (2.15) and (2.14) it was shown that a_m and $a_m^\dagger$ are unchanged by this transformation and pick up opposite phases $e^{i\omega_m t}$ and $e^{-i\omega_m t}$. Similarly the operators $\sigma_i^\pm$ pick up opposite phases. As each operator in Eq. (2.33) appears with its conjugate, these phases cancel. The only effect of transforming back to the Schrödinger picture is the conversion of the density matrix $\tilde{\rho}$ back into the Schrödinger form ρ , and the addition of the system Hamiltonian to the evolution.

$$\begin{aligned} \frac{d\rho_s(t)}{dt} = & -i \left[H_0 + \sum_{r,i} g_{r,i}^2 \left\{ \Im[J_r^{(1)}] a_r \sigma_i^+ a_r^\dagger \sigma_i^- + \Im[J_r^{(2)}] a_r^\dagger \sigma_i^- a_r \sigma_i^+ \right\}, \rho \right] + \\ & - \sum_{r,i} g_{r,i}^2 \left\{ \Re[J_r^{(1)}] \mathcal{L}[a_r^\dagger \sigma_i^-] \rho_s(t) + \Re[J_r^{(2)}] \mathcal{L}[a_r \sigma_i^+] \rho_s(t) \right\} \end{aligned} \quad (2.34)$$

The addition to the system Hamiltonian,

$$\Delta H = g_{r,i}^2 \left\{ \Im[J_r^{(1)}] a_r \sigma_i^+ a_r^\dagger \sigma_i^- + \Im[J_r^{(2)}] a_r^\dagger \sigma_i^- a_r \sigma_i^+ \right\}$$

may be transformed using the relations $aa^\dagger = a^\dagger a + 1$, $\sigma_i^+ \sigma_i^- = \frac{\mathcal{I} + \sigma_i^{(z)}}{2}$ and $\sigma_i^- \sigma_i^+ = \frac{\mathcal{I} - \sigma_i^{(z)}}{2}$ into

$$\Delta H = g_{r,i}^2 \left\{ \frac{\Im[J_r^{(1)}] + \Im[J_r^{(2)}]}{2} a_r^\dagger a_r + \frac{\Im[J_r^{(1)}] - \Im[J_r^{(2)}]}{2} a_r^\dagger a_r \sigma_i^{(z)} + \frac{\Im[J_r^{(1)}]}{2} \sigma_i^{(z)} + \Im[J_r^{(1)}] \right\} \quad (2.35)$$

The terms $a_r^\dagger a_r$ and $\sigma_i^{(z)}$ create shifts in the frequencies of the modes and the electronic transition frequency respectively, and may be absorbed into the definitions of ω and ξ respectively. The constant term commutes with the density matrix and may be dropped. The $a_r^\dagger a_r \sigma_i^{(z)}$ term couples diagonal elements of the density matrix to themselves, i.e. $a_r^\dagger a_r \sigma_i^{(z)} |\underline{n}, \underline{s}\rangle \langle \underline{n}, \underline{s}| \propto |\underline{n}, \underline{s}\rangle \langle \underline{n}, \underline{s}|$ (see Sec. 2.2.2 for the definition of the state $|\underline{n}, \underline{s}\rangle$). As the term $a_r^\dagger a_r \sigma_i^{(z)}$ appears in a commutator it will

therefore have no affect on the evolution of the diagonal elements of the density matrix, and may be excluded from the calculations performed in Secs. 2.2.2 and 2.3. This term would have to be included for any calculations involving the off diagonal matrix elements, for example the phase coherence of the light. The $\mathcal{L}[a_r\sigma_i^+]$ and $\mathcal{L}[a_r^\dagger\sigma_i^-]$ terms respectively describe the incoherent absorption and emission of a photon from or into mode m by molecule i . The rates describing these processes are relabelled as $\frac{\Lambda_\downarrow^{(m)}(r_j)}{2} = g_{m,i}^2 \Re[J_m^{(1)}]$ and $\frac{\Lambda_\uparrow^{(m)}(r_j)}{2} = g_{m,i}^2 \Re[J_m^{(2)}]$. The coupling between a mode and a molecule $g_{m,j}$ is dependent on the intensity of the mode at the position of the molecule therefore $g_{m,j}$ is replaced with a dependence of Λ on the molecular position r_j . This completes the transformation of the Hamiltonian into a master equation which does not contain molecular vibrations.

The pumping of molecules and the decay of molecular excitation not described by emission into cavity modes, are incoherent processes, due to the rapid dephasing of the molecules. The loss of photons from the cavity is also incoherent due to the negligible photon population outside the cavity. These processes may therefore be accounted for by adding Lindblad terms to the master equation, where $\frac{\kappa}{2}\mathcal{L}[\hat{a}_m]$, $\frac{\Gamma_\uparrow}{2}\mathcal{L}[\hat{\sigma}_i^+]$, and $\frac{\Gamma_\downarrow}{2}\mathcal{L}[\hat{\sigma}_i^-]$ correspond to the decay of photons from mode m with rate κ , the pumping of molecule i with rate $\Gamma_{\uparrow,i}$, and the decay of molecule i with rate $\Gamma_\downarrow$. The full master equation is therefore

$$\begin{aligned} \dot{\rho} = & -i[\tilde{H}_0, \rho] - \left\{ \sum_m \frac{\kappa}{2} \mathcal{L}[\hat{a}_m] + \sum_i \left[\frac{\Gamma_{\uparrow,i}}{2} \mathcal{L}[\hat{\sigma}_i^+] + \frac{\Gamma_\downarrow}{2} \mathcal{L}[\hat{\sigma}_i^-] \right] \right. \\ & \left. + \sum_{m,i} \left[\frac{\Lambda_\downarrow^{(m)}(r_j)}{2} \mathcal{L}[\hat{a}_m^\dagger \hat{\sigma}_i^-] + \frac{\Lambda_\uparrow^{(m)}(r_j)}{2} \mathcal{L}[\hat{a}_m \hat{\sigma}_i^+] \right] \right\} \rho. \end{aligned} \quad (2.36)$$

Where $\tilde{H}_0$ is the sum of the original system Hamiltonian and the additional terms ΔH .

2.2.1 Mode Molecule Coherence

In the previous section the term $-i[\tilde{V}, \tilde{\rho}(0)]$ in Eq. (2.18) was approximated to zero. A full justification of this is given in [105]. In the terminology used there: the rhodamine dye used to create photonic condensates has a dimensionless coupling strength η of 0.6. This leads to a reduction in the original mode molecule coupling from g (defined in the original Hamiltonian Eq. (2.2)). The paper [105] shows that this reduction is at least two orders of magnitude, and that the first order terms may be neglected in this case. Note that the laser regime discussed in [105] is achieved by changing the spectral density² of the dye, and is therefore different to the laser phase discussed in chapter 3.2.

An intuitive reason for discarding the first order coherence between modes and molecules may be seen by considering the environment term in the interaction Hamiltonian $B_{m,j} = e^{-i(\xi - \omega_m)t} D_j'(t)$. The environment term $B_{m,j}$ oscillates at the detuning frequency of a mode, which is of the order of 10THz. The other system processes have time scales of order 1ns [46], therefore the term $-i[\tilde{V}, \tilde{\rho}(0)]$ creates a fast oscillating phase which averages to zero.

²The density of ro-vibrational harmonic oscillator modes per unit harmonic oscillator frequency.

2.2.2 Diagonal Approximation



The formulae derived in this section are interesting but not used in the rest of this thesis.

You may skip to Sec. 2.3

The density matrix ρ gives complete information about the state of the system, which is required to calculate many properties of the system, for example the phase coherence between modes $\text{Tr}[a_m^\dagger a_l \rho]$, or between modes and molecules $\text{Tr}[a_m^\dagger \sigma_i^- \rho]$. There are however, many operators which are diagonal in the natural mode, molecule basis, and do not change the system state, for example, the mode population $a_m^\dagger a_m$, molecule excitation $\frac{\sigma_i^{(z)} + 1}{2}$, and second order coherence $a_m^\dagger a_l^\dagger a_m a_l$. The expectations of these operators may be calculated from just the diagonal elements of the density matrix. This section demonstrates that the off-diagonal elements of the density matrix do not couple to the diagonal elements. The off-diagonal elements may therefore be discarded for some analyses, and the system properties calculated from only the diagonal elements. This reduces the complexity of the equations and simulations.

As there are many modes their populations may be described by a vector $\underline{n}$, where n_i is the population in mode i . Similarly the excitation of the molecule i , $\frac{\langle \sigma_i^{(z)} \rangle + 1}{2}$, may be written as an element of the vector $\underline{s}$. A system state may therefore be written as $|\underline{n}, \underline{s}\rangle$. The expectation value of any operator O may be written as $\langle \hat{O} \rangle = \text{Tr}[\hat{O} \hat{\rho}]$. Writing $\hat{\rho}$ in terms of the basis vectors $|\underline{n}, \underline{s}\rangle$, and the matrix $\rho_{\underline{n}_2, \underline{n}_3, \underline{s}_2, \underline{s}_3}$ gives the operator expectation

$$\langle \hat{O} \rangle = \sum_{\underline{n}_1, \underline{s}_1} \langle \underline{n}_1, \underline{s}_1 | \hat{O} \left[\sum_{\underline{n}_2, \underline{n}_3, \underline{s}_2, \underline{s}_3} \rho_{\underline{n}_2, \underline{n}_3, \underline{s}_2, \underline{s}_3} |\underline{n}_2, \underline{s}_2\rangle \langle \underline{n}_3, \underline{s}_3| \right] | \underline{n}_1, \underline{s}_1 \rangle . \quad (2.37)$$

If the operator $\hat{O}$ does not change the system state, the product $\hat{O} |\underline{n}, \underline{s}\rangle$ is equal to $O(\underline{n}, \underline{s}) |\underline{n}, \underline{s}\rangle$, where $O(\underline{n}, \underline{s})$ is a number dependent on O , $\underline{n}$, and $\underline{s}$. The expectation then becomes

$$\langle \hat{O} \rangle = \sum_{\underline{n}_1, \underline{s}_1} O(\underline{n}_1, \underline{s}_1) \rho_{\underline{n}_1, \underline{n}_1, \underline{s}_1, \underline{s}_1} , \quad (2.38)$$

which involves only the diagonal elements of the density matrix. It may be shown that the diagonal elements of the density matrix only couple to other diagonal elements as follows. The master equation (2.36) contains the commutator of the modified system Hamiltonian with ρ . This Hamiltonian contains only photon number operators, and molecular excitation operators, neither of which change the states on which they act. The Lindblad superoperator groups operators with their Hermitian conjugates via two terms, Eq. (2.31). In the correlators³ the operators a_m and σ_i^+ are directly multiplied with their conjugates, and their products do not change the system state. The remaining Lindblad terms $-2\hat{X}\rho\hat{X}$, couples diagonal elements of the density matrix to other diagonal elements, for example the Lindblad term containing the operator a couples the matrix element $|n\rangle \langle n|$ to the matrix element $|n-1\rangle \langle n-1|$. As the master equation only couples the diagonal elements to other diagonal

³The correlator of A and B is $AB + BA$

elements the evolution of the diagonal elements may be calculated without considering the off diagonal elements.

To perform calculations using only the off diagonal elements the full density matrix is replaced with a vector of the diagonal elements $P_{\underline{n}, \underline{s}}$.

$$\rho = \sum_{\underline{n}, \underline{s}} P_{\underline{n}, \underline{s}} |\underline{n}, \underline{s}\rangle \langle \underline{n}, \underline{s}| . \quad (2.39)$$

In the rest of this section the coupling between the modes and the molecules is assumed to be homogeneous, *i.e.* $\Lambda_{\uparrow}^{(m)}(\underline{r}) = \Lambda_{\uparrow}^{(m)}$. As the coupling is a constant, the states of two molecules may be swapped without changing the dynamics of the modes. It is therefore more useful to use molecular states which are incoherent mixtures of molecular eigenstates. Each mixture is defined as the sum of all molecular eigenstates with the same total excitation

$$\nu_j = \frac{1}{J C_j} \sum_{\underline{s} \in \{\underline{s} : \underline{s} = j\}} |\underline{s}\rangle \langle \underline{s}| , \quad (2.40)$$

where $\sum_{\underline{s} \in \{\underline{s} : \underline{s} = j\}}$ is the sum over all $\underline{s}$ with excitation j . $J C_j = \frac{J!}{j!(J-j)!}$ is the binomial coefficient for exciting j molecules from J total molecules, this is included to ensure that the trace of ν_j is one.

! The normalisation $\frac{1}{J C_j}$ is omitted from Kirton and Keeling's derivation ([95], paragraph after equation (26)). Despite omitting the normalisation they achieve the correct result, presumably by using phenomenological derivations of Eqs. (2.50) and (2.51).

The

diagonal of the density matrix may be written using the incoherent sum as

$$\rho = \sum_{\underline{n}, j} P_{\underline{n}, j} |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j . \quad (2.41)$$

An equation for the evolution of the diagonal elements $P_{\underline{n}, j}$ may be obtained by substituting Eq. (2.41) into the master equation (2.36). As the substituted density matrix is diagonal, the commutator with the Hamiltonian is zero. The second term is equal to

$$\sum_{\underline{n}, j} \dot{P}_{\underline{n}, j} |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j \stackrel{\kappa}{=} - \sum_{m, \underline{n}, j} \frac{\kappa}{2} \mathcal{L}[\hat{a}_m] P_{\underline{n}, j} |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j , \quad (2.42)$$

where $\stackrel{\kappa}{=}$ indicates that only the part of $\sum_{\underline{n}, j} \dot{P}_{\underline{n}, j} |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j$ proportional to κ is being considered. Expansion of the Lindblad superoperator gives

$$\sum_{\underline{n}, j} \dot{P}_{\underline{n}, j} |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j \stackrel{\kappa}{=} - \sum_{m, \underline{n}, j} \frac{\kappa}{2} P_{\underline{n}, j} [a_m^\dagger a_m |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j + |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j a_m^\dagger a_m - 2a_m^\dagger |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j a_m] . \quad (2.43)$$

The operator a_m destroys a photon in mode m

$$a_m |n_0 \dots n_m \dots n_N\rangle = \sqrt{n_m - 1} |n_0 \dots n_m - 1 \dots n_N\rangle . \quad (2.44)$$

This may be written concisely as follows. Define the vector $\underline{\delta}^{(m)}$, using the Kronecker delta⁴, as $\underline{\delta}_i^{(m)} = \delta_{m, i}$. The state $|n_0 \dots n_m - 1 \dots n_N\rangle$ may therefore be written as $|\underline{n} - \underline{\delta}^{(m)}\rangle$. The cavity decay

⁴The Kronecker delta $\delta_{i, j}$ is defined as 1 if $i = j$ and 0 otherwise.

term may be written as

$$\sum_{\underline{n}, j} P_{\underline{n}, j} |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j \stackrel{\kappa}{=} - \sum_{m, \underline{n}, j} \kappa P_{\underline{n}, j} \left[n_m |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j - n_m |\underline{n} - \underline{\delta}^{(m)}\rangle \langle \underline{n} - \underline{\delta}^{(m)}| \otimes \nu_j \right] . \quad (2.45)$$

Applying $\langle \underline{n}'|$ to the left, and $|\underline{n}'\rangle$ to the right of this equation, and immediately changing variables from $\underline{n}'$ to $\underline{n}$ gives

$$P_{\underline{n}, j} \stackrel{\kappa}{=} \kappa \sum_m \left[-P_{\underline{n}, j} n_m + P_{\underline{n} + \underline{\delta}^{(m)}, j} (n_m + 1) \right] . \quad (2.46)$$

To apply this procedure to the molecular terms in the master equation, the action of $\sigma_i^- \sigma_i^+$ on the molecular state ν_j must be calculated

$$\sigma_i^- \sigma_i^+ \nu_j = \frac{1}{JC_j} \sigma_i^- \sigma_i^+ \sum_{\underline{s} \in \{\underline{s} \cdot \underline{s} = j\}} |\underline{s}\rangle \langle \underline{s}| . \quad (2.47)$$

The action of $\sigma_i^- \sigma_i^+$ on $|s_i\rangle$ gives zero unless $s_i = 0$. The operator $\sigma_i^- \sigma_i^+$ therefore acts on ν_j as

$$\sigma_i^- \sigma_i^+ \nu_j = \frac{1}{JC_j} \sum_{\underline{s} \in \{\underline{s} \cdot \underline{s} = j\}} \delta_{s_i, 0} |\underline{s}\rangle \langle \underline{s}| , \quad (2.48)$$

where $\delta_{s_i, 0}$ is a Krönecker delta. To recover the original state ν_j perform the sum over molecules i

$$\sum_i \sigma_i^- \sigma_i^+ \nu_j = \frac{1}{JC_j} \sum_{\underline{s} \in \{\underline{s} \cdot \underline{s} = j\}} \left(\sum_i \delta_{s_i, 0} \right) |\underline{s}\rangle \langle \underline{s}| . \quad (2.49)$$

The sum over krönecker deltas is equal to the number of unexcited molecules, and independent of the exact molecular eigenstate $\underline{s}$. Eq. (2.49) therefore becomes

$$\sum_i \sigma_i^- \sigma_i^+ \nu_j = \frac{1}{JC_j} \sum_{\underline{s} \in \{\underline{s} \cdot \underline{s} = j\}} (J - j) |\underline{s}\rangle \langle \underline{s}| = (J - j) \nu_j , \quad (2.50)$$

where J is the number of molecules, and j is the number of excited molecules. Similarly the operator $\sigma_i^+ \sigma_i^-$ acts on ν_j to give

$$\sum_i \sigma_i^+ \sigma_i^- \nu_j = j \nu_j \quad (2.51)$$

The master equation (2.36) applied to the density matrix also contains the term $\sigma_i^+ \nu_j \sigma_i^-$ which is calculated as follows

$$\sigma_i^+ \nu_j \sigma_i^- = \frac{1}{JC_j} \sum_{\underline{s} \in \{\underline{s} \cdot \underline{s} = j\}} \sigma_i^+ |\underline{s}\rangle \langle \underline{s}| \sigma_i^- \quad (2.52)$$

Similarly to previous case, some of the $|\underline{s}\rangle \langle \underline{s}|$ states are eliminated, and the remaining states gain one excitation

$$\sigma_i^+ \nu_j \sigma_i^- = \frac{1}{JC_j} \sum_{\underline{s} \in \{\underline{s} \cdot \underline{s} = j\}} \delta_{s_i, 0} |\underline{s} + \underline{\delta}^{(i)}\rangle \langle \underline{s} + \underline{\delta}^{(i)}| . \quad (2.53)$$

The state $|\underline{s} + \underline{\delta}^{(i)}\rangle$ (with $\underline{s} \cdot \underline{s} = j$) belongs in ν_{j+1} not ν_j , as it has $j + 1$ excitations. If the expression $\sigma_i^+ \nu_j \sigma_i^-$ is summed over i then every term in ν_{j+1} will appear in the sum. Each term has equal weight due to the symmetry of $\sum_i \sigma_i^+ \nu_j \sigma_i^-$ under the exchange of molecules. $\sum_i \sigma_i^+ \nu_j \sigma_i^-$ is therefore proportional to ν_{j+1}

$$\sum_i \sigma_i^+ \nu_j \sigma_i^- \propto \nu_{j+1} . \quad (2.54)$$

To calculate the constant of proportionality consider the sum over $\sigma_i^+ |\underline{s}\rangle \langle \underline{s}| \sigma_i^-$. This is proportional to the sum over $|\underline{s}'\rangle \langle \underline{s}'|$ due to symmetry, where $|\underline{s}'\rangle$ is a molecular eigenstate with $j + 1$ excitations

$$\sum_{\underline{s} \in \{\underline{s} \cdot \underline{s} = j\}} \sum_i \sigma_i^+ |\underline{s}\rangle \langle \underline{s}| \sigma_i^- = A \sum_{\underline{s}' \in \{\underline{s}' \cdot \underline{s}' = j+1\}} |\underline{s}'\rangle \langle \underline{s}'| . \quad (2.55)$$

Each term on the left hand side of Eq. (2.55) $\sigma_i^+ |\underline{s}\rangle \langle \underline{s}| \sigma_i^-$ is equal to a term on the right hand side $|\underline{s}'\rangle \langle \underline{s}'|$ or zero. The number of non-zero terms on the left hand side is therefore equal to A multiplied by the number of terms on the right hand side. Given a particular molecular eigenstate $|\underline{s}\rangle$ there are $J - j$ non-zero terms in $\sum_i \sigma_i^+ |\underline{s}\rangle \langle \underline{s}| \sigma_i^-$, and there are ${}^J C_j$ eigenstates $|\underline{s}\rangle$. There are therefore ${}^J C_j (J - j)$ terms on the left hand side. There are ${}^J C_{j+1}$ terms on the right hand side, therefore the constant of proportionality is

$$A = \frac{{}^J C_j}{{}^J C_{j+1}} (J - j) . \quad (2.56)$$

Substituting this into Eq. (2.55), and using the definitions of ν_j and ν_{j+1} gives

$$\sum_i \sigma_i^+ \nu_j \sigma_i^- = (J - j) \nu_{j+1} . \quad (2.57)$$

Similarly

$$\sum_i \sigma_i^- \nu_j \sigma_i^+ = j \nu_{j-1} . \quad (2.58)$$

Substituting the density matrix $\rho = \sum_{\underline{n}, j} P_{\underline{n}, j} |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j$ into the master equation (2.36) and considering only the molecular pumping and loss terms gives

$$\begin{aligned} \sum_{\underline{n}, j} \dot{P}_{\underline{n}, j} |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j &\stackrel{\Gamma_{\uparrow}, \Gamma_{\downarrow}}{=} \Gamma_{\uparrow} [-(J - j) P_{\underline{n}, j} |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j + (J - j) P_{\underline{n}, j} |\underline{n}\rangle \langle \underline{n}| \otimes \nu_{j+1}] \\ &+ \Gamma_{\downarrow} [-j P_{\underline{n}, j} |\underline{n}\rangle \langle \underline{n}| \otimes \nu_j + j P_{\underline{n}, j} |\underline{n}\rangle \langle \underline{n}| \otimes \nu_{j-1}] . \end{aligned} \quad (2.59)$$

Applying $\langle \underline{n}|$ to the left, and $|\underline{n}\rangle$ to the right of this equation, and matching ν_j terms gives

$$\begin{aligned} \dot{P}_{\underline{n}, j} &\stackrel{\Gamma_{\uparrow}, \Gamma_{\downarrow}}{=} \Gamma_{\uparrow} [-(J - j) P_{\underline{n}, j} + (J - j + 1) P_{\underline{n}, j-1}] \\ &+ \Gamma_{\downarrow} [-j P_{\underline{n}, j} + (j + 1) P_{\underline{n}, j+1}] . \end{aligned} \quad (2.60)$$

The procedure used to calculate the contribution to the diagonal elements $\dot{P}_{\underline{n}, j}$ of the κ , $\Gamma_{\uparrow, j}$, and $\Gamma_{\downarrow}$ terms can be applied to the absorption and emission terms. This gives a total equation for the evolution of the diagonal elements

$$\begin{aligned} \dot{P}_{\underline{n}, j} &= \kappa \sum_m \left[-n_m P_{\underline{n}, j} + (n_m + 1) P_{\underline{n} + \underline{\delta}^{(m)}, j} \right] \\ &+ \Gamma_{\uparrow} [-(J - j) P_{\underline{n}, j} + (J - j + 1) P_{\underline{n}, j-1}] \\ &+ \Gamma_{\downarrow} [-j P_{\underline{n}, j} + (j + 1) P_{\underline{n}, j+1}] \\ &+ \sum_m \Lambda_{\uparrow}^{(m)} \left[-(J - j) n_m P_{\underline{n}, j} + (J - j + 1) (n_m + 1) P_{\underline{n} + \underline{\delta}^{(m)}, j-1} \right] \\ &+ \sum_m \Lambda_{\downarrow}^{(m)} \left[-j (n_m + 1) P_{\underline{n}, j} + (j + 1) n_m P_{\underline{n} - \underline{\delta}^{(m)}, j+1} \right] . \end{aligned} \quad (2.61)$$

This allows the simulation of the evolution of any diagonal operator without having to use the full density matrix and master equation.



The following paragraph is original work.

As

$P_{\underline{n},j}$ is a vector of probabilities it must sum to one. Performing the sum of the individual rates $\sum_{\underline{n},j} \dot{P}_{\underline{n},j}$ shows that the rates sum to zero, indicating that probability is conserved, provided that the upper limit of the number of photons in infinity. In an actual simulation the upper limit for the photon number is finite and there are therefore unbalanced emission terms. The term $-j(n_m + 1)P_{\underline{n},j}$ for $\underline{n}$ and j is usually cancelled by the $(j + 1)n_m P_{\underline{n}-\underline{\delta}^{(m)},j+1}$ term for $\underline{n} = \underline{n} + \underline{\delta}^{(m)}$ and $j = j + 1$, however at the maximum simulated photon number $P_{\underline{n}+\underline{\delta}^{(m)}}$ does not exist, therefore probability will leak out of the system. This must be corrected in the simulation by removing the $-j(n_m + 1)P_{\underline{n},j}$ term from Eq. (2.61), when n_m is at the maximum value. A formal way of considering this is to remove the state above the maximum $|n_{max} + 1\rangle$ from the system, so that the action of the creation operator $a^\dagger$ on the maximum photon number state $|n_{max}\rangle$ is equal to zero. This creates the same probability conservation as setting $\dot{P}_{\underline{n},j}$ to zero for the maximum n . In addition to conserving probability it also alters the boundary terms in the equations for the off-diagonal elements of the density matrix, studied by Kirton and Keeling in [95]. Furthermore it alters the expectation values of certain operators, e.g. $aa^\dagger$, which equals zero when applied to $|n_{max}\rangle$ if the higher states have been removed and $(n_{max} + 1)|n_{max}\rangle$ otherwise. The conservation of probability, and correctly accounting for the effects this has on the off diagonal elements of the system, is essential for certain optimisation or root finding methods which fail to find the correct solution if probability is not conserved.

Given a starting probability, e.g. no photons or excited molecules $P_{\underline{0},0} = 1$, the probability vector may be found at all subsequent times. Various quantities may then be calculated e.g.

$$\langle a_m^\dagger a_l^\dagger a_m a_l \rangle = \sum_{\underline{n},j} (n_m n_l - \delta_{m,l} n_m) P_{\underline{n},j} \quad (2.62)$$

This is an instructive way to calculate such expectations and may be the optimal method for highly complicated or numerous expectations. However rate equations may be derived for the expectation values of operators as detailed in the next section. These rate equations produce the same results as Eq. (2.61), are usually computationally more efficient, and do not suffer from truncation errors.

2.3 Rate Equations

The majority of the original work in this thesis looks at the population in modes and the excitation of molecules. These properties do not require the calculation of the complete density matrix, and may instead be modelled by rate equations, as detailed in this section. Rate equations for the operator $\hat{O}$ may be calculated from the diagonal approximation outlined in Sec. 2.2.2 as $\frac{d\langle \hat{O} \rangle}{dt} = \sum_{\underline{n},j} \dot{P}_{\underline{n},j} O_{\underline{n},j}$. It is also instructive to calculate rate equations directly from the master equation (2.36), as this will be a better starting point for the later discussion of second order correlation in chapter 5. To do this substitute the equation for $\dot{\rho}$ given in the master equation into the derivative of the expectation of O , $\frac{d\langle O \rangle}{dt} = \text{Tr}[O\dot{\rho}]$.

The rate of change of mode population, calculated using the master equation (2.36), may be considered term by term. The system Hamiltonian $\tilde{H}_0$ does not contribute to the rate, as the mode population commutes with itself $[n_i, n_k] = 0$, and with the molecular operators. The contribution from cavity decay is

$$\frac{d\langle a_k^\dagger a_k \rangle}{dt} \stackrel{\kappa}{=} -\frac{\kappa}{2} \sum_m \text{Tr} \left[a_k^\dagger a_k a_m^\dagger a_m \rho + a_k^\dagger a_k \rho a_m^\dagger a_m - 2a_k^\dagger a_k a_m \rho a_m^\dagger \right], \quad (2.63)$$

where $\stackrel{\kappa}{=}$ indicates that only terms proportional to κ are considered. This may be split into a term where $k = m$ and other terms

$$\begin{aligned} \frac{d\langle a_k^\dagger a_k \rangle}{dt} \stackrel{\kappa}{=} & -\frac{\kappa}{2} \sum_{m \neq k} \text{Tr} \left[a_k^\dagger a_k a_m^\dagger a_m \rho + a_k^\dagger a_k a_m^\dagger a_m \rho - 2a_k^\dagger a_k a_m^\dagger a_m \rho \right] \\ & -\frac{\kappa}{2} \text{Tr} \left[a_k^\dagger a_k a_k^\dagger a_k \rho + a_k^\dagger a_k a_k^\dagger a_k \rho - 2a_k^\dagger a_k^\dagger a_k a_k \rho \right], \end{aligned} \quad (2.64)$$

where the commutation $[a_m, a_k] = 0$ for $m \neq k$, and the cyclicity of the trace have been used. The method used to solve all equations in this section is to transform the first two terms in a trace into the last term in a trace. As the last term is negative this will lead to cancellations and simplification of the trace. The term with $m \neq k$ is already of this form, and this trace is equal to zero. The term $a_k^\dagger a_k a_k^\dagger a_k$ may be transformed into $a_k^\dagger a_k^\dagger a_k a_k$ using the commutation relation $a_k a_k^\dagger = 1 + a_k^\dagger a_k$. The first two terms of the $m = k$ trace therefore cancel the last term with the remainder $2a_k^\dagger a_k \rho$

$$\frac{d\langle a_k^\dagger a_k \rangle}{dt} \stackrel{\kappa}{=} -\kappa \text{Tr} \left[a_k^\dagger a_k \rho \right] = -\kappa \langle a_k^\dagger a_k \rangle \quad (2.65)$$

So far the equation for $\langle a_k^\dagger a_k \rangle$ involves only $\langle a_k^\dagger a_k \rangle$, despite the fact that the derivation included larger powers of a . Keeping the number of required equations small is advantageous for efficient simulation, so this is a very useful fact.

The operators in the pumping $\Gamma_{\uparrow, j}$ and molecular decay $\Gamma_{\downarrow}$ terms commute with n_k , therefore these do not contribute to the rate of change of mode population. The contribution to the rate from molecular absorption is

$$\frac{d\langle a_k^\dagger a_k \rangle}{dt} \stackrel{\Lambda_{\uparrow}}{=} -\sum_{m, j} \frac{\Lambda_{\uparrow}^{(m)}(r_j)}{2} \text{Tr} \left[a_k^\dagger a_k a_m^\dagger a_m \sigma_j^- \sigma_j^+ \rho + a_k^\dagger a_k \rho a_m^\dagger a_m \sigma_j^- \sigma_j^+ - 2a_k^\dagger a_k a_m \sigma_j^+ \rho a_m^\dagger \sigma_j^- \right] \quad (2.66)$$

The photon operator may be moved to the front of each expression and the molecule operators to the back using the cyclicity of the trace and the commutation of photon and molecule operators

$$\frac{d\langle a_k^\dagger a_k \rangle}{dt} \stackrel{\Lambda_{\uparrow}}{=} -\sum_{m, j} \frac{\Lambda_{\uparrow}^{(m)}(r_j)}{2} \text{Tr} \left[a_k^\dagger a_k a_m^\dagger a_m \rho \sigma_j^- \sigma_j^+ + a_m^\dagger a_m a_k^\dagger a_k \rho \sigma_j^- \sigma_j^+ - 2a_m^\dagger a_k^\dagger a_k a_m \rho \sigma_j^- \sigma_j^+ \right] \quad (2.67)$$

As in the cavity decay case κ , the photon operators for $m \neq k$ commute and do not contribute to the rate. The commutation of the photon operators in the $k = m$ term behave identically to the cavity decay case, and $\sigma_i^- \sigma_i^+ = \frac{1 - \sigma_i^{(z)}}{2}$. The contribution of absorption to the rate of population change is therefore

$$\frac{d\langle a_k^\dagger a_k \rangle}{dt} \stackrel{\Lambda_{\uparrow}}{=} -\sum_j \frac{\Lambda_{\uparrow}^{(m)}(r_j)}{2} \langle a_k^\dagger a_k (1 - \sigma_j^z) \rangle \quad (2.68)$$

The contribution from emission has a similar form

$$\frac{d\langle a_k^\dagger a_k \rangle}{dt} \stackrel{\Lambda_\downarrow}{=} \sum_j \frac{\Lambda_\downarrow^{(m)}(r_j)}{2} \langle (a_k^\dagger a_k + 1)(1 + \sigma_j^z) \rangle \quad (2.69)$$

where the change in sign comes from using $\sigma_i^+ \sigma_i^-$ instead of $\sigma_i^- \sigma_i^+$, and the addition of 1 to $a_k^\dagger a_k$ comes from the commutation of $a_k^\dagger$ and a_k . These terms may be combined into a total rate equation for the mode population

$$\frac{d\langle n_k \rangle}{dt} = -\kappa \langle n_k \rangle - \sum_j \frac{\Lambda_\uparrow^{(m)}(r_j)}{2} \langle n_k(1 - \sigma_j^z) \rangle + \sum_j \frac{\Lambda_\downarrow^{(m)}(r_j)}{2} \langle (n_k + 1)(1 + \sigma_j^z) \rangle. \quad (2.70)$$

This equation contains the expectation of the product of photon and molecule operators $\langle n_k \sigma_i^{(z)} \rangle$. The rate equation for this expectation would contain expectations of three operators e.g. $\langle n_k n_l \sigma_i^{(z)} \rangle$, and in general the equation for the expectation of q operators will contain the expectation of $q + 1$ operators. To obtain a closed set of equations this infinite set of equations must be truncated. Kirton and Keeling make the semi-classical approximation $\langle n_k \sigma_i^{(z)} \rangle \approx \langle n_k \rangle \langle \sigma_i^{(z)} \rangle$. This removes any contribution to the rate equations from correlated fluctuations in mode population and molecular excitation. This is discussed further in Sec. 5, where the semi-classical approximation is not made. This approximation leads to coupled equations for $\langle n_k \rangle$ and $\langle \sigma_i^{(z)} \rangle$.

The equation for the rate of change of molecular excitation $\langle \sigma_i^{(z)} \rangle$ may be calculated in an identical fashion to the equation for $\langle n_k \rangle$. As before the Hamiltonian $\tilde{H}_0$ commutes with $\sigma_i^{(z)}$, and therefore makes zero contribution to the rate of molecular excitation change. The cavity decay term also commutes with $\sigma_i^{(z)}$ and does not contribute. The first contribution is therefore pumping

$$\frac{d\langle \sigma_j^z \rangle}{dt} \stackrel{\Gamma_\uparrow}{=} -\frac{\Gamma_{\uparrow,j}}{2} \text{Tr} [\sigma_j^z \sigma_j^- \sigma_j^+ \rho + \sigma_j^z \rho \sigma_j^- \sigma_j^+ - 2\sigma_j^z \sigma_j^+ \rho \sigma_j^-] . \quad (2.71)$$

As the molecular operators of different molecules commute $[\sigma_i^{(z)}, \sigma_j^+] = 0, \forall i \neq j$, terms with $i \neq j$ are not included. The cyclicity of the trace allows this to be written as

$$\frac{d\langle \sigma_j^z \rangle}{dt} \stackrel{\Gamma_\uparrow}{=} -\frac{\Gamma_{\uparrow,j}}{2} \text{Tr} [\sigma_j^z \sigma_j^- \sigma_j^+ \rho + \sigma_j^- \sigma_j^+ \sigma_j^z \rho - 2\sigma_j^- \sigma_j^z \sigma_j^+ \rho] \quad (2.72)$$

As in the derivation of the rate of mode population change, the goal is to transform the first two terms into the same form as the last term so that they cancel. After this cancellation the following terms are left

$$\frac{d\langle \sigma_j^z \rangle}{dt} \stackrel{\Gamma_\uparrow}{=} -\frac{\Gamma_{\uparrow,j}}{2} \text{Tr} [[\sigma_j^z, \sigma_j^-] \sigma_j^+ \rho + \sigma_j^- [\sigma_j^+, \sigma_j^z] \rho] . \quad (2.73)$$

Using the relations $[\sigma_j^z, \sigma_j^\pm] = \pm \sigma_j^\pm$, and $2\sigma_j^- \sigma_j^+ = 1 - \sigma_j^z$ gives

$$\begin{aligned} \frac{d\langle \sigma_j^z \rangle}{dt} &\stackrel{\Gamma_\uparrow}{=} -\frac{\Gamma_{\uparrow,j}}{2} \text{Tr} [-\sigma_j^- \sigma_j^+ \rho - \sigma_j^- \sigma_j^+ \rho] \\ \frac{d\langle \sigma_j^z \rangle}{dt} &\stackrel{\Gamma_\uparrow}{=} \Gamma_{\uparrow,j} \langle \sigma_j^- \sigma_j^+ \rangle \\ \frac{d\langle \sigma_j^z \rangle}{dt} &\stackrel{\Gamma_\uparrow}{=} \Gamma_{\uparrow,j} \frac{1 - \langle \sigma_j^z \rangle}{2} \end{aligned} \quad (2.74)$$

The contribution to the rate of change of molecular excitation from molecular decay may be calculated identically as

$$\begin{aligned}
\frac{d\langle\sigma_j^z\rangle}{dt} &\stackrel{\Gamma_\downarrow}{=} -\frac{\Gamma_\downarrow}{2} \text{Tr} [\sigma_j^z \sigma_j^+ \sigma_j^- \rho + \sigma_j^z \rho \sigma_j^+ \sigma_j^- - 2\sigma_j^z \sigma_j^- \rho \sigma_j^+] \\
\frac{d\langle\sigma_j^z\rangle}{dt} &\stackrel{\Gamma_\downarrow}{=} -\frac{\Gamma_\downarrow}{2} \text{Tr} [\sigma_j^z \sigma_j^+ \sigma_j^- \rho + \sigma_j^+ \sigma_j^- \sigma_j^z \rho - 2\sigma_j^+ \sigma_j^z \sigma_j^- \rho] \\
\frac{d\langle\sigma_j^z\rangle}{dt} &\stackrel{\Gamma_\downarrow}{=} -\frac{\Gamma_\downarrow}{2} \text{Tr} [[\sigma_j^z, \sigma_j^+] \sigma_j^- \rho + \sigma_j^+ [\sigma_j^-, \sigma_j^z] \rho] \\
\frac{d\langle\sigma_j^z\rangle}{dt} &\stackrel{\Gamma_\downarrow}{=} -\frac{\Gamma_\downarrow}{2} \text{Tr} [\sigma_j^+ \sigma_j^- \rho + \sigma_j^- \sigma_j^+ \rho] \\
\frac{d\langle\sigma_j^z\rangle}{dt} &\stackrel{\Gamma_\downarrow}{=} -\Gamma_\downarrow \frac{1 + \langle\sigma_j^z\rangle}{2}
\end{aligned} \tag{2.75}$$

The calculations for the contributions from emission and absorption are identical to pumping and molecular decay, with the addition of n_m terms. As the n_m operator commutes with the molecular operators it may simply be included in copies of the contributions from pumping and molecular decay

$$\begin{aligned}
\frac{d\langle\sigma_j^z\rangle}{dt} &\stackrel{\Lambda_\uparrow}{=} -\sum_m \frac{\Lambda_\uparrow^{(m)}(\underline{r}_j)}{2} \text{Tr} [\sigma_j^z a_m^\dagger \sigma_j^- a_m \sigma_j^+ \rho + \sigma_j^z \rho a_m^\dagger \sigma_j^- a_m \sigma_j^+ - 2\sigma_j^z a_m \sigma_j^+ \rho a_m^\dagger \sigma_j^-] \\
&\stackrel{\Lambda_\uparrow}{=} \sum_m \Lambda_\uparrow^{(m)}(\underline{r}_j) \frac{\langle a_m^\dagger a_m (1 - \sigma_j^z) \rangle}{2} \\
\frac{d\langle\sigma_j^z\rangle}{dt} &\stackrel{\Lambda_\downarrow}{=} -\sum_m \frac{\Lambda_\downarrow^{(m)}(\underline{r}_j)}{2} \text{Tr} [\sigma_j^z a_m \sigma_j^+ a_m^\dagger \sigma_j^- \rho + \sigma_j^z \rho a_m \sigma_j^+ a_m^\dagger \sigma_j^- - 2\sigma_j^z a_m^\dagger \sigma_j^- \rho a_m \sigma_j^+] \\
&\stackrel{\Lambda_\downarrow}{=} -\sum_m \Lambda_\downarrow^{(m)}(\underline{r}_j) \frac{\langle (a_m^\dagger a_m + 1)(1 + \sigma_j^z) \rangle}{2}
\end{aligned} \tag{2.76}$$

The total rate equation for the molecular excitation $\langle\sigma_i^{(z)}\rangle$ is therefore

$$\frac{d\langle\sigma_j^z\rangle}{dt} = \Gamma_{\uparrow,j} \frac{(1 - \langle\sigma_j^z\rangle)}{2} - \Gamma_\downarrow \frac{(1 + \langle\sigma_j^z\rangle)}{2} + \sum_m \Lambda_\uparrow^{(m)}(\underline{r}_j) \frac{\langle n_m (1 - \sigma_j^z) \rangle}{2} - \sum_m \Lambda_\downarrow^{(m)}(\underline{r}_j) \frac{\langle (n_m + 1)(1 + \sigma_j^z) \rangle}{2} . \tag{2.77}$$

A few minor transformations bring the rate equations (2.70) and (2.77) to a more useful form. It is convenient to think of molecular excitation as ranging from zero (not excited), to one (excited), instead of from -1 to 1 as is the case for $\langle\sigma_i^{(z)}\rangle$. The excitation f_j is therefore defined as $\frac{\langle\sigma_j^z\rangle+1}{2}$. If the coupling between modes and molecules was a constant in space, then the absorption and emission coefficients $\Lambda_\uparrow^{(m)}(\underline{r}_j)$ and $\Lambda_\downarrow^{(m)}(\underline{r}_j)$ would become spatially independent, $\Lambda_\uparrow^{(m)}$ and $\Lambda_\downarrow^{(m)}$. If the molecular pumping was also constant then the excitation of each molecule would be identical $f_j = f_i = f$. The sum over molecules in the rate equation for mode population (2.70) may then be replaced by the total number of molecules J to create the homogeneous coupling rate equations

$$\begin{aligned}
\frac{dn_k}{dt} &= -\kappa n_k - \Lambda_\uparrow^{(m)} n_k (1 - f) J + \Lambda_\downarrow^{(m)} (n_k + 1) f J \\
\frac{df}{dt} &= \Gamma_{\uparrow,j} (1 - f) - \Gamma_\downarrow f + \sum_m \Lambda_\uparrow^{(m)} n_m (1 - f) - \sum_m \Lambda_\downarrow^{(m)} (n_m + 1) f .
\end{aligned} \tag{2.78}$$

A rate equation with homogeneous coupling is good at describing equilibrium systems. This is because molecular homogeneity is obtained if the thermalisation between molecules is stronger than other non-equilibrium processes. The molecules in a homogeneous system have a single chemical potential,

therefore the photons also have a single chemical potential. As the condensation of a mode clamps a chemical potential, discussed in Sec. 3.1, multimode condensation is impossible in a homogeneous system. If the homogeneous system is well thermalised then the mode populations will follow a Bose-Einstein distribution, as described in Sec. 1.2.

2.3.1 Inhomogeneous Coupling Rate Equation

To see multimode condensation, and better describe the dynamics of photonic condensates, a model with inhomogeneous coupling is required, where the coupling between a mode and a molecule depends on the intensity of the mode at the molecular position. The derivation of this begins from the rate equations which use the excitation of individual molecules (2.70) and (2.77). As the coupling is not homogeneous, the coupling between each molecule and each mode must be derived by considering the probability of a photon being absorbed at position $\underline{r}$ as it travels across the cavity. The probability of a photon being absorbed by an unexcited molecule may be described by the molecule's cross-section $\bar{\sigma}(\delta_m)$, which is a function of photon detuning. If the photon passes through this cross-sectional area, it will be absorbed by the molecule. Assuming the cross-section is small compared to the variation of the photon's wavefunction ψ_m , the probability that a photon will be absorbed as it passes the molecule is $\bar{\sigma}(\delta_m)|\psi_m(\underline{r})|^2$, where $\underline{r}$ is the position of the molecule. If the 2D molecular density $\bar{\rho}$ is a constant, then there are $\bar{\rho}d^2\underline{r}$ molecules in the infinitesimal region $d^2\underline{r}$, a fraction $(1 - f(\underline{r}))$ of which are not excited. The probability of a photon being absorbed as it passes through this infinitesimal region is therefore

$$P = (1 - f(\underline{r})) \bar{\sigma}(\delta_m) |\psi_m(\underline{r})|^2 \bar{\rho} d^2\underline{r} . \quad (2.79)$$

If the length of the cavity is L , and the photons are travelling at speed $c^* = \eta c$, where η is the refractive index of the dye and solvent, then a photon will cross the cavity at a rate c^*/L . The rate of absorption in the infinitesimal region $d^2\underline{r}$ is therefore

$$dR = (1 - f(\underline{r})) \frac{c^* \bar{\sigma}(\delta_m) |\psi_m(\underline{r})|^2 \bar{\rho}}{L} d^2\underline{r} . \quad (2.80)$$

The total rate of absorption is the integral of the infinitesimal rate dR over the entire cavity. The total rate may be split into the following terms: a spatial term

$$f_m = \int f(\underline{r}) |\psi_m(\underline{r})|^2 d^2\underline{r} , \quad (2.81)$$

which is the weighted average of molecular excitation fraction with respect to the mode intensity, a frequency term

$$\Lambda_{\uparrow}^{(m)} = \frac{c^* \bar{\sigma}(\delta_m)}{L} , \quad (2.82)$$

and the 2D density of molecules $\bar{\rho}$. Note that the absorption rate $\Lambda_{\uparrow}^{(m)}$ has units of area/time, which cancel the units of inverse area in the molecular density leaving the units of frequency.



Terminology: The inhomogeneous rate equation uses ‘the fraction of molecules at a given position which are excited’ $f(\underline{r})$. This is a long description and will be shortened to ‘excited fraction of molecules’, ‘excited fraction’, ‘fraction of excited molecules at position $\underline{r}$ ’ or similar. ‘The weighted average, with respect to the intensity of mode m , of the fraction of molecules at a given position which are excited’, f_m Eq. (2.81) will be shortened to ‘excited fraction overlapping mode m ’ or ‘excited overlap’.

The absorption term in Eq. (2.70) may therefore be written as $\bar{\rho} \Lambda_{\uparrow}^{(m)} (1 - f_m) n_m$ (again using the semi-classical approximation, and that the integral $\int |\psi_m(\underline{r})|^2 d^2 \underline{r} = 1$). The emission rate may be similarly calculated to give the following inhomogeneous rate equation for mode population

$$\frac{dn_m}{dt} = -\kappa n_m + \bar{\rho} \Lambda_{\downarrow}^{(m)} f_m (n_m + 1) + \bar{\rho} \Lambda_{\uparrow}^{(m)} (f_m - 1) n_m , \quad (2.83)$$

which requires the fraction of excited molecules overlapping mode m .

A similar calculation may be made to calculate the rate of change of the fraction of excited molecules at position $\underline{r}$. The rate of photons in mode m intersecting a single molecular cross-section is

$$R' = \frac{|\psi_m(\underline{r})|^2 \bar{\sigma}(\delta_m) c^* n_m}{L} = |\psi_m(\underline{r})|^2 \Lambda_{\uparrow}^{(m)} n_m . \quad (2.84)$$

The rate of absorption by N_{mol} molecules in an infinitesimal region at $\underline{r}$, is the intersection rate R' multiplied by the number of unexcited molecules $(1 - f(\underline{r}))N_{\text{mol}}$. The rate of change of excited fraction is the rate of change of excited number divided by the total number N_{mol} . Therefore the absorption rate for the excited fraction $f(\underline{r})$ is $(1 - f(\underline{r}))R'$ summed over all modes m . The rate of emission may be similarly calculated. The pumping rate is position dependent and is therefore labelled by $\Gamma_{\uparrow}(\underline{r})$ instead of $\Gamma_{\uparrow,i}$. Equation (2.77) therefore becomes

$$\frac{\partial f(\underline{r})}{\partial t} = -\Gamma_{\downarrow}^{tot}(\underline{r}) f(\underline{r}) + \Gamma_{\uparrow}^{tot}(\underline{r}) (1 - f(\underline{r})) , \quad (2.85)$$

where the total rates of gain and loss are

$$\begin{aligned} \Gamma_{\uparrow}^{tot}(\underline{r}) &= \Gamma_{\uparrow}(\underline{r}) + \sum_m |\psi_m(\underline{r})|^2 \Lambda_{\uparrow}^{(m)} n_m \\ \Gamma_{\downarrow}^{tot}(\underline{r}) &= \Gamma_{\downarrow} + \sum_m |\psi_m(\underline{r})|^2 \Lambda_{\downarrow}^{(m)} (n_m + 1) \end{aligned} \quad (2.86)$$

The equations (2.83), (2.85), (2.81), and (2.86) form a closed set of equations which describe the evolution of mode population and molecular excitation over time, and form the starting point of the temporal analysis described in chapter 4.

2.3.2 Steady State

If only the steady state of the system is required, instead of the full temporal dynamics, the molecular excitation may be eliminated. At steady state the rate of molecular excitation change, $\frac{\partial f(\underline{r})}{\partial t}$ in

equation (2.85) may be set to zero, and the equation rearranged to give an expression for $f(\underline{r})$. This expression may be substituted into the equation for f_m , (2.81) to give

$$f_m = \int d^2r |\psi_m(\underline{r})|^2 \frac{\Gamma_{\uparrow}^{tot}(\underline{r})}{\Gamma_{\uparrow}^{tot}(\underline{r}) + \Gamma_{\downarrow}^{tot}(\underline{r})} . \quad (2.87)$$

As this equation for f_m does not explicitly depend on the molecular excitation at position $f(\underline{r})$, the molecular excitation at each position is not required to find the steady state. If a mode population generates a set of f_m using Eq. (2.87), which give a zero mode population rate (using Eq. (2.83)), then the mode population is a steady state. If Eq. (2.87) is not used to find the excited overlap f_m then the steady state excitation at each point must be calculated using Eq. (2.85), and then integrated using Eq. (2.81). As the number of molecular positions is orders of magnitudes larger than the number of modes, calculating the excited overlap f_m using Eq. (2.87) instead of Eq. (2.81) greatly improves computational efficiency. Equations (2.83), and (2.87) are used to find steady state in chapter 3.

2.4 Limitations

The model presented in this section makes a number of assumptions which are summarised here to highlight the limitations of the model. Firstly the Hamiltonian expressed the photon state in terms of modes spanning the entire cavity. These modes are constant and not affected by the photon or molecular state. This assumption breaks down under strong de-phasing of the photons by the molecules, in which case describing the photon population at each spatial position would be more appropriate. The rotating wave approximation is also made to achieve a Jaynes-Cummings rather than a Tavis-Cummings coupling between the modes and molecules. This is appropriate as the oscillation of the additional terms would be many orders of magnitude faster than the evolution of the system. The molecules are modelled as having two electronic levels. In reality a third level exists which may be populated by the pump laser, thereby bleaching the dye and preventing the absorption and emission of cavity photons. This is an area for experimental optimisation rather than theoretical study and is best included in the model by reducing the concentration of the dye when it is bleached. Additional molecular states may also absorb cavity photons and then not re-emit them, and this process should be included in the loss rate of the photons κ . The molecules may also emit into cavity modes with a different longitudinal frequency which are not included in the model, and this process should similarly be included in the photon loss rate.

The molecular vibrations included in this derivation are single frequency harmonic oscillators. As shown in [95] the main effect of lifting this restriction is on the derivation of the absorption and emission spectra. This thesis uses experimentally measured absorption and emission spectra so this is a safe assumption. The vibrational state of the molecules is assumed to be constant and not coupled to the electronic state or the photons (the Born approximation). This is justified by the rapid thermalisation of the vibrational state due to frequent collisions of the molecules with the solvent. The coupling between modes and molecules is assumed to be weak, thereby allowing the truncation of the perturbative expansion after the second term (after Eq. (2.18)). Additionally the first order term is approximated as zero due to its rapid oscillation. The weak coupling is demonstrated in [106], which thereby shows that the photons and molecules do not form polaritons.

The photon-molecule correlation $\langle n\sigma \rangle$ is approximated as separable which is a potential source of error investigated in chapter 5. The pumping of the molecules is assumed to be incoherent. This is reasonable as the pump laser is usually aligned at an angle to the axis of the cavity and at a frequency higher than the cavity modes of interest, therefore it does not couple directly to the cavity modes. As the photon population is transferred to the lower photon modes incoherently, any coherence between the pump laser and the molecules is destroyed before the pump excitations reach the condensate. When estimating the number of dye molecules, care should be taken to distinguish between the cavity volume occupied by the molecules, and the volume occupied by the photons. The latter is larger due to the penetration of the photons partway into the dielectric stacks which form the cavity mirrors. Finally the photon state is approximated as constant along the longitudinal axis. This is reasonable for a cavity with a large radius as used in [45, 46], but may be violated for cavities with stronger curvatures. This would cause particular problems for the inhomogeneous model derived in Sec. 2.3.1, which treats the varying molecular excitation as two dimensional.

2.5 Kennard-Stepanov Relation

This section shall prove that the absorption and emission spectra of the dye are related by a Boltzmann factor

$$\Lambda_{\downarrow}^{(m)} = \Lambda_{\uparrow}^{(m)} e^{-\frac{\hbar\delta_m}{k_B T}}, \quad (2.88)$$

where k_B is the Boltzmann constant, T is the temperature of the dye, and δ_m is the detuning of light from the molecular resonance. This is called the Kennard-Stepanov relation [107] for molecules, and the McCumber relation [108] for semiconductors. It is sometimes known as the fluctuation-dissipation relation of the system and may be derived from the fluctuation-dissipation theorem. In this thesis it is derived by considering black body radiation in thermal equilibrium with a group of molecules. This derivation is similar to the derivation of Einstein A and B coefficients [109] for a two level atom. Define the black body photon density $D(\omega)$ so that $D(\omega)d\omega$ is the number of photons in the frequency range ω to $\omega + d\omega$. Plank's law requires the density to be [109]

$$D(\omega) = \frac{\hbar\omega^3}{4\pi^3 c^2} \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}. \quad (2.89)$$

As the light is in thermal equilibrium with the dye, the rate of absorption and emission at each frequency must cancel. The rate of spontaneous emission at frequency ω is $A(\omega)j$, where j is the number of unexcited molecules. The rate of stimulated absorption and emission is $B_{\uparrow}(\omega)D(\omega)(J - j)$, and $B_{\downarrow}(\omega)D(\omega)j$ respectively, where J is the total number of molecules. These rates must balance giving

$$A(\omega)j + B_{\downarrow}(\omega)D(\omega)j - B_{\uparrow}(\omega)D(\omega)(J - j) = 0, \quad (2.90)$$

which may be rearranged to get the photon density $D(\omega)$

$$D(\omega) = \frac{A(\omega)j}{B_{\uparrow}(\omega)(J - j) - B_{\downarrow}(\omega)j} = \frac{\frac{A(\omega)}{B_{\downarrow}(\omega)}}{\frac{B_{\uparrow}(\omega)(J - j)}{B_{\downarrow}(\omega)j} - 1}. \quad (2.91)$$

This expression for the photon density is equal to the Planck distribution for all temperatures and frequencies if and only if both of the following equalities hold

$$\begin{aligned}\frac{B_{\uparrow}(\omega)(J-j)}{B_{\downarrow}(\omega)j} &= e^{\frac{\hbar\omega}{k_B T}} , \\ \frac{A(\omega)}{B_{\downarrow}(\omega)} &= \frac{\hbar\omega^3}{4\pi^3 c^*{}^2} .\end{aligned}\tag{2.92}$$

These may be simplified by calculating the number of excited molecules at thermal equilibrium. The number of molecules in each state is given by the Boltzmann factor

$$N_{k,v} = C e^{-\frac{E_k + E_v}{k_B T}} ,\tag{2.93}$$

where k and v are the electronic and vibrational quantum numbers, E_k and E_v are the electronic and vibrational energies of the state, and C is a constant. The number of molecules in the excited state is the sum over the number in each excited vibrational state. Similarly the number in the unexcited state is also a sum over vibrational states. The excitation ratio may therefore be written as

$$\frac{j}{J-j} = \frac{\sum_v e^{-\frac{E_{\uparrow} + E_v}{k_B T}}}{\sum_v e^{-\frac{E_{\downarrow} + E_v}{k_B T}}} .\tag{2.94}$$

Where $E_{\uparrow}$ and $E_{\downarrow}$ are respectively the energies of the excited and ground electronic states. The electronic energy may be factored out of each sum. The remaining sums over vibrational energies in the numerator and denominator are identical, and therefore cancel. The excitation ratio may then be given in terms of the electronic transition frequency $\hbar\xi = E_{\uparrow} - E_{\downarrow}$

$$\frac{j}{J-j} = e^{-\frac{\hbar\xi}{k_B T}} .\tag{2.95}$$

Substitution of Eq. (2.95) into the first of the equations in (2.92) gives the Kennard-Stepanov relation,

$$\frac{B_{\downarrow}(\omega)}{B_{\uparrow}(\omega)} = e^{-\frac{\hbar\delta}{k_B T}} ,\tag{2.96}$$

where δ is the detuning from the electronic transition $\delta = \omega - \xi$. The various rates used in this thesis are related to the B coefficients by constant factors e.g. the speed of light, cavity length, and molecular density at a particular position, therefore the ratios of these rates are also given by the Kennard-Stepanov relation.

An additional property of the dye absorption and emission often used in conjunction with the Kennard-Stepanov relation is the symmetry of the absorption and emission spectra about the electronic transition

$$B_{\downarrow}(\delta) = B_{\uparrow}(-\delta) .\tag{2.97}$$

To show this consider the vibrational levels of the ground and excited states. The vibrational potential is approximately identical for each electronic state but shifted in position [110]. The vibrational states for each electronic state may therefore be approximated as identical but shifted. This is shown in

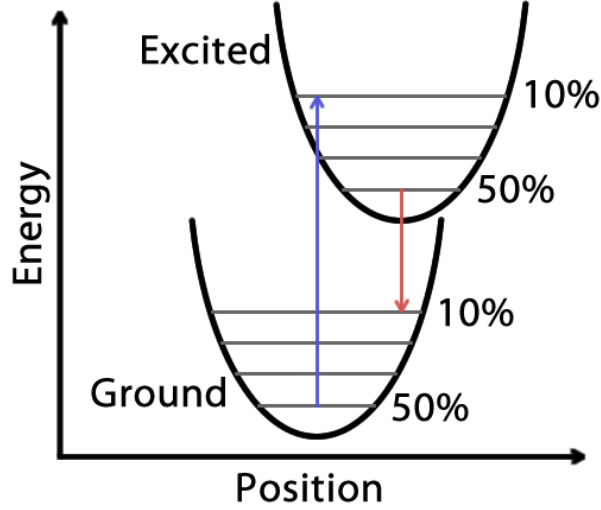


Figure 2.1: Example energy level diagram of the ground and excited electronic states of the molecule. For each electronic state the vibrational potential is plotted (black curves) as well as the four lowest energy vibrational levels (grey lines). In this example the lowest vibrational level contains 50% of the population in each electronic state and the highest vibrational level contains 10%. The transitions between the electronic states and vibrational levels 0 and 3 are shown as blue and red arrows.

Fig. 2.1. The rate of emission from the excited electronic state vibrational ground state ($|1, 0\rangle$) to the ground electronic state, vibrational level 3 ($|0, 3\rangle$) (shown as the red arrow in Fig. 2.1), is dependent on the spatial overlap of the vibrational states [111, 112] and the percentage of population in vibrational level 0. The spatial overlap and percentage population is identical for the transition of a molecule from $|0, 0\rangle$ to $|1, 3\rangle$ (shown as the blue arrow in Fig. 2.1). Both of these transitions therefore have equal rates. As the detuning of the emission event is the negative of the absorption event, the absorption and emission rates are symmetric, and equation (2.97) has been proven.

2.6 Applications of the Microscopic Model

The microscopic model has generated many theoretical predictions which match the observed properties of photonic condensates. It has also been used to successfully model plasmonic condensates Sec. 1.3. Both of these applications are discussed in this section. The early work on photonic condensates focused on demonstrating Bose-Einstein condensation in order to establish the thermodynamic nature of the system. In [94] Kirton and Keeling demonstrate that the mode populations produced by the macroscopic model fit a Bose-Einstein distribution when the cavity loss permits thermalisation, Fig. 2.2(LEFT)(a), and do not fit this distribution when cavity loss prevents thermalisation, Fig. 2.2(LEFT)(b). This demonstrates that the model reproduces thermal equilibrium theory [20], and experimental results [45]. Fig. 2.2(RIGHT) shows the theoretical total photon population N_{phot} , molecular excitation p_e , and chemical potential μ , as the pump power is varied. At the critical pump power there is a sharp increase in photon population, and capping of the molecular excitation and chemical potential. This matches thermal equilibrium BEC theory Sec. 1.2.1.

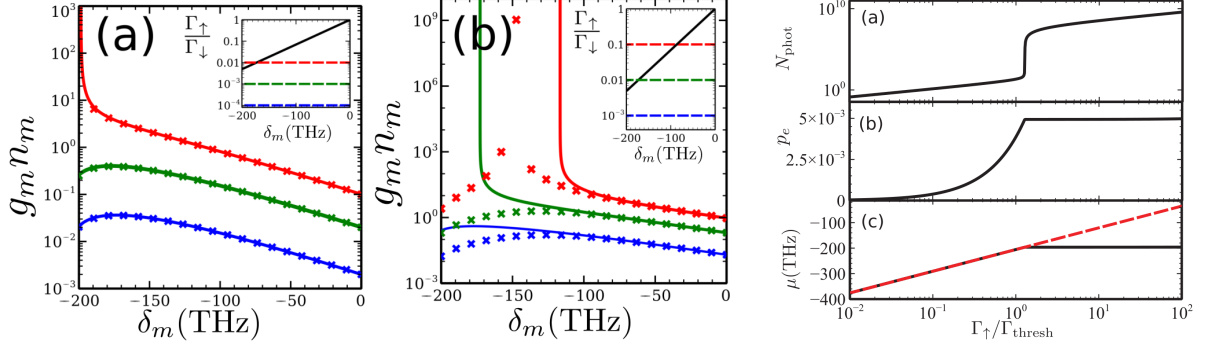


Figure 2.2: (LEFT) The level population^a predicted by the rate equations for good thermalisation (a), and bad thermalisation (b). (RIGHT) Mode population N_{phot} , molecular excitation p_e , and chemical potential μ as pump power $\Gamma_{\uparrow}$ is varied. The simulation uses homogeneous coupling between modes and molecules. Both figures were generated using homogeneous coupling between modes and molecules Eq. 2.78 [94].

^aThe sum of the population in all modes of a particular frequency.

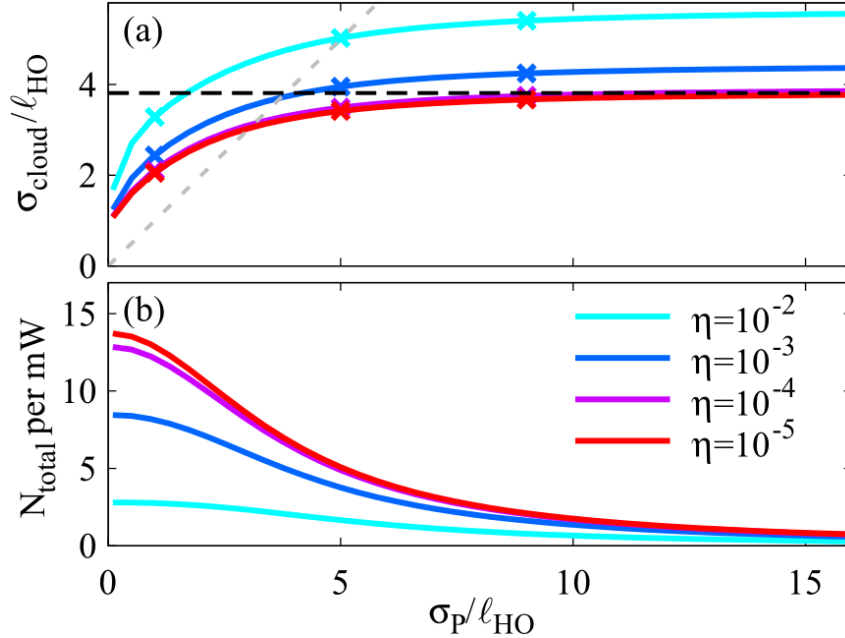


Figure 2.3: (TOP) The size of the output photon cloud as a function of pump spot size, given in units of harmonic oscillator length of the cavity. (BOTTOM) The total number of photons per unit power as a function of pump spot size [94].

The mode populations are affected by varying the pump spot size [96]. Simulating this requires inhomogeneous coupling between modes and molecules, as described in Sec. 2.3.1. The output mode populations may be viewed collectively as a cloud of photons with a characteristic width. Larger pump spots result in larger cloud widths, as the wider modes are being pumped more. This effect is reduced by increasing the thermalisation of the system, as this redistributes photons from the wide, high frequency modes, to the narrow, low frequency modes. This is shown in Fig. 2.3(TOP), where η is the inverse thermalisation. Fig. 2.3(BOTTOM) shows the normalised photon number as a function of pump spot size. For narrow pump spots the overlap between pump and mode profiles for even modes

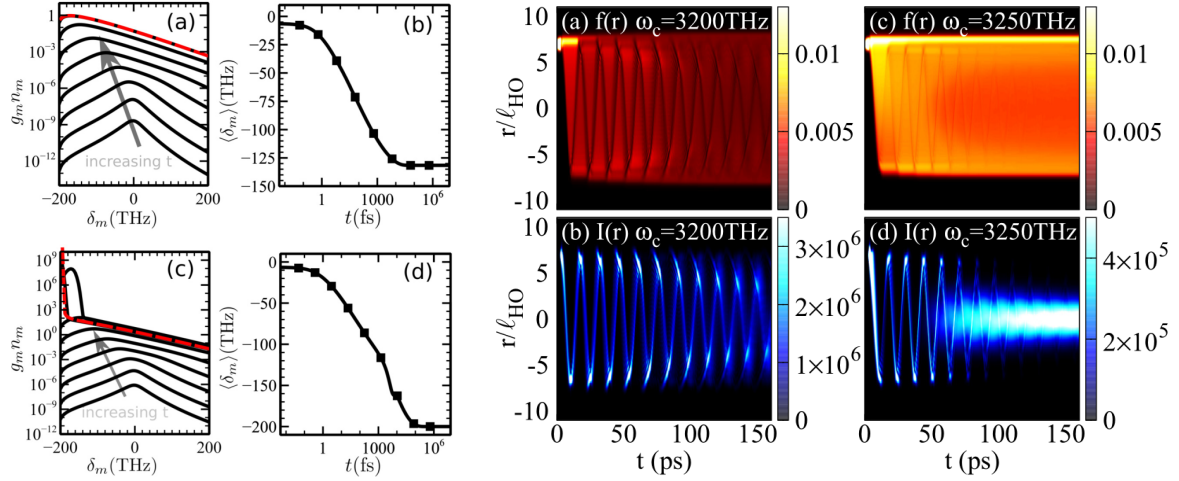


Figure 2.4: (LEFT) (a) and (c) show the evolution of mode population towards steady state over time below (a) and above (c) threshold. (b) and (d) show the mean frequency over time [95]. (RIGHT) The theoretical oscillations of photon intensity in a well thermalised system (d) and a poorly thermalised system (b); the plots (c) and (a) show the corresponding molecular excitation as a function of position [57].

is constant with respect to the pump, and the population of odd modes is negligible as they have approximately zero mode profile at the origin. Therefore the photon number becomes independent of the pump spot size as small sizes. At large pump spot sizes increasing the pump spot spreads the pump energy over a larger area, so less of the pump energy is in the region occupied by the low frequency, high population modes. Therefore the mode population decays polynomially for large pump spot sizes.

Integrating the rate equations (2.78) with respect to time gives the mode populations and molecular excitation as a function of time. This has been done for homogeneous coupling between modes and molecules [95] and is shown in Fig. 2.4(LEFT). Plots (a) and (c) show the evolution of the mode population as time increases for below and above threshold respectively. Plots (b) and (d) show the average frequency of the light within the cavity. This shows that photons are initially pumped into higher frequency states and then thermalise to the Bose-Einstein distribution. If a cavity is pumped with a narrow off centre pump, the peak of the photon intensity within the cavity oscillates, this is shown experimentally in [57]. It is possible to generalise the rate equations derived in 2.3 for $a_m^\dagger a_m$ to rate equations for the first order correlation between modes $a_m^\dagger a_k$ [96]. Including these first order coherences allows these oscillations to be modelled. Fig. 2.4(RIGHT) shows the theoretical oscillations of photon intensity in a well thermalised system (d) and a poorly thermalised system (b); the plots (c) and (a) show the corresponding molecular excitation as a function of position. This shows that thermalisation destroys first order coherence, leaving a state which is stationary in space.

The rate equations (2.78) may be extended to include two polarisations of light [113]. The electronic transition of a molecule may be modelled as a dipole. The coupling of the molecule to light is dependent on the projection of this dipole onto the polarisation of the light; if the dipole is perpendicular to the polarisation then there is no coupling, if it is parallel then the coupling is maximal. If a molecule does not rotate it therefore has a tendency to emit light of the same polarisation that it absorbed.

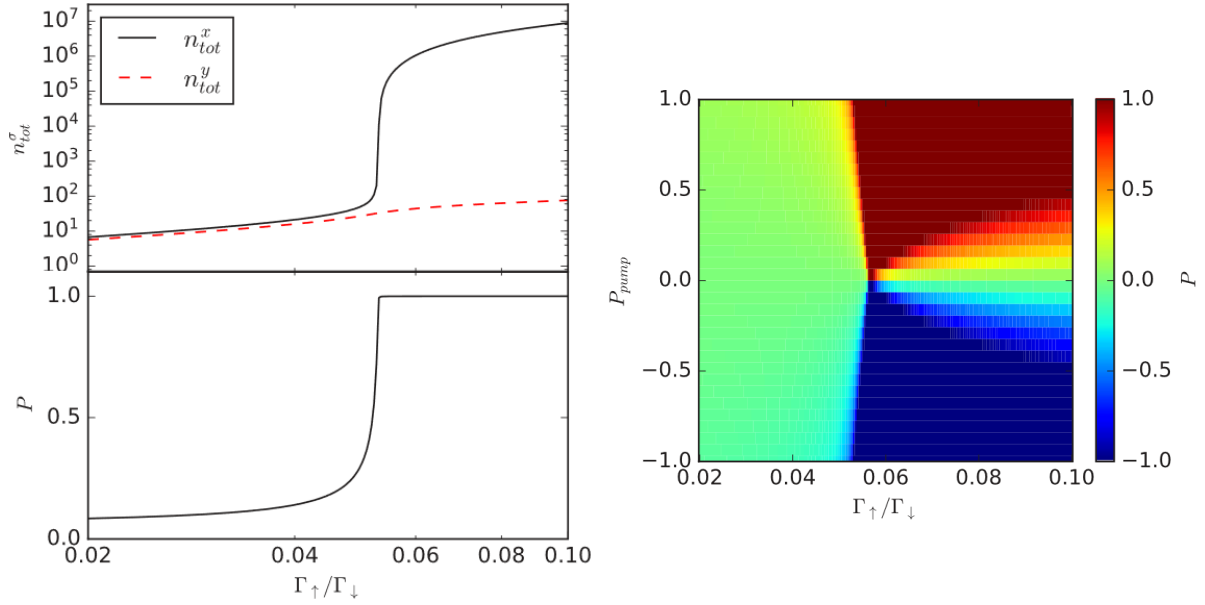


Figure 2.5: (LEFT, TOP) The population of x and y polarised light in the cavity when pumped with an x polarised pump. (LEFT BOTTOM) The polarisation of the light in the cavity. (RIGHT) The Polarisation P of the light in the cavity as a function of pump power $\Gamma_{\uparrow}$ and pump polarisation P_{pump} . Figure taken from [113]

If the rotation of a molecule is faster than emission then the emitted photon polarisation will not be correlated with the absorbed photon polarisation. The theoretical output polarisation of light is shown in Fig. 2.5(LEFT) for an x polarised pump. When no modes are condensed the molecular emission is of the order of spontaneous emission and slower than the molecular rotation, the population in each polarisation is therefore approximately equal. When a mode is condensed then the stimulated emission is faster than molecular rotation and the majority of emission is into the condensed mode, and the output may become polarised. A phase diagram of the polarisation as functions of pump power and pump polarisation is shown in Fig. 2.5(RIGHT). The pump polarisation is varied by incoherently increasing and decreasing x and y components of the pump *not* by rotating the pump polarisation. As the pump polarisation of the pump increases the threshold for condensation decreases as more of the pump light is emitted into the condensing mode. When the polarisation of the pump is close to zero both mode polarisations are pumped and both may condense resulting in an unpolarised output. As the pump is usually well polarised, and the uncondensed modes do not contribute to the molecular excitation (see Sec. 3), only one polarisation of light needs to be considered.

The rate equations for inhomogeneous coupling may also be applied to the plasmonic BECs discussed in Sec. 1.3. Fig. 2.6 shows the evolution of the plasmonic system from a state with plasmons in the vicinity of the pump spot, to a thermally distributed BEC. The experiment and theory both show a movement of population from high to low energies and a final BEC state, indicating that the microscopic model is a good description of the plasmonic system.

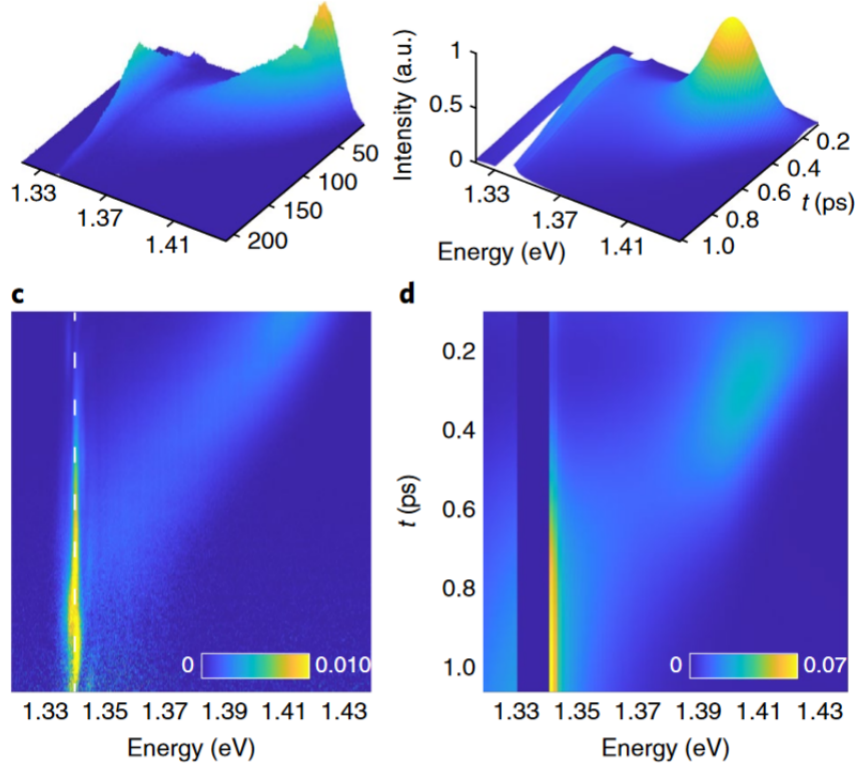


Figure 2.6: (LEFT) The experimentally measured formation of a plasmon BEC. (RIGHT) The predicted formation of a plasmon BEC using the rate equations for inhomogeneous coupling described in 2.3.1. The vertical axis of the left plot is scaled to correspond to the time axis of the right plot. The upper plots show the raw intensity, the bottom plots show the normalised intensity at each time; average population is not conserved due to loss. Figure taken from [42].

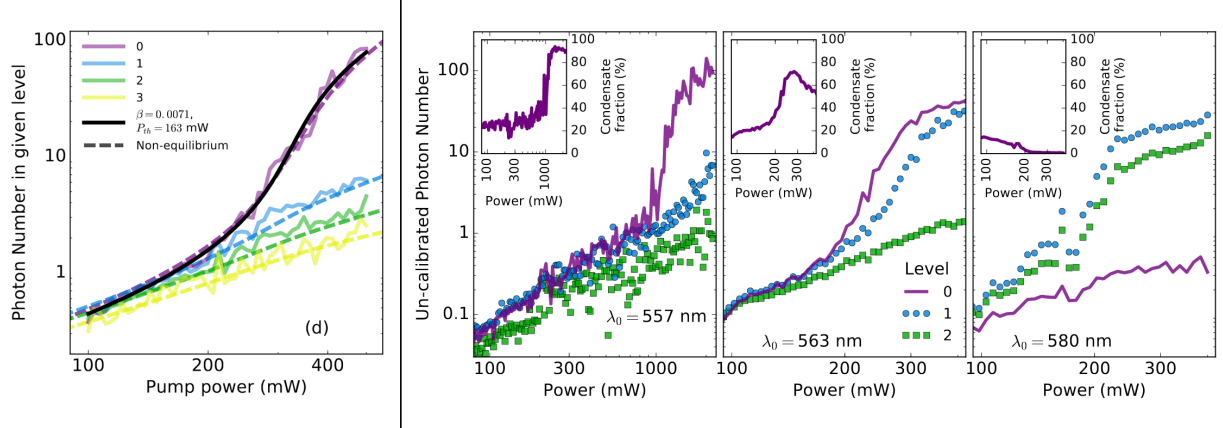


Figure 2.7: Figure taken from [5]. (LEFT) Solid colours: The number of photons in each energy level as pump power is varied. Dashed colours: the theoretical fit to the experimental data generated by the author. (RIGHT) the number of photons in each energy level as function of pump power. Left to right shows increasing cut-off wavelength, varied by changing the spacing between cavity mirrors.

Multimode Condensation

If a mirror with a small radius of curvature is used in an experimental setup then the cavity modes have a wide frequency spacing and are therefore resolvable using a spectrometer [5]. This allows

the population in each mode to be directly measured and plotted as a function of pump power. Fig. 2.7 (left) shows the experimentally measured photon population in each energy level⁵ as solid coloured lines and a theoretical fit as coloured dashed lines. The theoretical line was fitted using the inhomogeneous rate equations (2.83) by varying the cavity decay rate κ , the molecular decay rate $\Gamma_{\downarrow}$, the pump width and power, and the strength of absorption and emission. Fig. 2.7 (right) shows similar plots of population for various mode frequencies. The spacing between cavity mirrors was varied to apply a constant shift to all mode frequencies (see Sec. 1.7). At low wavelengths absorption and emission are strong, and the system is thermalised, the plot therefore shows Bose-Einstein condensation of the ground mode. The middle plot shows multimode condensation of the ground mode and level one. The right plot was generated with a large wavelength; the absorption and emission are therefore weak and the system is not thermalised. The condensed modes are therefore not the ground mode. The non-equilibrium theory fits the data up to a factor of two in a data range of two orders of magnitude. The strong agreement between experiment and theory is an excellent justification for using this model.



This experiment was performed after, and inspired by the work discussed in Chapter 3.1. The Non-equilibrium fits in Fig. 2.7 were generated with code produced by the author of this thesis.

2.7 Summary

To summarise, the initial system Hamiltonian is

$$H = \sum_m \omega_m a_m^\dagger a_m + \sum_i \left[\frac{\xi}{2} \sigma_i^{(z)} + \Omega b_i^\dagger b_i \right] + \sum_{m,i} g_{m,i} (a_m \sigma_i^+ + a_m^\dagger \sigma_i^-) + \sum_i \Omega \sqrt{S} \sigma_i^z (b_i + b_i^\dagger). \quad (2.98)$$

This is transformed using the polaron transform to combine the two coupling terms

$$H = \sum_m \omega_m a_m^\dagger a_m + \sum_i \left[\frac{\xi}{2} \sigma_i^{(z)} + \Omega b_i^\dagger b_i \right] + \sum_{m,i} g_{m,i} (a_m \sigma_i^+ \hat{D}_i + a_m^\dagger \sigma_i^- \hat{D}_i^\dagger). \quad (2.99)$$

The Born-Markov approximations are performed, and pumping and loss terms are included to give the master equation

$$\begin{aligned} \dot{\rho} = & -i[\tilde{H}_0, \rho] - \left\{ \sum_m \frac{\kappa}{2} \mathcal{L}[\hat{a}_m] + \sum_i \left[\frac{\Gamma_{\uparrow,i}}{2} \mathcal{L}[\hat{\sigma}_i^+] + \frac{\Gamma_{\downarrow}}{2} \mathcal{L}[\hat{\sigma}_i^-] \right] \right. \\ & \left. + \sum_{m,i} \left[\frac{\Lambda_{\downarrow}^{(m)}(r_j)}{2} \mathcal{L}[\hat{a}_m^\dagger \hat{\sigma}_i^-] + \frac{\Lambda_{\uparrow}^{(m)}(r_j)}{2} \mathcal{L}[\hat{a}_m \hat{\sigma}_i^+] \right] \right\} \rho. \end{aligned} \quad (2.100)$$

This may be used to calculate rate equations for the mode population and molecular excitation for homogeneous coupling between modes and molecules

$$\begin{aligned} \frac{dn_k}{dt} = & -\kappa n_k - \Lambda_{\uparrow}^{(m)} n_k (1-f) J + \Lambda_{\downarrow}^{(m)} (n_k + 1) f J \\ \frac{df}{dt} = & \Gamma_{\uparrow,j} (1-f) - \Gamma_{\downarrow} f + \sum_m \Lambda_{\uparrow}^{(m)} n_m (1-f) - \sum_m \Lambda_{\downarrow}^{(m)} (n_m + 1) f. \end{aligned} \quad (2.101)$$

⁵An energy level is defined as all modes of a particular energy. As the cavity is harmonic the number of modes in energy level n is $n + 1$.

Rate equations may also be calculated for inhomogeneous coupling between modes and molecules

$$\begin{aligned}
\frac{dn_m}{dt} &= -\kappa n_m + \bar{\rho} \Lambda_{\downarrow}^{(m)} f_m (n_m + 1) + \bar{\rho} \Lambda_{\uparrow}^{(m)} (f_m - 1) n_m \\
\frac{\partial f(\underline{r})}{\partial t} &= -\Gamma_{\downarrow}^{tot}(\underline{r}) f(\underline{r}) + \Gamma_{\uparrow}^{tot}(\underline{r}) (1 - f(\underline{r})) \\
\Gamma_{\uparrow}^{tot}(\underline{r}) &= \Gamma_{\uparrow}(\underline{r}) + \sum_m |\psi_m(\underline{r})|^2 \Lambda_{\uparrow}^{(m)} n_m \\
\Gamma_{\downarrow}^{tot}(\underline{r}) &= \Gamma_{\downarrow} + \sum_m |\psi_m(\underline{r})|^2 \Lambda_{\downarrow}^{(m)} (n_m + 1) \\
f_m &= \int f(\underline{r}) |\psi_m(\underline{r})|^2 d^2 \underline{r} .
\end{aligned} \tag{2.102}$$

In the steady state f_m may be directly calculated as a function of mode population as

$$f_m = \int d^2 r |\psi_m(\underline{r})|^2 \frac{\Gamma_{\uparrow}^{tot}(\underline{r})}{\Gamma_{\uparrow}^{tot}(\underline{r}) + \Gamma_{\downarrow}^{tot}(\underline{r})} . \tag{2.103}$$

Chapter 3

Multimode Phases and Clamping

The experiments discussed in Sec. 2.6, show clear evidence of multiple modes exhibiting macroscopic occupation. In [96] Kirton and Keeling demonstrate that this phenomena may be observed using the inhomogeneous rate equation model, and hypothesise that this may be explained by gain clamping. This chapter explores my work on the multimode phases of photonic condensates at steady state. It begins by discussing how steady state may be calculated, and the system parameters used in the simulations. Then definitions of threshold and the different phases are given. The impact of molecular clamping on condensate phase is then discussed. A phase diagram is presented which shows how changing the thermalisation rate and pump power of the condensate affects its phase. Finally analytic formula for the phase boundaries are derived.

The simulations in this chapter and chapter 4 use a 2D parabolic cavity¹. The mode intensity profiles will therefore be the eigenmodes of a 2D harmonic oscillator, which are the Hermite-Gauss modes discussed in Sec. 1.7. The derivation of the master equation 2.36 requires that all modes have different frequencies, as this is required to go from Eq. (2.24) to Eq.(2.25). The cavity simulated must therefore be anisotropic, so that the frequency spacing between modes in the y direction is 1.01 the spacing in the x direction, $\epsilon_y = 1.01\epsilon_x$. These, and other parameters are given in Table 3.1. As the anisotropy is weak, the populations in modes $[p_0, p_1]$ and $[p_1, p_0]$ are almost identical, therefore this chapter only refers to modes with $p_x < p_y$. The remaining parameters may be justified as follows. The molecular density was chosen to give large and sharp increases in mode population when a mode condenses. The range of the detuning of the lowest mode δ_0 was chosen to give both laser and BEC phases (discussed later). This requires the ratio of absorption to cavity decay (called the thermalisation coefficient) to be between 0.1 and 10. As the cavity decay rate and molecular density are known the absorption peak is therefore fixed. The pump profile used was Gaussian with a width twenty times larger than the standard deviation of the ground mode $\left(L = \sqrt{\langle x^2 \rangle_{[0,0]}}\right)$, and is therefore approximately flat over the low energy modes.

Finding the steady state of the system given these parameters is difficult to do analytically, due to the non-linearity of the equations, and is therefore obtained numerically. The steady state may be found using the rate of change of mode population Eq. (2.83), and the steady state molecular excitation

¹Note that Kirton and Keeling use a 1D cavity in [96].

Quantity	Symbol	Value
Cavity decay rate	κ	$1 \times \kappa$
Detuning of the lowest mode	δ_0	$(-55.7 \rightarrow -30.1)$ OR -39.4 THz
Cavity mode spacing in x direction	ϵ_x	4.77 THz
Cavity mode spacing in y direction	ϵ_y	$1.01\epsilon_x$
Free space emission	$\Gamma_{\downarrow}$	$\kappa/4$
Absorption from cavity mode m	$\Lambda_{\uparrow}^{(m)}$	Peak: $1.2 \times 10^{-9} \kappa L^2$
Emission into cavity mode m	$\Lambda_{\downarrow}^{(m)}$	Peak: $1.2 \times 10^{-9} \kappa L^2$
Spatial width of ground mode	L	L
2 dimensional density of molecules	$\bar{\rho}$	$10^{12}/L^2$
Pump beam width		$20 L$
Thermalisation coefficient	$\gamma = \bar{\rho}\Lambda_{\uparrow}^{[0,0]}/\kappa$	$(0.1 \rightarrow 10)$ OR 1.8
Number of modes		28 (7 levels)

Table 3.1: The default values used in the simulations presented in chapter 3, unless otherwise specified. Rates are invariant under a global scaling, and are therefore given in units of cavity decay rate. Similarly lengths are given in terms of the spatial width of ground mode, which may be freely scaled without affecting the simulation. Scaling would change the mode frequencies however these are not defined in terms of the length scale.

fraction overlapping each mode Eq. (2.87), as explained in Sec. 2.3.1. There are two algorithms capable of finding the steady state, the first is a root finding algorithm which varies the mode population to minimise the rate. The second algorithm propagates the mode population over time until steady state is reached using the rate equation (2.83). Note that this propagation is not a true propagation over time as the molecular excitation is always assumed to be in the steady state (Eq. (2.87)), it is just exploiting the fact that the propagation algorithms in python are more stable than the root finding algorithms. The intermediate mode populations generated by the propagation algorithm are therefore meaningless. The root finding algorithm makes larger changes in mode population between iterations when compared to the propagation algorithm, this makes the root finding algorithm faster but also less stable. The propagation algorithm was chosen because it is more reliable than the root finding algorithm. The runtime of the propagation algorithm may be dramatically shortened when simulating many similar systems (e.g. when constructing a phase diagram) by setting the initial conditions of a

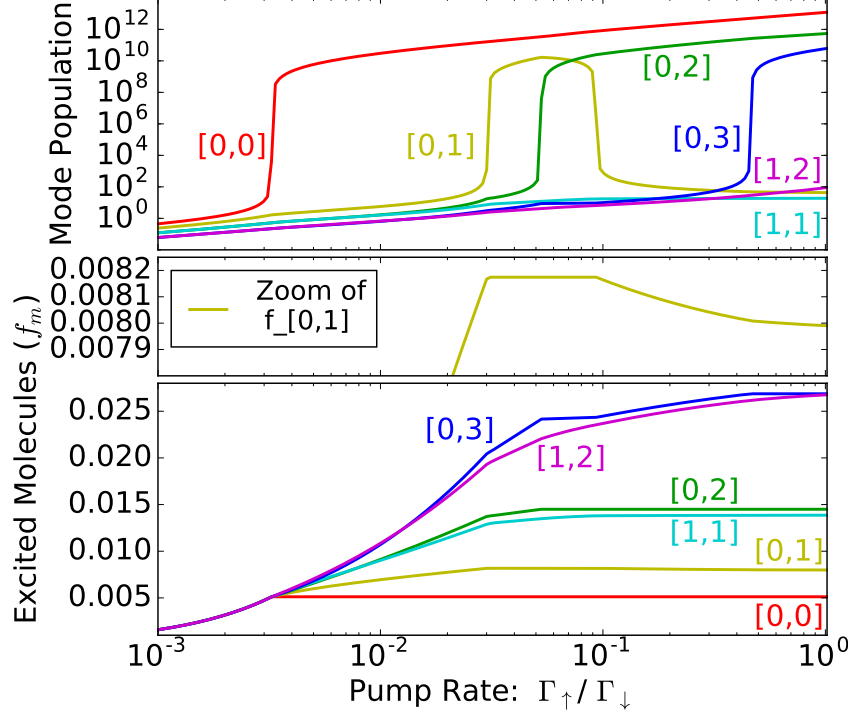


Figure 3.1: (TOP) the steady state population in each mode as a function of pump power. The label $[p_x, p_y]$ corresponds to the population in the mode with quantum numbers p_x and p_y . (BOTTOM) The molecular excitation fraction f_m overlapping each mode, Eq. (2.81). The label $[p_x, p_y]$ corresponds to the mode in the overlap integral. (MIDDLE) A zoom of the bottom figure to show the reduction in $f_{[0,1]}$ after the decondensation of mode $[0, 1]$.

simulation to the steady state of a similar system. The runtime of the propagation algorithm on a single core varies from a minute for uncondensed systems of 10 modes, to tens of minutes for systems of 28 modes in condensed states.

The steady state mode population as a function of pump rate is shown in Fig. 3.1 (top). Clear jumps in population of approximately 8 orders of magnitude are visible and correspond to the condensation of modes. Each condensation event changes the phase of the system, as there are numerous possible phases they are grouped as follows. At low pump rate none of the modes are condensed, this is called the uncondensed phase. A phase with only the ground mode condensed is called the BEC phase, and can be seen in Fig. 3.1 as the pump rate is increased from the uncondensed phase. If the ground mode and at least one other mode are condensed then the system is in a multimode phase. Fig. 3.1 transitions through four different multimode phases as the pump rate increases. The final phase is called the laser phase, in this thesis it is defined as multiple condensed modes excluding the ground mode, see Sec. 1.4. Fig. 3.1 does not show the laser phase. There is an 8 order of magnitude loss of population in mode $[0, 1]$ after the condensation of mode $[0, 2]$. This loss of condensation under increasing pump power is called decondensation and is counter-intuitive, usually increasing the pump power increases the number of photons in a mode. To the author's best knowledge this decondensation phenomena has barely been investigated. Vorberg *et al.* [114] presents a similar phenomenon as the coupling between two different heat baths is varied. A form of decondensation with far smoother

transitions is also predicted in diffuse random lasers [115]. The remainder of this chapter will explain the origins of decondensation and discuss how it may be either achieved or avoided.

3.1 Molecular Clamping

In order to understand decondensation and the transitions between the multimode phases it is instructive to study the clamping of molecular excitation by condensed modes. The theory is well established in laser physics [59], and may be adapted to analyse condensates. The effect of molecular excitation on the condensation of modes may be seen by deriving a threshold condition for condensation in terms of the molecular excitation fraction overlap f_m . In the steady state the rate of mode population change $\frac{dn_m}{dt}$ in Eq. (2.83) is equal to zero. This may be rearranged to give the steady state mode population in terms of molecular excitation f_m

$$n_m = \frac{\Lambda_{\downarrow}^{(m)} f_m}{\frac{\kappa}{\bar{\rho}} - \Lambda_{\downarrow}^{(m)} f_m - \Lambda_{\uparrow}^{(m)} (f_m - 1)} . \quad (3.1)$$

Condensation occurs when the mode population diverges, therefore a possible threshold condition is for the denominator of Eq. (3.1) to equal zero². This may be rearranged to give a threshold value for f_m

$$f_m^{crit} = \frac{\Lambda_{\uparrow}^{(m)} + \frac{\kappa}{\bar{\rho}}}{\Lambda_{\uparrow}^{(m)} + \Lambda_{\downarrow}^{(m)}} . \quad (3.2)$$

For reference, if the molecular excitation is shifted by the critical value $y_m = f_m^{crit} - f_m$, then the steady state mode population, Eq. (3.1) becomes

$$n_m = \frac{\Lambda_{\downarrow}^{(m)}}{\Lambda_{\uparrow}^{(m)} + \Lambda_{\downarrow}^{(m)}} + \frac{\Lambda_{\downarrow}^{(m)} \Lambda_{\uparrow}^{(m)} + \Lambda_{\downarrow}^{(m)} \frac{\kappa}{\bar{\rho}}}{(\Lambda_{\uparrow}^{(m)} + \Lambda_{\downarrow}^{(m)})^2} \frac{1}{y_m} , \quad (3.3)$$

which clearly diverges as the excitation fraction approaches the critical value $y_m \rightarrow 0$. If the molecular excitation fraction leaves the critical value the corresponding mode will decondense. This can be seen in Fig. 3.1, when the value of $f_{[0,1]}$ is at the plateau (and close to the critical value), mode $[0,1]$ is condensed. This section looks at the excitation of molecules at different cavity positions to explain why the excitation fraction for individual modes f_m is at or below the critical value, causing those modes to either condense or decondense. As an excitation fraction greater than the critical value would cause a negative mode population the excitation fraction for each may not exceed the critical value $f_m < f_m^{crit}$.

The molecular excitation fraction for a mode is given by the overlap integral of the mode wavefunction and the excitation fraction as a function of position Eq. (2.81). If the molecular excitation varies with position then different modes can have different excitation fractions f_m corresponding to their mode profiles. It is therefore possible for multiple modes to simultaneously condense³. The excitation fraction at each position depends on the total rates of molecular gain and loss at that position, given

²The denominator will never actually equal zero at steady state but it will be close to zero, see Sec. 3.2.1.

³In a system with homogeneous mode molecule coupling f_m is identical for each mode, so multimode condensation is impossible

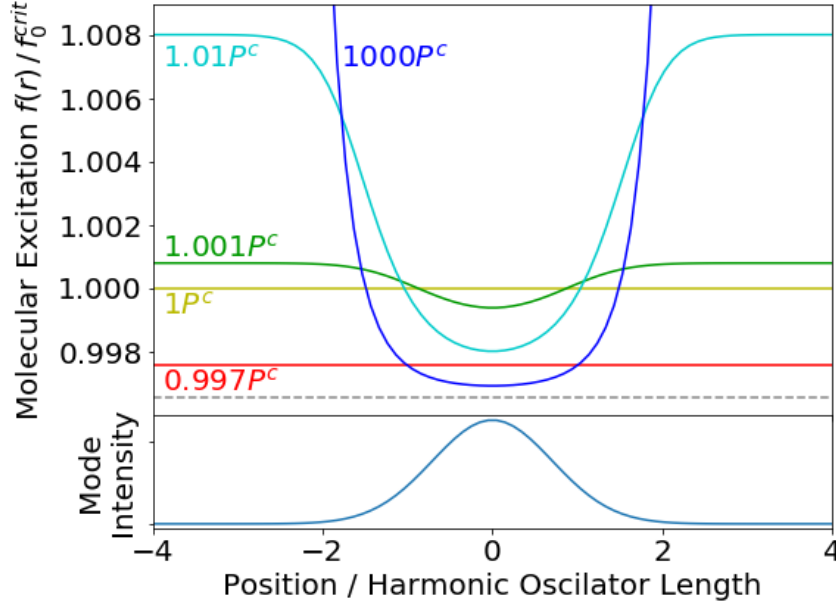


Figure 3.2: (TOP) The molecular excitation fraction as a function of cavity position. The cavity position is the 1D distance from the centre of the cavity in units of harmonic oscillator length L . Molecular excitation fraction is given in units of the critical excitation fraction for mode $[0, 0]$, $f_{[0,0]}^{\text{crit}}$, given by Eq. (3.2). Different lines correspond to different pump powers given in units of the threshold power of mode $[0, 0]$, P^c . The grey dashed line show the limit of molecular excitation at infinite population of mode $[0, 0]$, given by Eq. (3.6). (BOTTOM) The mode profile of mode $[0, 0]$ which determines the coupling to the molecules at position r .

by Eqs. (2.86). These rates contain absorption and emission terms, which depend on mode population, and pumping and loss terms, which do not. If the mode populations are small then the pumping and loss terms dominate and the molecular excitation may be written as

$$f(\underline{r}) = \frac{\Gamma_{\uparrow}(\underline{r})}{\Gamma_{\uparrow}(\underline{r}) + \Gamma_{\downarrow}}. \quad (3.4)$$

In this regime the molecules are said to be unclamped. If the mode intensity is large at a particular position then absorption and emission dominate and the molecular excitation may be written as

$$f(\underline{r}) = \frac{\sum_m |\psi_m(\underline{r})|^2 n_m \Lambda_{\uparrow}^{(m)}}{\sum_m |\psi_m(\underline{r})|^2 n_m (\Lambda_{\uparrow}^{(m)} + \Lambda_{\downarrow}^{(m)})}. \quad (3.5)$$

Molecules at point $\underline{r}$ are said to be clamped by mode m if the rates of absorption and emission at point $\underline{r}$ dominate: $|\psi_m(\underline{r})|^2 n_m \Lambda_{\uparrow}^{(m)} \gg \Gamma_{\uparrow}$ and $|\psi_m(\underline{r})|^2 n_m \Lambda_{\downarrow}^{(m)} \gg \Gamma_{\downarrow}$. If the population in one mode dominates all other populations then the equation for clamped excitation, Eq. (3.5) simplifies to

$$f(\underline{r}) = \frac{\Lambda_{\uparrow}^{(m)}}{\Lambda_{\uparrow}^{(m)} + \Lambda_{\downarrow}^{(m)}}. \quad (3.6)$$

This is guaranteed to be less than the critical value for condensation given in Eq. (3.2). This demonstrates why the excitation fraction for a mode f_m never exceeds the critical value: as f_m approaches

the critical value the mode population tends to infinity, this large population clamps f_m to a value less than the critical value. The clamping prevents f_m from reaching the critical value⁴ and thereby prevents the population from becoming infinite.

The transition from unclamped to clamped molecules is shown in Fig. 3.2, for a uniform pump profile. As the pump power is increased the excitation of unclamped molecules increases monotonically, as can be seen from Eq. (3.4). When the uniform distribution of $f(r)$ reaches the critical value for mode $[0, 0]$ (yellow line), mode $[0, 0]$ condenses. As the excitation fraction for mode $[0, 0]$, $f_{[0,0]}$ may not exceed the critical value, the weighted average of $f(r)$ is constant for all higher pump powers (where the weight is the mode profile shown in the bottom of Fig. 3.2). The unclamped molecules at the edges of the cavity gain excitation as pump power is increased (Eq. (3.4)), the clamped molecules at the centre of the cavity must therefore lose excitation to keep $f_{[0,0]}$ constant. As the pump power increases the population in mode $[0, 0]$ increases and the excitation of clamped molecules approaches⁵ the value given in Eq. (3.6), shown as a dashed grey line in Fig. 3.2. If multiple modes are condensed then the general trend is for increasing pump power to decrease the excitation of clamped modes, but there are exceptions.

The decrease in molecular excitation at particular cavity positions explains the decondensation seen in Fig. 3.1, and is represented by the diagram Fig. 3.3. When mode $[0, 0]$ condenses it clamps the molecules in the centre of the cavity to an excitation below the critical excitation for mode $[0, 0]$, indicated by the black double arrow in Fig. 3.3. The critical excitation for mode $[0, 1]$ is higher than mode $[0, 0]$, therefore mode $[0, 1]$ must use unclamped molecules in the middle⁶ of the cavity to condense, *i.e.* the integral (2.81) is only larger than the critical value Eq. (3.2) if unclamped molecules contribute to it. The strong emission of middle and central molecules into mode $[0, 1]$ is indicated by solid green lines in Fig. 3.3. Unclamped molecules can emit into mode $[0, 1]$ because its mode profile is spatially wider than the profile of mode $[0, 0]$. In order for mode $[0, 1]$ to condense the middle molecules must have an excitation larger than the critical excitation for mode $[0, 1]$, because they must compensate for the clamped central molecules. In some systems the excitation of middle molecules required for the condensation of mode $[0, 1]$ exceeds the critical excitation of mode $[0, 2]$, $f(r_{middle}) > f_{[0,2]}^{crit}$. In Fig. 3.3 the dashed circle is the excitation of middle molecules required to make mode $[0, 1]$ condense, and the solid circle is the actual excitation when clamped by mode $[0, 2]$. When mode $[0, 2]$ condenses the middle molecules may be clamped to values below what is required to make mode $[0, 1]$ condense. The molecules emitting into mode $[0, 1]$ may be clamped by mode $[0, 0]$ in the centre of the cavity, and by mode $[0, 2]$ in the middle of the cavity. As mode $[0, 2]$ is spatially larger than mode $[0, 1]$ there are no remaining unclamped molecules which can maintain the condensation of mode $[0, 1]$. As the pump power is increased the excitation of the clamped molecules decreases (as shown in Fig. 3.2) and the excitation fraction overlapping mode $[0, 1]$ drops below the critical excitation, this causes mode $[0, 1]$ to decondense. Mode $[0, 2]$ has a higher critical excitation than mode $[0, 1]$ but mode $[0, 2]$ does not decondense because unclamped molecules at the edge of the cavity emit into mode $[0, 2]$ but not mode

⁴but f_m gets very close to the critical value

⁵The excitation never reaches the value given in Eq. (3.6) because the mode population is proportional to the pump power at infinite pump power (proven in Box. 4.3), therefore the molecules are never completely clamped.

⁶Here “middle” means in between the centre and the edge of the cavity.

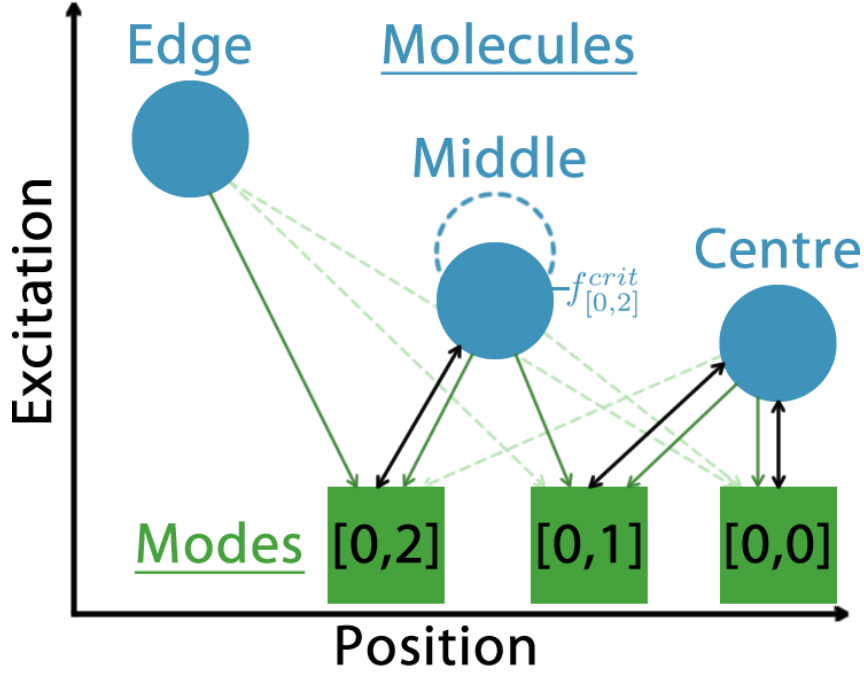


Figure 3.3: A diagram representing the clamping required for the decondensation of mode $[0, 1]$. Green squares represent modes, blue circles represent molecules. The height of the circle indicates the excitation of the molecules. The right molecules are in the centre of the cavity, the left molecules are at the edge of the cavity, and the middle molecules are in between. Black double arrows indicate that the molecules are clamped by the mode. Solid green arrows indicate strong emission from the molecule into the mode. Dashed pale arrows indicate weak emission into the mode and should be ignored. The dashed circle indicates the excitation of middle molecules required for the condensation of mode $[0, 1]$, as this excitation is not achieved, mode $[0, 1]$ decondenses.

$[0, 1]$. This process is analogous to gain stealing in lasers.

3.2 Phase Diagram

The previous section showed that the strong interaction of condensed modes, via molecular clamping, causes changes in the multimode phase. This section investigates the phases changes caused by varying pump power and thermalisation. This requires a measure of thermalisation which, in this text, is defined as the ratio of absorption to cavity loss, for the lowest mode, $\gamma = \rho\Lambda_{\uparrow}^{[0,0]}/\kappa$. This is chosen because thermalisation occurs when a photons are absorbed and re-emitted. If the absorption rate is much larger than the cavity loss ($\gamma \gg 1$), then the photons will be absorbed and emitted multiple times before escaping the cavity, and therefore be thermalised. If the cavity loss is much larger than emission ($\gamma \ll 1$), then the photons will not be reabsorbed, and the emission spectrum of the cavity will depend purely on the emission spectrum of the molecules. Condensation will therefore occur in the mode with the largest rate of emission, as in a laser. The identification of phases requires a method of detecting when a mode is condensed. The jumps in population shown in Fig. 3.1 are representative

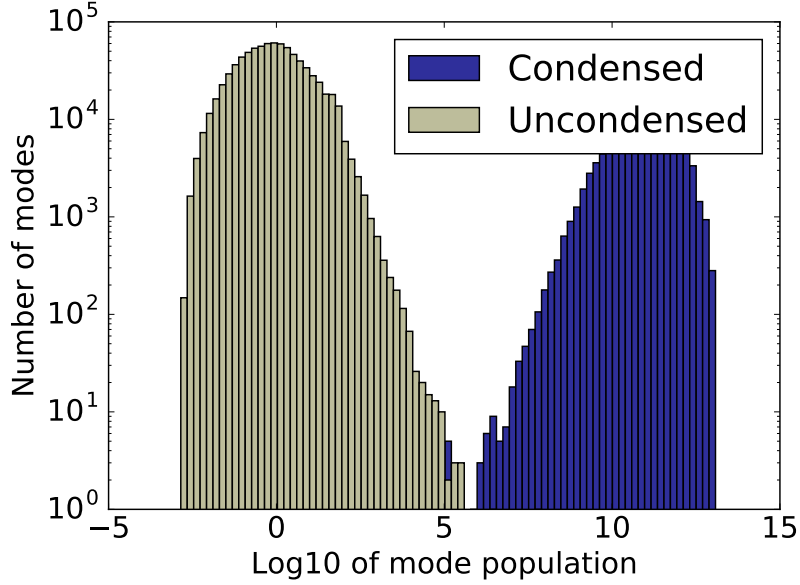
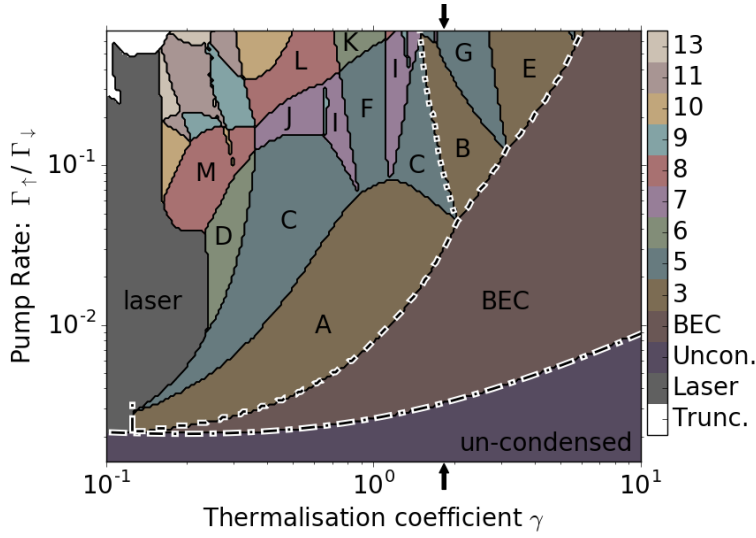


Figure 3.4: A histogram of the populations of modes classified as condensed or uncondensed using the criteria: 3 orders of magnitude increase or decrease in population over an increase in pump power of 10%. The set of mode populations used in are taken from the phase diagram, Fig 3.5. The population of each mode at each point on the phase diagram (containing 200 by 200 points) is added to a single set of populations and the histogram is generated from this set. Note that changing the threshold condition to an increase of 3.4 orders of magnitude over a 10% increase in pump power would remove the anomalous condensed modes with populations of 10^5 .

of all jumps discussed in this chapter, and, as they are sharp and large, they may be used as criteria for threshold. In this thesis the threshold for condensation (decondensation) is defined as a mode population increase (decrease) of three orders of magnitude over a 10% increase in pump power. This threshold condition will be used later when creating the phase diagram Fig. 3.5. To verify that it is a sensible threshold condition for every point on the phase diagram the population in each mode at every point on the phase diagram may be plotted on a histogram Fig. 3.4. This shows that there is a clear separation in mode population between condensed modes, with populations greater than 6.3×10^5 , and uncondensed modes, which validates the choice of threshold condition. There are a few anomalies where a mode with population less than 6.3×10^5 has been classified as condensed, however all of these anomalies are near phase boundaries and reclassifying them as uncondensed would result in an insignificant shift of the phase boundary.

Fig. 3.5 shows the phase of the system as the thermalisation coefficient and pump rate are varied. The “laser” phase contains many phase changes between different laser phases, however these are not shown to maintain clarity. The un-condensed phase has no condensed modes, and in the BEC phase only the ground mode is condensed. The small anisotropy of the cavity causes modes $[q, p]$ and $[p, q]$ to condense at slightly different pump or thermalisation rates, this creates additional phase boundaries and narrow intermediate phases in-between all the phases shown (where $[q, p]$ is condensed but not $[p, q]$). These intermediate phases have been removed for clarity by considering both $[p, q]$ and $[q, p]$



	Condensed Modes
BEC	[0,0]
A	[0,0] [0,1]
B	[0,0] [0,2]
C	[0,0] [0,1] [0,2]
D	[0,0] [0,1] [0,2] [1,1]
E	[0,0] [0,3]
F	[0,0] [0,1] [0,3]
G	[0,0] [0,2] [0,3]
I	[0,0] [0,1] [0,2] [0,3]
J	[0,0] [0,1] [0,2] [0,4]
K	[0,0] [0,1] [0,3] [2,2]
Lleft	[0,0] [0,1] [0,2] [0,4] [2,2]
Lright	[0,0] [0,1] [0,2] [0,3] [2,2]
M	[0,0] [0,1] [0,2] [1,1] [0,3]

Figure 3.5: (LEFT) The phase of the condensate as a function of thermalisation coefficient $\gamma = \bar{\rho}\Lambda_{\uparrow}^{[0,0]}/\kappa$ and pumping. Each colour corresponds to a different number of condensed modes, except the “laser” phase, where modes other than the ground modes are condensed, and the “trunc” region which contains truncation errors. (RIGHT) The modes which are condensed in each section of the phase diagram (and the corresponding modes: $[q, p]$ indicates that modes $[q, p]$ and $[p, q]$ are condensed). There is a boundary in phase *L*, directly above the *J*, *I* boundary, where both sides have 8 condensed modes. The left side of the boundary has mode $[0, 4]$ condensed, and the right has mode $[0, 3]$ condensed.

to be condensed if either is condensed. At the boundary between phases *I* and *J* the condensed mode $[0, 3]$ decondenses and the mode $[0, 4]$ condenses simultaneously. The mode $[3, 0]$ decondenses as mode $[4, 0]$ condenses at a slightly larger thermalisation coefficient. Due to the procedure of considering both modes in a pair condensed if either is condensed this creates a narrow region between *J* and *I* where 9 modes appear condensed instead of 7; this is an artefact of the plot and not an error in the simulation. The narrow phases between *M* and the unlabelled phase to the right of *M*, and between *I* and the unnamed phase to the right of *I* are caused by the same plotting artefact. The rough phase boundaries in the top left of the diagram are due to limited numerical accuracy. The arrow on the thermalisation axis shows the thermalisation coefficient used to create Fig. 3.1 ($\gamma = 1.8$). The dashed lines are analytic phase boundaries discussed in Sec. 3.2.1.

At low pump rates the system is in the uncondensed phase, as the pump rate is increased a single mode condenses, followed by the condensation of other modes. At high thermalisation coefficient the threshold pump rate for multimode condensation increases, and the system remains in the BEC phase

for a greater range of pump rates. This is because the high thermalisation transfers population from the higher modes to the ground mode, preventing the higher modes from condensing and enforcing a Bose-Einstein distribution. An equivalent explanation is that as the thermalisation rate increases, and the pump rate is kept constant, the spatial region clamped by the condensed ground state becomes larger. As the clamped region is larger, the higher modes require a larger unclamped excitation level in order to condense, which is only produced by a higher pump rate. Both explanations also explain which mode condenses to form the multimode condensate (in phases *A*, *B*, and *E*). Any mode in complete thermal equilibrium with the ground mode cannot condense due to the transfer of population from the higher mode to the ground mode. The number of molecules shared by the higher modes and the ground mode is smaller than the number shared by the lower modes and the ground mode. Formally, a pair of modes are coupled by a molecule absorbing and emitting into both modes, therefore the strength of the coupling between modes *a* and *b* may be expressed as the integral

$$C_{a,b} = \int d\underline{r} |\psi_a(\underline{r})|^2 |\psi_b(\underline{r})|^2 \quad (3.7)$$

As the profile of the ground mode is more similar to the lower modes than the higher modes, the thermal equilibrium between the ground mode and the lower modes is stronger than between the ground modes the higher modes. Strong equilibrium prevents multimode condensation, therefore as the thermalisation coefficient increases the lower modes are prevented from condensing, and the higher modes form the multimode condensates. This may also be explained with clamping, as the thermalisation coefficient increases the spatial region of molecules clamped by the ground mode becomes larger. Multimode phases require unclamped molecules, and higher frequency modes have wider mode profiles. As the thermalisation coefficient is increased the lower modes lose access to unclamped molecules, but the higher modes do not.

There is also an increase in the uncondensed-BEC threshold as thermalisation rate increases. The thermalisation rate is varied by changing the frequency of the lowest mode, which changes the absorption and emission strengths, given in Fig. 1.6. The BEC phase requires a critical number of photons in the cavity and as the thermalisation rate is increased the ratio of absorption to emission increases for all modes. This increases the fraction of system excitations which are excited molecules rather than cavity photons. The pump rate required to produce the critical number of cavity photons therefore increases with thermalisation coefficient. As the thermalisation coefficient is decreased the system transitions from the BEC phase to the multimode phase, with increasing numbers of condensed modes, and finally to the laser phase. This is because multimode condensation is a non-equilibrium phenomena and is therefore suppressed by strong thermalisation, which redistributes photons from higher modes to the ground mode, and allows the condensed ground mode to clamp a larger area of molecules. There are multiple cases of decondensation under increasing pump power in Fig. 3.5: e.g. the *CB*, *IF*, *LK*, and *GE* boundaries. Note that decondensation does not occur at every thermalisation rate, reducing the thermalisation coefficient from the arrows in Fig. 3.5 will cause the system to transition from phase *C* to phase *I*, instead of to phase *B*. If decondensation occurs at this thermalisation coefficient it will be at a larger pump power. Searches for decondensation in parameter space must therefore be thorough and involve a large sampling of potential system parameters.

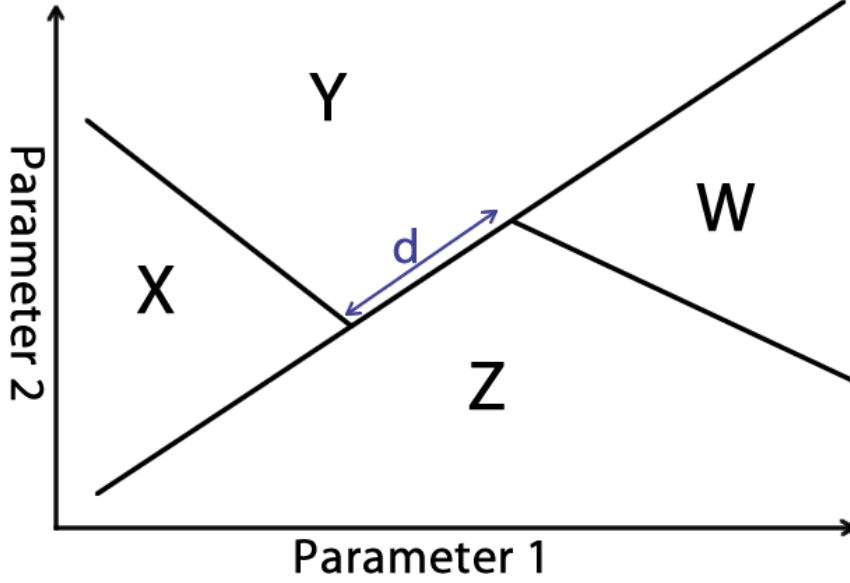


Figure 3.6: An example phase diagram with the four phases W , X , Y , and Z , and arbitrary parameters 1 and 2. The intersection points XYZ and WYZ are separated by phase space distance d .

In thermodynamic systems whose phases are unique⁷ functions of N parameters, the boundaries between phases form $N - 1$ dimensional planes in the N dimensional parameter space. Most thermodynamic systems do not contain critical points where more than $N + 1$ phases meet because there is usually no correlation between the phase boundaries in these systems. An example system with two parameters and the phases W , X , Y , and Z in shown in Fig. 3.6. If the intersection points between the phases XYZ and WYZ are uncorrelated, the distance between these points in phase space d is therefore random and unlikely to be close to zero. The phase diagram Fig. 3.5 has two types of points where four phases meet. The first type occurs when two unrelated phase boundaries intersect. The boundary between the right side of L and I corresponds to the condensation of mode $[2, 2]$, as does the boundary between F and K . Similarly the IF and LK boundaries correspond to the condensation of mode $[0, 2]$. As the location of the $[2, 2]$ boundary is almost unaffected by the condensation of mode $[0, 2]$ the boundaries intersect and form a four phase point. An example of the second type of four phase point is $ABCBEC$. At this type of phase point an additional mode condenses under increasing pump power. Which additional mode condenses depends on which reaches threshold first. The threshold condition is derived in Sec. 3.2.1 and is a smooth condition. As the thermalisation coefficient is increased along the phase boundary between the BEC and multimode phases, there exists a thermalisation coefficient where the threshold conditions for modes $[0, 1]$ and $[0, 2]$ are simultaneously satisfied, *i.e.* $f_{[0,1]} = f_{[0,1]}^{crit}$ at the same pump power as $f_{[0,2]} = f_{[0,2]}^{crit}$. Moving along the phase boundary between BEC and multimode phases results in either mode $[0, 1]$ or mode $[0, 2]$ condensing and clamping the other mode. Moving away from the phase boundary, in a specific direction, allows both modes to maintain condensation. System configurations where the condensation conditions for different modes are simultaneously satisfied get are therefore four phase points.

⁷*i.e.* there is no hysteresis or memory

3.2.1 Analytic Boundaries

This section details the derivation of the analytic boundaries between the uncondensed, BEC, and multimode phases, in addition to a decondensation boundary. These analytic boundaries are shown as white dashed lines in Fig. 3.5. This section draws heavily on Sec. 3.1, which must be understood before proceeding with this section. The uncondensed-BEC threshold will be derived first, and the method will then be generalised to calculate the other boundaries. This section assumes that uncondensed modes do not significantly contribute to the molecular excitation fraction. This holds if $\Lambda_{\uparrow}^{(m)} \ll \Gamma_{\uparrow}$ and $\Lambda_{\downarrow}^{(m)} \ll \Gamma_{\downarrow}$, as can be seen from Eqs. (2.85) and (2.86), and is the case for the considered system.

The calculation of a phase boundary involves proof by contradiction, and shall be demonstrated on the uncondensed-BEC boundary. Assume that the mode of interest is not condensed and calculate the excitation fraction as a function of increasing pump power. As no modes are condensed in the uncondensed phase the only contribution to molecular gain and loss is pumping and molecular decay

$$\begin{aligned}\Gamma_{\uparrow}^{tot}(r) &= \Gamma_{\uparrow} \\ \Gamma_{\downarrow}^{tot} &= \Gamma_{\downarrow} .\end{aligned}\tag{3.8}$$

The equation for the molecular excitation overlap Eq. (2.87), therefore reduces to

$$f_m = \frac{\Gamma_{\uparrow}}{\Gamma_{\uparrow} + \Gamma_{\downarrow}} .\tag{3.9}$$

Equating this with the critical excitation fraction for mode m to condense, Eq. (3.2), gives the pump rate required to achieve the threshold molecular excitation in the uncondensed phase

$$\frac{\Gamma_{\uparrow}^{thresh}}{\Gamma_{\downarrow}} = \frac{\bar{\rho}\Lambda_{\uparrow}^{(m)} + \kappa}{\bar{\rho}\Lambda_{\downarrow}^{(m)} - \kappa} .\tag{3.10}$$

Given the pump power derived in Eq. (3.10), and the assumption that all modes are uncondensed, mode m must condense as the molecular excitation has reached its critical value. This is a contradiction, therefore the steady state phase of the system is not uncondensed. To find which phase the system is in, the mode which condenses at the lowest pump rate is calculated using Eq. (3.10). This gives the pump rate of the uncondensed phase boundary, and the phase on the other side of the boundary: if mode $[0, 0]$ condenses at the boundary it is the BEC phase, otherwise it is the laser phase.

This procedure may be used to calculate the next phase boundary encountered as the pump rate is increased whilst the system is in the BEC phase. Eq. (3.9) is no longer valid, as the ground mode contributes to the excitation fraction in the BEC phase. Using Eqs. (2.86) and (2.87) the equation for molecular overlap f_m becomes

$$f_m = \int d^2r \frac{\Gamma_{\uparrow} + |\psi_0(r)|^2 \Lambda_{\uparrow}^{[0,0]} n_{[0,0]}}{\Gamma_{\downarrow} + \Gamma_{\uparrow} + |\psi_0(r)|^2 n_{[0,0]} (\Lambda_{\uparrow}^{[0,0]} + \Lambda_{\downarrow}^{[0,0]})} |\psi_m(r)|^2 .\tag{3.11}$$

As before, this equation may be equated with the critical excitation fractions Eq.(3.2) to find the threshold pump rate, but this requires knowledge of the population in the ground mode $n_{[0,0]}$. This population $n_{[0,0]}$ may be calculated from the knowledge that mode $[0, 0]$ is condensed, and therefore

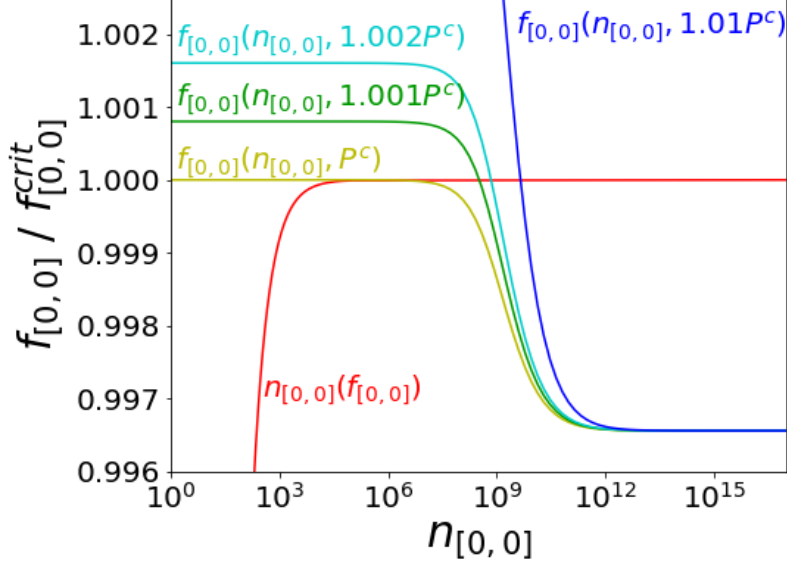


Figure 3.7: The red line is the steady state population of mode $[0, 0]$ in terms of the molecular excited fraction for mode $[0, 0]$, as given by Eq. (3.1). The other lines are the steady state molecular overlap for mode $[0, 0]$ in terms of the population of mode $[0, 0]$ as given by Eq. 3.11, for different pump powers given in terms of the critical pump power P^c . The molecular excitation axis is given in units of the critical excited fraction for mode $[0, 0]$.

$f_{[0,0]} \approx f_{[0,0]}^{crit}$. The problem with using the equality $f_{[0,0]} = f_{[0,0]}^{crit}$ to find the mode population is demonstrated in Fig. 3.7. This equality cannot be put into the equation for mode population $n_{[0,0]}(f_{[0,0]})$, Eq. (3.1), as this would produce an infinite mode population due to the high sensitivity of n_m to changes in f_m at threshold. Instead the equation for the excited fraction overlapping mode $[0, 0]$, $f_{[0,0]}(n_{[0,0]})$, Eq. (3.11), is equated with the critical value $f_{[0,0]}^{crit}$, as this equality is not sensitive to small changes in $f_{[0,0]}$. Fig. 3.7 shows that equation $n_{[0,0]}(f_{[0,0]})$ does not intersect the critical excitation at finite $n_{[0,0]}$, whereas the equation $f_{[0,0]}(n_{[0,0]}) = f_m^{crit}$, has a single well defined solution for $n_{[0,0]}$, at non-critical pump powers. The equation $f_{[0,0]} = f_{[0,0]}^{crit}$ may therefore be solved transcendently using Eq. (3.11) to find the mode population $n_{[0,0]}$ at a particular pump power. The mode population $n_{[0,0]}$ may then be used to find the molecular overlap f_m for other modes using Eq. (3.11), which may be solved analytically, this derivation is given in appendix A.1. As with the uncondensed boundary the solution of equation

$$f_m^{crit} = \int d^2r \frac{\Gamma_{\uparrow} + |\psi_0(r)|^2 \Lambda_{\uparrow}^{[0,0]} n_{[0,0]}}{\Gamma_{\downarrow} + \Gamma_{\uparrow} + |\psi_0(r)|^2 n_{[0,0]} (\Lambda_{\uparrow}^{[0,0]} + \Lambda_{\downarrow}^{[0,0]})} |\psi_m(r)|^2 \quad (3.12)$$

with the lowest pump power gives the pump power required to change phase. It also gives the additional mode which will condense in that phase.

To calculate the decondensation boundary the molecular excitation in multimode phases is required. The equation for this is

$$f_m = \int d^2r |\psi_m(r)|^2 \frac{\Gamma_{\uparrow}(r) + \sum_{p \in C} |\psi_p(r)|^2 \Lambda_{\uparrow}^{(p)} n_p}{\Gamma_{\uparrow}(r) + \Gamma_{\downarrow} + \sum_{p \in C} |\psi_p(r)|^2 (\Lambda_{\uparrow}^{(p)} + \Lambda_{\downarrow}^{(p)}) n_p} \quad (3.13)$$

where p is summed over all condensed modes. In general this cannot be solved analytically, however it may be numerically integrated and used to calculate phase boundaries as previously demonstrated. The population in each condensed mode may be found by requiring that $f_m = f_m^{crit}$ for each condensed mode. The decondensation boundaries may be calculated in two ways. The first method is to start in the decondensed phase e.g. phase B in Fig. 3.5, and reduce the pump power until the excitation fraction for the decondensed mode reaches critical value. This method is identical to the method for condensing modes except that the pump rate is reduced instead of increased. The second calculation method is to start in the multimode phase before decondensation e.g. phase C in Fig. 3.5. The pump power is increased until a solution to the threshold condition $f_m = f_m^{crit}$ cannot be found by varying the condensed populations n_p , for one of the modes. This mode will then decondense.

The entire phase diagram shown in Fig. 3.5 could be constructed using the methods described in this section as follows:

1. Start in the uncondensed phase with no condensed modes. The molecular excitation is given by Eq. (3.9).
2. Find the mode which condenses at the lowest pump power, set the pump power to this phase boundary.
3. Use the condition that $f_m = f_m^{crit}$ for condensed modes to find the population in each condensed mode, using Eq. (3.13).
4. Increase the pump power until the molecular overlap for an uncondensed mode reaches threshold, or until a solution for the condensed mode population cannot be found.
5. Add/remove the relevant mode to/from the list of condensed modes
6. Repeat from point 3.

The analytic phase boundaries shown in Fig. 3.5 did not use this full procedure as the locations of the phase boundaries were already known. The high degree of agreement between the analytic phase boundaries and the simulated steady state shows that the multimode phase changes are caused by molecular clamping.

3.3 Other Phase Diagrams

The technique used to create the phase diagram Fig. 3.5 may be used to generate phase diagrams of other system parameters. Due to the large number of system parameters and potential phase diagrams it is impractical to investigate each phase diagram to the same degree as Fig. 3.5. This section therefore presents a series of medium resolution phase diagrams created from systems with fewer modes, causing fewer multimode phases to be observed.

The first phase diagram is Fig. 3.8, and plots the phase against pump width and pump rate. As the pump width increases the uncondensed-BEC threshold pump rate increases. This is because the

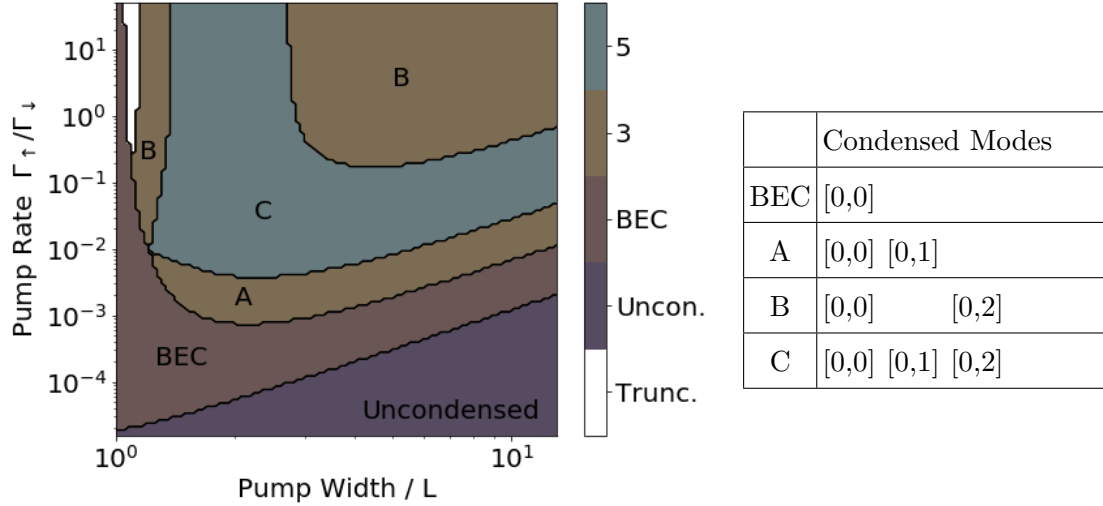


Figure 3.8: (LEFT) The phase of the system as pump rate and pump width are varied. Each colour corresponds to a number of condensed modes, as in Fig. 3.5. Pump width is given in units of harmonic oscillator length L . Pump rate is given in units of molecular decay $\Gamma_{\downarrow}$. (RIGHT) The modes which are condensed in each section of the phase diagram (and the corresponding modes: $[q, p]$ indicates that modes $[q, p]$ and $[p, q]$ are condensed).

ground mode is narrow, and the fraction of pump excitations which thermalise to the ground mode before being lost decreases as pump width increases. This also explains the other upwards trends in pump rate seen on the right side of Fig. 3.8. If the pump width is decreased below twice the harmonic oscillator length L , the threshold between the BEC and multimode phases increases. This is because a majority of the pump is directed into the spatial region clamped by the ground state. The unclamped molecules mode $[0, 1]$ uses to condense are therefore less excited and mode $[0, 1]$ requires a larger pump rate to condense. As the threshold pump rate increases, the width of the spatial region clamped by the ground mode increases. Mode $[0, 1]$ is narrower than mode $[0, 2]$, and is affected more by the expansion of the clamped region. If the pump width is decreased sufficiently then mode $[0, 2]$ condenses at a lower pump rate than mode $[0, 1]$. The pump width where modes $[0, 1]$ and $[0, 2]$ have the same threshold pump power is the intersection of the BEC, A, B, and C phases in Fig. 3.8. As explained in Sec. 3.1 the decondensation of mode $[0, 1]$ is due to the combined clamping of molecules by modes $[0, 0]$ and $[0, 2]$. Fig. 3.8 shows two cases of decondensation, at low and high pump widths. Both cases require clamping by modes $[0, 0]$ and $[0, 2]$, however in the high pump width case, the clamping of mode $[0, 2]$ is more significant than mode $[0, 0]$ and visa versa. At intermediate pump widths there is no decondensation because the pump width is large enough that the ground mode is not clamping all the excited molecules. Simultaneously the pump width is small enough that mode $[0, 2]$ does not receive enough population to clamp mode $[0, 1]$ and cause it to decondense. This again shows that decondensation only occurs in a restricted parameter space, and is therefore difficult to find.

Fig. 3.9 shows the phase of the system as pump rate and mode spacing are varied. As the frequency of the ground mode is constant, the threshold between the uncondensed and BEC phases is constant with respect to mode spacing. The threshold pump power increases as the mode spacing increases

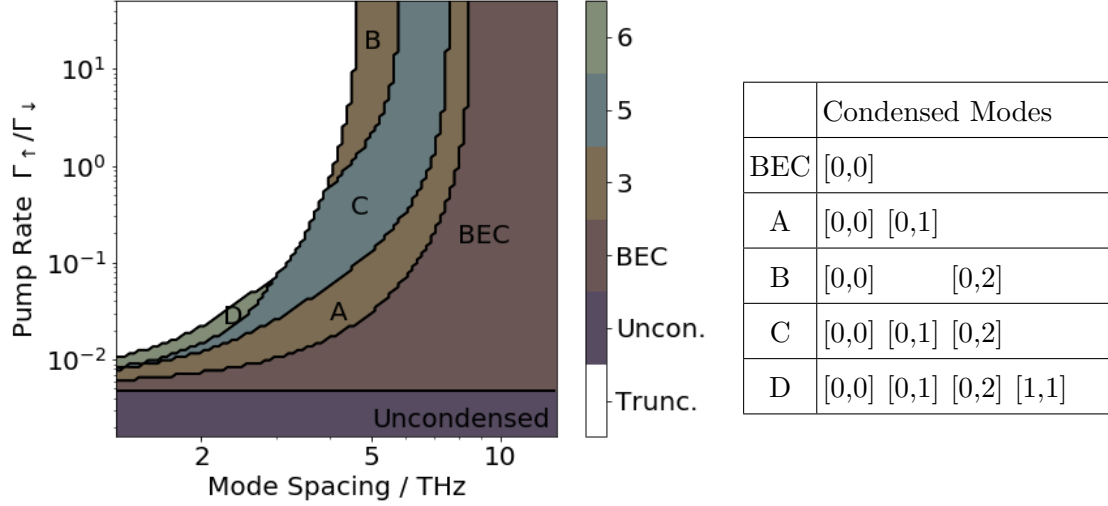


Figure 3.9: (LEFT) The phase of the system as pump rate and mode spacing are varied. Each colour corresponds to a number of condensed modes, as in Fig. 3.5. Pump rate is given in units of molecular decay $\Gamma_{\downarrow}$. (RIGHT) The modes which are condensed in each section of the phase diagram (and the corresponding modes: $[q, p]$ indicates that modes $[q, p]$ and $[p, q]$ are condensed).

which may be explained as follows. For the system parameters used, given in Tab. 3.1, the cavity loss rate κ is smaller than the absorption rate $\Lambda_{\uparrow}^{(m)}\bar{\rho}$ for all modes. The critical molecular excitation overlap f_m^{crit} , Eq. (3.2) may therefore be approximated as

$$f_m^{crit} = \frac{1}{\frac{\Lambda_{\downarrow}^{(m)}}{\Lambda_{\uparrow}^{(m)}} + 1} . \quad (3.14)$$

As the mode spacing increases the ratio of absorption $\Lambda_{\uparrow}^{(m)}$ to emission $\Lambda_{\downarrow}^{(m)}$ increases, which increases the critical excitation required for the condensation of the higher modes. As higher pump rates are required to create higher molecular excitation, increasing the mode spacing increases all of the multimode threshold pump rates. Decreasing the mode spacing reduces the critical excitation of mode $[0, 1]$ to below the value mode $[0, 2]$ is clamping the excitation to, and thereby prevents its decondensation. At very large mode spacings the ground state clamps the molecular excitation to values below the critical excitations of all modes, at all pump powers. An intuitive investigation of this phenomena is given in Sec. 4.3.

3.4 Outlook

The phase of the system has only been studied in detail as the thermalisation coefficient and pump rate are varied. There are many other system parameters which could affect the multimode phase and promote or suppress decondensation, for example: spatial pump profile, molecular decay, and mode profiles. Investigating how the phase diagram Fig. 3.5 changes as these system parameters are

varied could find an enhancement or suppression of decondensation. The decondensation mechanism presented here requires inhomogeneous coupling between a reservoir of excitations and multiple modes. This is an uncommon setup, for example polariton condensates do not have a reservoir of molecules and thermalise via collisions. It remains to be seen whether similar decondensation processes can occur in systems with different configurations. In order to experimentally create the phases in the high pump rate region of the phase diagram 3.5, powerful lasers are required. Current experiments currently do not use CW lasers with these powers. This could be circumvented by using pulsed lasers which easily reach powers three orders of magnitude larger than CW lasers, however the system would not reach steady state during the pulse duration. The temporal dynamics required to analyse the effects of pulsed pumping and identify phenomena similar to decondensation are discussed in the next chapter.

Chapter 4

Temporal Dynamics and a Rotated Basis

The previous chapter analysed the steady state of photonic condensates and demonstrated strong interactions between modes which may cause the decondensation of modes. This chapter analyses the evolution of the system to steady state, and shows the effects of strong interactions on the dynamics of photonic condensates. The evolution of mode population towards steady state is non-monotonic and exhibits numerous interesting features. It is well established that systems with parameters which are close to the parameters required for a phase transition experience an increase in the time taken to reach equilibrium, tending to infinite time at the phase boundary [116, 117, 20]. This has been observed in many systems from Josephson junction arrays in optical lattices [118], Kagome spin ices of interacting nano-magnets [119], and species extinction models [120]. This analysis chapter predicts critical slowing close to the phase boundaries of photonic condensates. Interestingly it also predicts dramatic slowing of equilibration far away from phase transitions which, to the author's knowledge, has not been predicted in any other system.

The steady state of the system may be obtained without directly simulating the molecular excitation, which may be instantaneously calculated using Eq. (2.81). This simplification may not be applied to the simulation of the system dynamics as the steady state assumption used to derive Eq. (2.81) is not valid. To simulate the system dynamics with 100% accuracy the molecular excitation at each spatial position¹ must be known at each point in time, in order to perform the integral in Eq. (2.81). As this requires storing an infinite number of molecular excitations, this is impossible. The molecules must instead be grouped into a finite number of spatial bins, and the integral approximated as a sum. This transforms the rate equation for the population n_m in mode m , Eq. (2.83) into

$$\dot{n}_m = -\kappa n_m + (n_m + 1)\Lambda_{\downarrow}^{(m)} \sum_j g_{m,j} M_j f_j - n_m \Lambda_{\uparrow}^{(m)} \sum_j g_{m,j} M_j (1 - f_j) , \quad (4.1)$$

where f_j is the fraction of molecules in bin j which are excited, M_j is the number of molecules in bin j , and $g_{m,j}$ is the average coupling between mode i and the molecules in bin j . As the coupling

¹Simulating the position of each molecule would also work but also requires an exceptionally large amount of computational storage.

between the molecules in a bin and a particular mode is approximated as constant across the bin, the excitation of each molecule within the bin has the same rate equation

$$\dot{f}_j = P(1 - f_j) - f_j \Gamma_\downarrow - f_j \sum_i g_{m,j} \Lambda_{\downarrow}^{(m)} (n_m + 1) + (1 - f_j) \sum_i g_{m,j} \Lambda_{\uparrow}^{(m)} n_m , \quad (4.2)$$

where P is the homogeneous pump rate². As the density of bins tends to infinity, the accuracy of the simulation approaches 100%. The choice of the number of bins is therefore a trade-off between computational difficulty and accuracy.

This chapter shall introduce a transformation of the rate equations Eqs. (4.1) and (4.2), which greatly reduces the system size, and thereby increases the computational speed. This permits the study of equilibration time and non-critical slowing down. The remainder of the chapter exploits the transformed system to generate new insights about photonic condensates.

4.1 Molecular Ordering

When studying photonic condensates, the quantities of interest are usually derived from the mode populations, and the molecular excitations are required only to derive the mode populations. To improve the simulation efficiency, therefore, the molecular information most relevant to the evolution of mode population is kept and the rest is discarded. This information is a collective excitation of molecules. Each collective excitation has a profile which describes the excitation or de-excitation³ molecules as the collective gains excitation. In mathematical terms the molecular excitation vector $\underline{f}$ in Eq. (4.1) may be written as the weighted sum of normalised vectors $\underline{v}_k$: $\underline{f} = \sum_k \underline{v}_k c_k$ where $\underline{v}_k$ is the collective excitation profile and c_k is the collective excitation. This requires representing the molecular excitation in different bases, therefore bracket notation is used. In Eqs. (4.1) and (4.2) the molecular excitation $|f\rangle$ is represented as a vector f_j where each element of the vector corresponds to a spatial position $|j\rangle$.

! The molecular excitation vector may be described using a variety of bases which shall be denoted using bracket notation. The basis-vectors corresponding to each spatial bin shall be denoted by a ket containing a single index $|j\rangle$ or $|k\rangle$. The alternative representation consists of multiple orders, denoted by the letters p , or q , and the vectors within each order are denoted by the letters l , or h . A ket in the ordered representation therefore reads $|p, l\rangle$ or $|q, h\rangle$. The basis vector describing cavity mode m shall be denoted by the ket $|\gamma_m\rangle$.

Using bracket notation the rate equation for mode population may be written compactly as

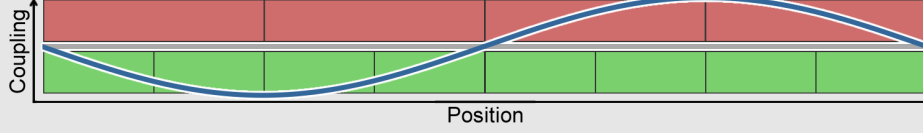
$$\dot{n}_m = C_m n_m + (n_m (\Lambda_{\uparrow}^{(m)} + \Lambda_{\downarrow}^{(m)}) + \Lambda_{\downarrow}^{(m)}) \langle \gamma_m | G_m | f \rangle , \quad (4.3)$$

²To use an inhomogeneous pump, promote P to a vector P_j , and ensure that the pump rate is approximately constant across each molecular bin.

³Profiles may have negative elements describing the transfer of excitation from one set of molecules to another.

Box 4.1: Spatial Molecular Sampling

The coupling of each molecule in a bin to every mode must be approximately identical in order to model the bin as a single entity, and the bins must be made as large as possible to decrease computational costs. Sampling four bins per oscillation of a mode wavefunction results in a large variation of coupling across each bin, as shown below by the red boxes.



A sampling of 8 bins per oscillation (the next highest power of two) is shown in green, and is a lower bound on the spatial molecular sampling. A system with 4 levels (10 modes) requires 39 bins in each spatial dimension to fully sample the highest modes. This gives 1521 bins in total.

where $C_m = -\kappa - \Lambda_{\uparrow}^{(m)} \sum_j g_{m,j} m_j$, and $\langle \gamma_m | G_m | j \rangle = g_{m,j} m_j$. Inserting the identity (the sum over all spatial basis vectors $\mathbb{1} = \sum_j |j\rangle \langle j|$) between G_m and $|f\rangle$, and identifying the vector elements f_j as $\langle j|f\rangle$ recovers the form of Eq. (4.1).

A basis of molecular excitation must now be constructed which encapsulates the coupling to the cavity modes, allowing the complement to the basis to be discarded. In most cases the N_c cavity modes have continuous profiles, and therefore the number of molecular bins N_m is much greater than the number of cavity modes $N_c \gg N_m$; in the system modelled in this chapter $N_m = 1521$ and $N_c = 10$, see Box 4.1. The operator G has rank N_m and, by the rank-nullity theorem, has $N_m - N_c$ null-vectors⁴. There are therefore only N_c vectors $|0, k\rangle$ for which $G|0, k\rangle \neq 0$, which shall comprise order 0. Only the projection of the molecular excitation onto these vectors affects the mode populations, and the vectors may be chosen so that $G_m|0, l\rangle = \delta_{m,l} W_m |\gamma_m\rangle$, where W_m is a constant, providing further simplification⁵. The remaining $N_m - N_c$ vectors $|p>0, k\rangle$, for which $G|p>0, k\rangle = 0$, shall be sorted into higher orders later in this derivation.

Inserting the identity between G_m and $|f\rangle$ (see Box. 4.2) transforms Eq. (4.3) to

$$\dot{n}_m = C_m n_m + (n_m (\Lambda_{\uparrow}^{(m)} + \Lambda_{\downarrow}^{(m)}) + \Lambda_{\downarrow}^{(m)}) W_m \langle 0, m | f \rangle . \quad (4.4)$$

The rate equation for mode population has therefore been reduced from one containing N_m molecular degrees of freedom, to one containing N_c . In order to computationally implement this reduction and increase computational efficiency, rate equations for the zeroth order molecular excitation profile $\langle 0, m | f \rangle$ must be obtained. These may be derived by applying the bra $\langle 0, m |$ to the bracket form of

⁴This may be seen from the singular value decomposition of $\langle \gamma_m | G | j \rangle$ which is $UDV^\dagger$. As the non-square diagonal matrix D contains only N_c non-zero columns, only N_c columns of V produce a non-zero result when multiplied by G_i

⁵This choice of definition results in non-orthogonal vectors in the zeroth order.

Box 4.2: Zeroth-Order identity

The identity which must be inserted into Eq.(4.3) in order to simplify it is non-trivial. As, by construction, the vectors in different orders are orthogonal, the identity may be constructed from the tensor product of the identities of each order $I = I_0 \otimes I_1 \otimes \dots$. Vectors in orders above zero are orthonormal and therefore the construction of the identity $I_{p>0}$ is trivially $\sum_l |p, l\rangle \langle p, l|$. As the zeroth-order vectors are not orthogonal, the operator $\sum_l |0, l\rangle \langle 0, l|$ is not the zeroth-order identity. Instead a different identity is constructed for each mode: for mode m the vector $|0, m\rangle$ is taken as the first vector in an orthonormal basis, and the other orthonormal basis vectors are constructed from superpositions of the remaining zeroth-order vectors $|0, l \neq m\rangle$. The zeroth-order identity which must be inserted into Eq.(4.3) is $|0, m\rangle \langle 0, m| + \sum_{l \neq m, h \neq m} Q_{l,h}^{(m)} |0, l\rangle \langle 0, h|$. As the operator G_m destroys any vector which is not $|0, m\rangle$ the exact form of the matrix $Q^{(m)}$ is irrelevant.

Eq. (4.2)

$$\langle 0, m | \dot{f} \rangle = \langle 0, m | D(n) \sum_j |j\rangle + \langle 0, m | E | f \rangle + \sum_m n_m \langle 0, m | B_m | f \rangle , \quad (4.5)$$

In terms of the operators

$$\begin{aligned} D(n) &= P \mathbb{1} + \sum_{m,j} g_{m,j} \Lambda_{\uparrow}^{(m)} n_m |j\rangle \langle j| \\ E &= -P \mathbb{1} - \sum_{m,j} g_{m,j} \Lambda_{\downarrow}^{(m)} |j\rangle \langle j| \\ B_m &= - \sum_j g_{m,j} (\Lambda_{\downarrow}^{(m)} + \Lambda_{\uparrow}^{(m)}) |j\rangle \langle j| . \end{aligned} \quad (4.6)$$

The operators D , E , and B couple vectors in the zeroth order to vectors in higher orders, i.e. $\langle 0, m | B_m | p > 0, m \rangle \neq 0$. Therefore the higher orders cannot currently be discarded without impacting the evolution of the system. Instead the remaining excitation profiles are arranged into a hierarchical ordering of excitation profiles. The evolution of the excitation of profiles in a given order is dependent only on the excitation profiles in or below the next highest order, i.e. $\langle q, m | B_m | p, m \rangle = 0$ for $p > q + 1$. By this construction excitations in high orders affect the mode populations indirectly and may therefore be discarded without greatly affecting the simulation accuracy.

Formally, the excitation profiles in orders $p > 0$ may be defined as all degrees of freedom which couple to order $p - 1$, and are orthogonal to each other and all vectors in orders less than p ; i.e. all the vectors $|p, l\rangle$ such that $\langle p - 1, h | B_m | p, l \rangle \neq 0$ for at least one mode m , and $\langle p, l | q, h \rangle = \delta_{p,q} \delta_{l,h}$ for p or q greater than zero. If the mode populations were known and constant then only one condition would be required:

$$\langle p - 1, h | D + E + \sum_m n_m B_m | p, l \rangle \neq 0.$$

As this is not the case then the operators B must be treated independently. A potential collective excitation is therefore only excluded from the next order if it does not couple to the current order for any mode population. The operator E is composed of the identity, which does not couple different

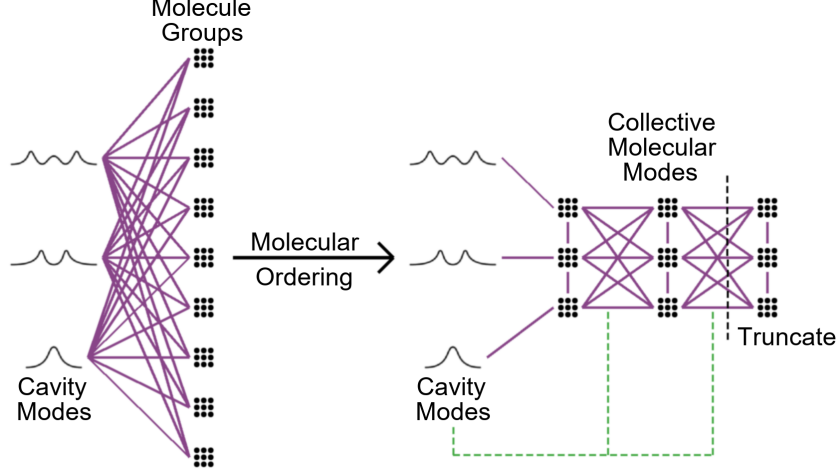


Figure 4.1: Diagram depicting the coupling between the cavity modes and the molecules grouped into spatial bins (LEFT), and between the cavity modes and the collective molecular modes (RIGHT). Each box of black dots represents a group of molecules, or a collective mode. The each column of collective modes represents an order. Purple lines indicate coupling between the connected objects, green dashed lines indicates that the cavity mode population affects the strength of the inter-molecule coupling.

collective excitations, and a weighted sum of operators B . The operator E may therefore be excluded from the ordering process as any coupling it induces is already covered by the operators B .

There is a further restriction on the coupling between orders caused by the Hermiticity of the system. By construction a vector in order p does not couple to orders less than $p - 1$, otherwise it would have been included in order $p - 1$; i.e. $\langle p - k, h | B_m | p, l \rangle = 0$ for $k > 1$. As the operator B_m is hermitian, this restriction may be reversed: $\langle p, h | B_m | p - k, l \rangle = 0$ for $k > 1$, therefore each order only couples to adjacent orders and itself. The structure of the coupling between cavity modes and ordered collective molecular modes is shown on the right of Fig. 4.1. The additional constraint allows an easier construction of each order: instead of finding all vectors which couple to the highest order, which scales with the number of molecular bins, the vectors which the highest order couples to may be identified, a much easier task. These vectors may then be orthonormalised and any linearly dependent vectors removed⁶.

The rate equation for the excitation in collective excitation profile l in order p may be written as

$$\langle p, l | \dot{f} \rangle = \langle p, l | D(n) \sum_j | j \rangle + \sum_{q=p-1}^{p+1} \sum_h \left[\langle p, l | E | q, h \rangle + \sum_m n_m \langle p, l | B_m | q, h \rangle \right] \langle q, h | f \rangle . \quad (4.7)$$

None of the elements in Eq. (4.7) has a size equal to the number of molecular bins N_m . The excitations of the profiles in order p may be stored as a vector $\hat{f}^{(p)}$, where $(\hat{f}^{(p)})_l = \langle p, l | f \rangle$, the length of which is equal to the number of profiles in order p . Similarly the matrices $\langle p, l | E | q, h \rangle$ and $\langle p, l | B_m | q, h \rangle$ have dimensions equal to the number of profiles in orders p and q . The goal of reducing the system size

⁶Due to the relative similarity of the cavity modes there can be many dependent modes to the extent that the number of profiles in each order is approximately constant

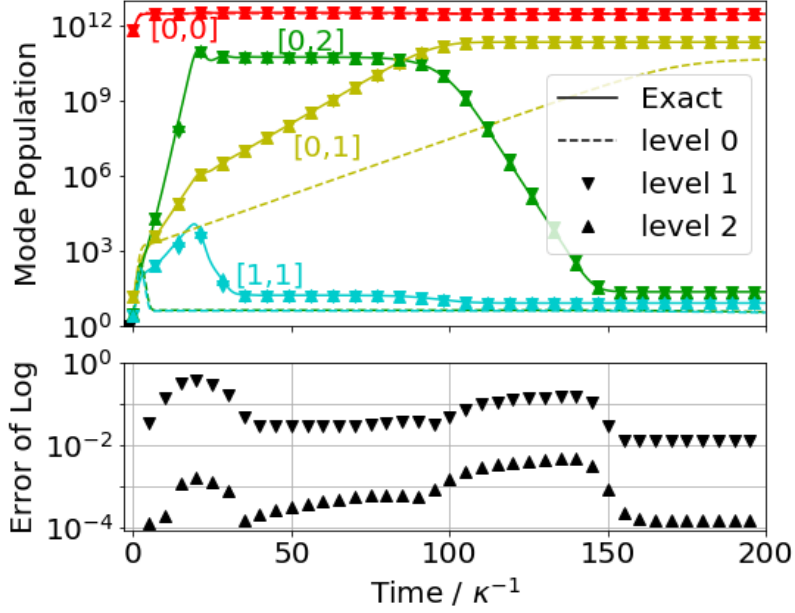


Figure 4.2: (TOP) The mode populations as a function of time for a variety of truncations. ‘Level x ’ corresponds to the truncation of all orders above x . The ‘Exact’ simulation uses the un-truncated spatial molecular basis, i.e. Eqs. (4.1) and (4.2). The label $[x, y]$ indicates the 2D harmonic oscillator quantum numbers for that mode (and also mode $[y, x]$). (BOTTOM) The error of the level 1 and level 2 approximations measured against the exact simulation. The error is defined as $E = \max_i \left[\log_{10} \left(n_i^{(x)} \right) - \log_{10} \left(n_i^{(e)} \right) \right]$ where $n_i^{(x)}$ is the population in mode i predicted by the truncated simulation and $n_i^{(e)}$ is the population predicted by the exact simulation. The system parameters used are: the lowest mode wavelength is $585nm$, the maximum absorption and emission is $1e - 9\kappa$, $M_j = 10^{12}$, $\Gamma_{\downarrow} = 1/4$.

has therefore been achieved. The rate of change of mode population depends only on the zeroth order excitation profiles, which in turn depend only on the first order etc. If the hierarchy is truncated then the number of excitation profiles which must be simulated is considerably smaller than the number of molecular bins.

4.1.1 Accuracy

The truncation of the hierarchy of collective excitation profiles reduces the accuracy of the simulation. This reduction in accuracy must be balanced against the increase in simulation speed. Fig. 4.2 shows the evolution of mode populations over time as predicted by simulations which truncate the molecular orders after order 0, 1, and 2, and also an exact simulation produced using Eqs. (4.1) and (4.2). The system starts in the steady state with a pump of $6.58 \times 10^{-6}\kappa$ and is quenched to a pump power of $2 \times 10^{-5}\kappa$ at time 0. The ground mode quickly re-equilibrates due to the small change in steady state population. Modes $[0, 1]$ and $[0, 2]$ both initially condense, with mode $[0, 2]$ achieving condensation earlier because the ground mode clamps of mode $[0, 1]$ much more than it clamps mode $[0, 2]$. When mode $[0, 1]$ condenses it clamps mode $[0, 2]$ causing it to decondense.

Unsurprisingly the level 0 approximation produces a sizeable deviation from the exact solution. A good approximation of the numerically exact solution is, however, achievable with only the zeroth and first orders of excitation profiles. The bottom of Fig. 4.2 shows that the level 1 approximation typically has an error (defined in the caption) less than $1/10$. This error can increase, to a maximum of 0.44, which is indicative more of a slight error in the timing of the transition to condensation, rather than an error in the mode population. An error in the timing of an event is far better than an error in the event itself, as most predictions about a system (e.g. the pattern of modes condensing) are unaffected by small scalings in time. Additionally the random nature of spontaneous emission causes uncertainty in the experimental timing of condensation, so precise predictions of individual condensation times are impossible, and only ensemble averages may be predicted. The level two approximation has an error approximately two orders of magnitude smaller than level one, and the level three approximation (not shown) has an error two orders of magnitude below that.

Fig. 4.2 is a typical example of how each approximation level performs. A small number of poor simulations show worse performance: the level 0 approximation may fail to achieve the correct steady state phase, and the level 1 approximation may display substantially different equilibration times compared to the exact simulation. These poor cases appear near phase boundaries and may be attributed to the truncation inducing a small shift in the steady state phase boundary, and are therefore not a fundamental error of the simulation. Instead the level 1 simulations may be interpreted as giving quantitatively correct results in a majority of cases, and qualitatively correct results in the remaining cases. Level 1 is therefore appropriate for studying the general causes of phenomena and identifying broad patterns, but may be unreliable when precise values of time or system parameters are required.

4.1.2 Runtime

The benefits of decreased accuracy are, of course, decreased runtime (i.e. the real time taken for a single core to perform the necessary calculations). A histogram of relative runtime is shown in Fig. 4.3, for a variety of quenches between pump powers. The test simulations were taken from a 33×33 log-uniform⁷ grid of the points shown in Fig. 4.6. This corresponds to both initial and final pump powers ranging from $10^{-3.5}\kappa$ to 10κ . The computational time taken to reach steady state was measured at each grid point, for each level of approximation, and compared to the computational time required for a numerically exact simulation. The system chosen requires 1521 spatial molecular bins but has only 10 excitation profiles in the zeroth order. When the 10 cavity modes are included this constitutes a reduction in computational system size⁸ to 1.3%, it is therefore unsurprising that the zeroth order simulation is almost two orders of magnitude faster than an exact simulation. The level 1 and level 2 simulations provide an accurate representation of the system in less than $1/10$ of the computational time, and even the highly accurate level 3 approximation is still faster than the numerically exact solution. Note that due to the linear dependence of many collective excitation profiles, the number of profiles in each order does not scale exponentially. For this system the number of profiles in orders zero to three is: 10, 27, 42, 31 respectively. The scaling of computational time is therefore far more

⁷The logarithms of the pump powers are uniformly spaced

⁸The size of the array required to store the state of the system

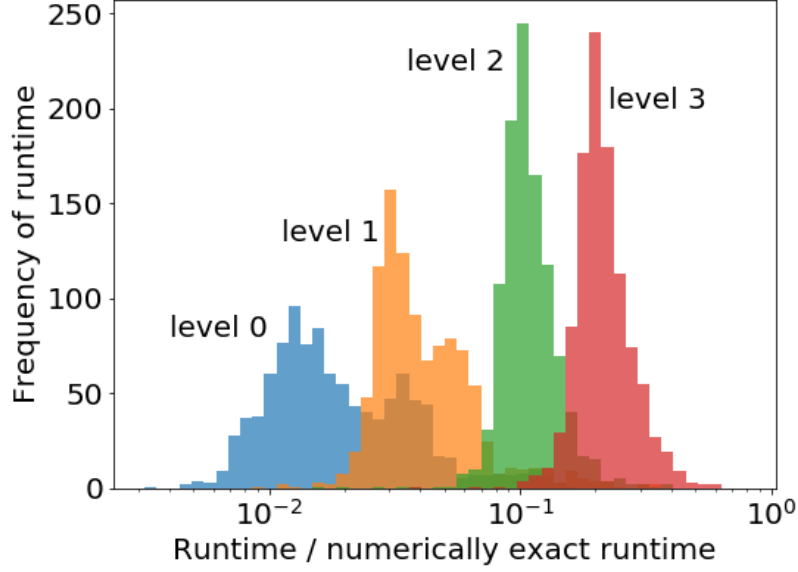


Figure 4.3: The frequency of runtime for approximation level x relative to the runtime of an numerically exact simulation.

favourable than would be expected for an exponentially increasing order size. Exponential scaling of order size is not expected for other cavity shapes which also exhibit smooth overlapping modes, as these will also produce many dependent excitation profiles. More exotic cavities have not been investigated.

4.2 Equilibration Time

A large portion of this thesis is dedicated to the steady state of photonic condensates. To experimentally use this information steady state must be reached, which motivates the study of system dynamics over time. Experiments which pump the system with a short pulse and observing the subsequent evolution will also benefit from a theoretical model of the system dynamics. This section shows that the equilibration time varies by many orders of magnitude and shows critical slowing close to thresholds. The system also exhibits a kind of non-critical slowing which, to the knowledge of the author, has not been observed or predicted in any other system.

Identifying slow processes requires a measure of either the rate of the process or it's duration, which poses a small problem. The system dynamics, as described by Eqs. (4.1) and (4.2), are coupled and non-linear, and therefore cause a variety of dynamical behaviours. In particular most behaviours are not described by exponential decay, and it is therefore very difficult for a single algorithm to assign a rate of decay to an arbitrary system evolution. Even fitting an exponential to the mode populations in the final section of a system evolution is not guaranteed to produce an accurate and reliable measure, and additionally discards any evolution not in this final section. Exponential fits to system decays are therefore only used as an approximate or illustrative measure. For the purposes of this section, a

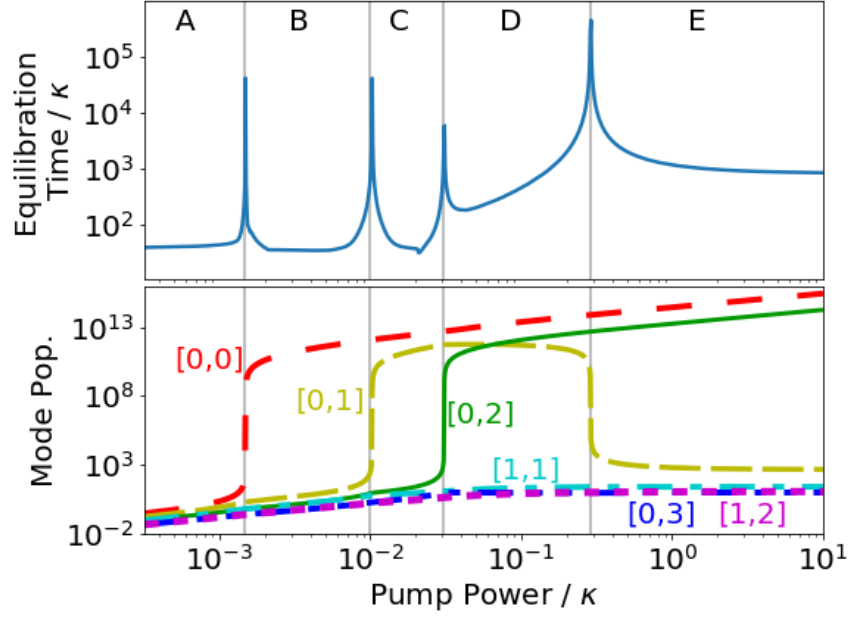


Figure 4.4: (TOP) The time taken for the system to reach equilibrium after a 1% quench in pump power, as a function of final pump power. (BOTTOM) The steady state mode population after the quench. The system parameters used are identical to those given in the caption of Fig. 4.2.

better measure of the equilibration rate is the time⁹ taken for the system to decay to within 10^{-6} of the steady state. Formally this condition is expressed as

$$\left| \frac{n_i - n_i^{(s)}}{n_i^{(s)}} \right| < 10^{-6} , \forall i , \quad (4.8)$$

where n_i is the population in mode i , and $n_i^{(s)}$ is the steady state mode population at infinite time. Provided that the system evolution results in a relative change in mode population much greater than 10^{-6} then this is an accurate measure for any system evolution. It is biased towards the slowest portion of the system evolution, however this is acceptable as this section examines critical and non-critical slowing down.

To identify systems with slow equilibration a system at steady state is perturbed by a 1% change in pump power. Fig. 4.4 (TOP) shows the time taken to reach steady state after the pump power quench. Fig. 4.4 (BOTTOM) shows the steady state population in each mode after the quench. The top plot shows clear peaks in equilibration time at phase boundaries, as predicted by prior work on critical slowing. In regions ‘A’, ‘B’, and ‘C’ the non-critical equilibration time is approximately 10κ which may be explained as follows. Due to the joint evolution of the coupled mode population and molecular excitation, the decay of mode population is not always exponential. It is however instructive to define an exponential rate of decay

$$E_m = \frac{dn_m}{dt} \frac{1}{n_m - n_m^{(s)}} , \quad (4.9)$$

⁹Simulated system time, not the time taken for the simulation to run, as in previous sections.

where $n_m^{(s)}$ is the steady state population in mode m . This definition is chosen because, if the exponential rate is constant in time, then the population decays exponentially to the steady state: $n_m = n_m^{(s)} + Ae^{E_mt}$ where A is a constant. It is useful to split the exponential rate into an approximately constant, relative rate of population change

$$\frac{\dot{n}_m}{n_m} = R_m = -\kappa - \left(\sum_j g_{m,j} M_j - W_m f_m \right) \Lambda_{\uparrow}^{(m)} + W_m f_m \Lambda_{\downarrow}^{(m)} \left(1 + \frac{1}{n_m} \right), \quad (4.10)$$

and the relative change in mode population $(n_m - n_m^{(s)})/n_m$, to give

$$E_m = R_m \frac{n_m}{n_m - n_m^{(s)}}. \quad (4.11)$$

To approximate the equilibration time for the considered system the $W_m f_m \Lambda_{\uparrow}^{(m)}$ term may be removed from the relative rate, as the molecular excitation fraction overlap f_m is small¹⁰. Furthermore the system is tuned so that interesting multimode condensation occurs and, as discussed in Chapter 3, this requires the cavity loss rate κ to be approximately equal to the absorption rate $g_{i,j} M_j \Lambda_{\uparrow}^{(m)}$. Finally the steady state value of excitation overlap $f_m^{(s)}$ exactly cancels the other relative rate terms. This allows the relative rate to be approximated as

$$R_m \approx 2\kappa \frac{f_m - f_m^{(s)}}{f_m^{(s)}}. \quad (4.12)$$

As the fractional change in molecular excitation after a quench in pump power is approximately constant, the change in relative rate after the quench is also approximately constant. Fig. 4.5 shows the population in mode $[0,0]$, the excitation of molecular profile $[0,0]$, and the exponential rate of mode $[0,0]$ over time after a 1% quench in pump power. Away from threshold the change in relative overlap is approximately 1%. After the quench the relative rate decays with a rate ζ

$$R_m(t) = R_m(0)e^{-\zeta t}.$$

Away from threshold the quench causes a change in the steady state of the mode population of approximately 2%. As the molecular excitation evolution is faster than the mode population evolution, their decay rates are approximately equal, and the mode population therefore decays as

$$\frac{(n_m - n_m^{(s)})}{n_m} = e^{-\zeta t}.$$

The identical decay rates cancel when calculating the exponential rate Eq. (4.11), which may therefore be approximated as constant in time. In the BEC and uncondensed regimes the exponential rate is approximately $2\kappa(1\%)/(2\%) = \kappa$. This approximately matches the values plotted in Fig 4.5. The time taken for the mode population to decay from a relative value of 2% to the arbitrary threshold of 10^{-6} with an exponential rate of κ is approximately 10κ . This explains the low equilibration times away from threshold in regions ‘A’, ‘B’, and ‘C’ in Fig 4.4.

Explaining the longer equilibrations seen in Fig 4.4 requires the approximations previously made to be dropped, and the exact exponential rates, shown in Fig. 4.5, to be studied. In the uncondensed regime

¹⁰This approximation is easier to see in Eq. (4.1) which contains a $1 - f$ term.

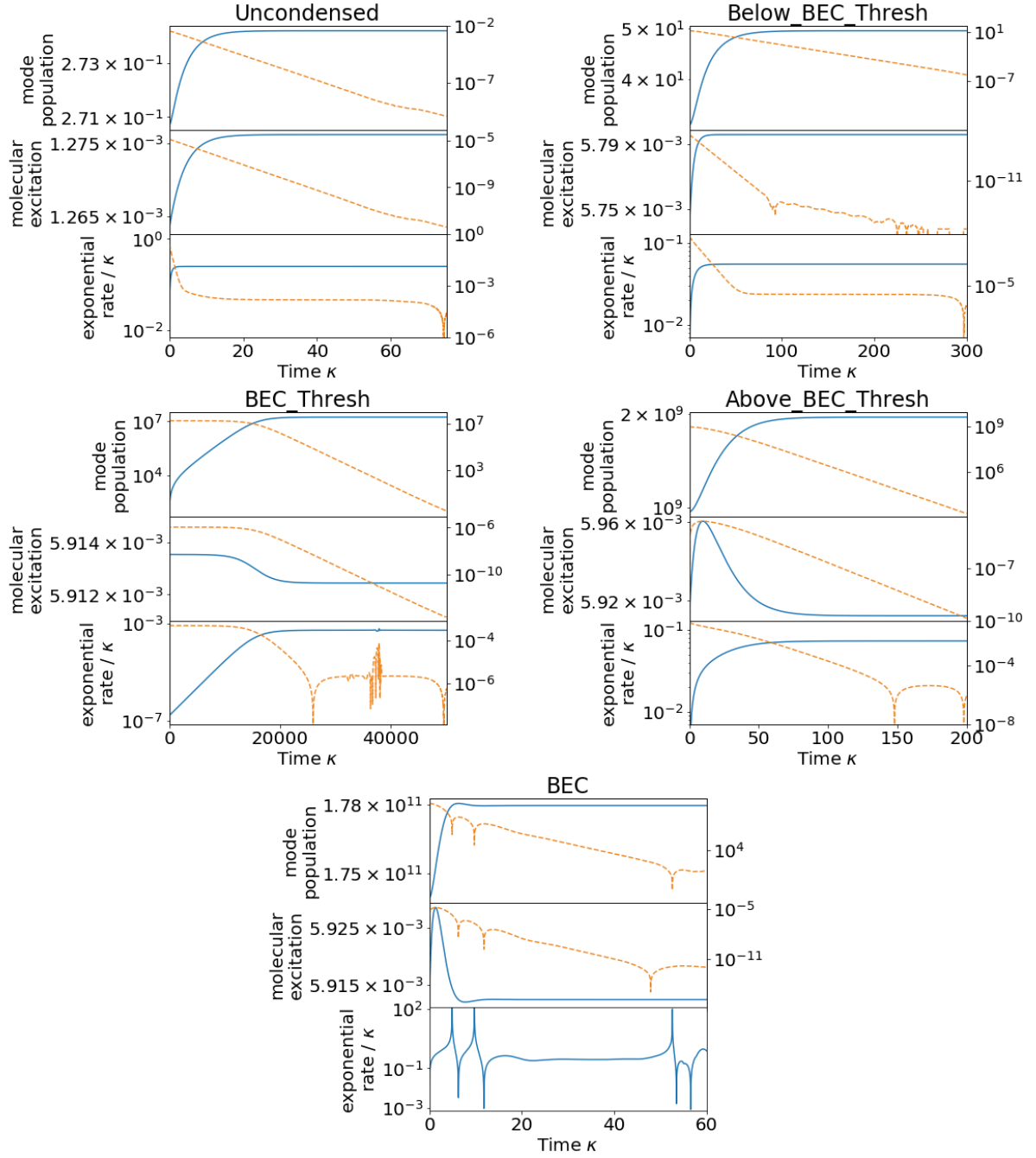


Figure 4.5: Five pump powers were chosen to characterise the system evolution from: the uncondensed region ‘A’ (a pump rate of $3.19 \times 10^{-4}\kappa$), just below the BEC threshold ($1.46 \times 10^{-3}\kappa$), at threshold ($1.49 \times 10^{-3}\kappa$), just above threshold ($1.52 \times 10^{-3}\kappa$), and far above threshold in the BEC region ‘B’ ($3.27 \times 10^{-3}\kappa$). In solid blue is plotted the population in mode $[0, 0]$ over time after a 1% quench in pump power, the excitation of the molecular profile corresponding to mode $[0, 0]$, and the exponential rate of decay of mode $[0, 0]$ (Eq. (4.9)). In dashed orange is plotted the difference between each property and it’s steady state value. As the exponential rate is theoretically zero at steady state the value of the exponential rate at the right edge of the plot is used instead. The *magnitude* of each property is plotted on a log scale, therefore abrupt dips of a plot to zero indicate that the property has changed sign. Rapid oscillations indicate that numerical precision has been reached. Note that drastically different time scale are used in each plot.

the molecular excitation is not affected by the population in the uncondensed modes, and reaches steady state quickly (compared to the evolution of mode population). The exponential rate in the uncondensed regime is therefore approximately constant. In the BEC regime the molecular excitation is strongly affected by the mode population and both experience coupled oscillations about the steady state values, causing the peaks and dips in mode population, molecular excitation, and exponential rate. Never-the-less the exponential rate in the BEC regime is approximately constant and therefore a good measure of the decay towards steady state. Close to threshold the exponential rate achieves the maximum value over a longer period of time than it does far from threshold. The maximum value is however maintained for the majority of the evolution, and is therefore an accurate measure of the rate of decay, up to a factor of two.

The plateau of the exponential rate at the BEC threshold is $5.2 \times 10^{-4}/\kappa$, which is nearly three orders of magnitude smaller than the median exponential rates in the uncondensed and BEC regimes, 0.25 and 0.3 respectively. This matches the increase in equilibration time of three orders of magnitude at threshold, seen in Fig. 4.4. As the relative rate is approximately constant far below, at, and far above the BEC threshold, the increased equilibration time at threshold may be explained by the large relative changes in mode population created by quenches close to a phase boundary.

In contrast to this, the slow rate of equilibration in region ‘E’ and part of region ‘D’, far from threshold, is caused by a reduction in the relative rate, and not an increase in the relative change of mode population. In these regions mode $[0, 1]$ is strongly clamped by modes $[0, 0]$ and $[0, 2]$. The quench causes fluctuations in the molecular excitations which drive all modes out of equilibrium. Most modes decay back to steady state at the same rate as their molecular excitation overlap, and this does not cause excessively long equilibration times. The excitation overlap of mode $[0, 1]$ however is clamped close to the steady state by modes $[0, 0]$ and $[0, 2]$ early in the evolution, before mode $[0, 1]$ has a chance to reach steady state. The relative rate for mode $[0, 1]$ is therefore much lower than for all the other modes, and lower than the corresponding relative rates in regions ‘A’, ‘B’, and ‘C’. This causes a large delay in the equilibration of mode $[0, 1]$, and the non-critical slowing down shown in Fig 4.4. It is difficult to graphically show this phenomena for small quenches, however non-critical slowing down after large quenches is shown in the next section.

4.2.1 Equilibration for a Variety of Quenches

The equilibration time after larger quenches in pump power may also be studied using equations (4.4) and (4.7), and is shown in Fig. 4.6 for a variety of initial and final pump powers. The increase in equilibration time is correlated more with the pump power after the quench than before the quench due to the fast equilibration of molecules. The mode populations are only affected by the quench via the molecules, and the molecular excitation has a maximum change of one compared to the macroscopic changes in photon population. The molecular excitation therefore reaches steady state before the mode populations, and any clamping based slowing of equilibration is based on the pump power after the quench.

As expected from Fig. 4.4 there is an increase in equilibration time for final pump powers in regions ‘D’ and ‘E’ due to the clamping of mode $[0, 1]$ in these regions. Fig. 4.6 also reveals a change in

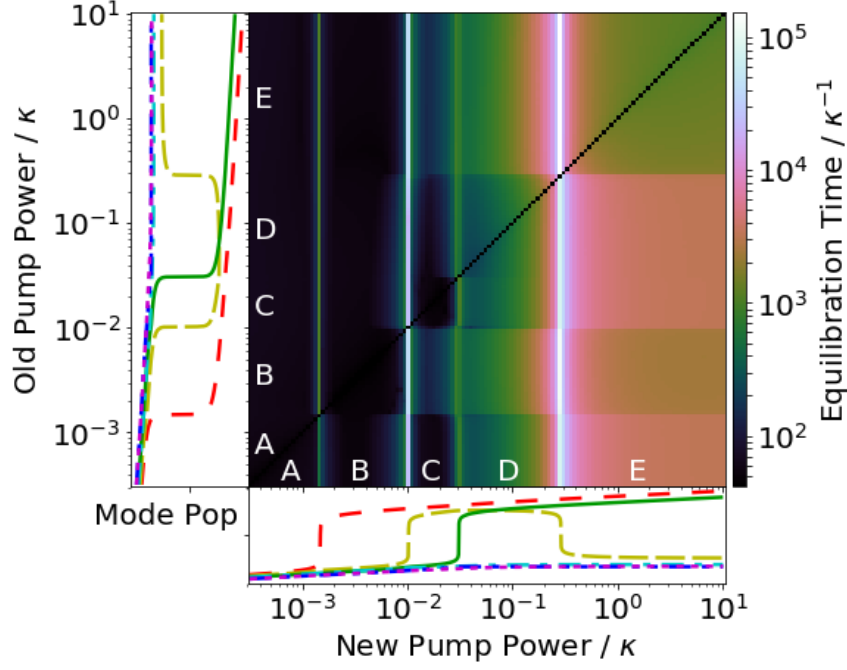


Figure 4.6: The time taken to reach steady state after a quench from the old pump power to the new pump power. The plots on each axis show the steady state of the system at either the old or new pump power, and correspond to the bottom of Fig. 4.4. The diagonal represents a zero change in pump power and therefore has an equilibration time of zero. Pump powers are grouped together based on which modes are condensed at steady state, the groups are labelled A to E.

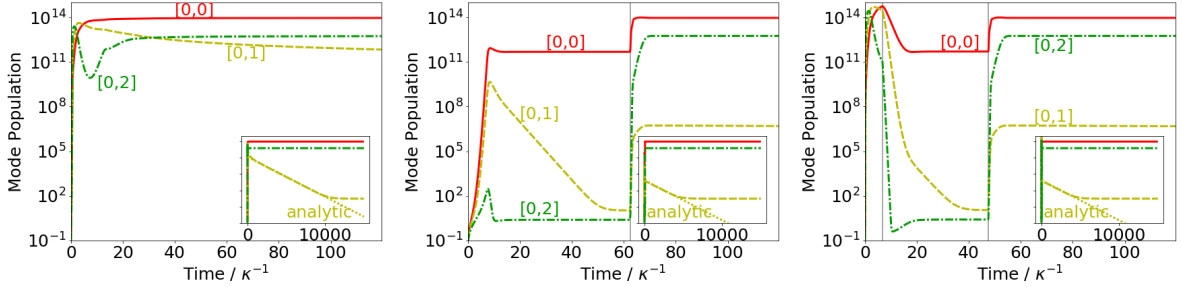


Figure 4.7: The evolution of mode population from the steady state of pump power $3.16 \times 10^{-4} \kappa$ to the steady state of pump power $3.34 \times 10^{-1} \kappa$. From left to right the plots show the evolution after a single quench, an intermediate quench to a pump power of $5.54 \times 10^{-3} \kappa$, and two intermediate quenches to pump powers of 3.69κ and $5.71 \times 10^{-3} \kappa$. These are the fastest ways to achieve the steady state from the initial state with 1, 2, and 3 quenches. The insets show the evolution over the entire decay to steady state, the dashed line shows the analytic prediction of the evolution of the population in mode $[0, 1]$.

equilibration time based on the pump power before the quench. For final pump powers in ‘E’ the equilibration time is faster when starting from region ‘B’ than regions ‘A’ and ‘C’. The middle plot of Fig. 4.7 shows the evolution to the (approximate) steady state of ‘B’ at time $60/\kappa$, followed by a quench and the evolution to the steady state of ‘E’. This may be compared to the evolution to the

steady state of ‘E’ when starting from zero mode population (region ‘A’) in the left plot. In both cases the long equilibration time is due to the slow decay of mode $[0, 1]$, which is exponential due to the clamping of the molecular excitation to a constant value. As the clamping is independent of the population in mode $[0, 1]$, the rate of decay in region ‘E’ is independent of the pump power before the quench. Starting the evolution from region ‘B’ results in a maximum population in mode $[0, 1]$ of approximately 3×10^6 , in contrast to the maximum of 10^{13} when starting from region ‘A’. As the decay rate is constant, this results in a halving of the equilibration time, shown by the insets of Fig. 4.4.

The initial rise in the population of mode $[0, 1]$ is caused by the excitation of molecules beyond their steady state to an excitation level sufficient to cause the condensation of mode $[0, 1]$. If there were no clamping then mode $[0, 1]$ would remain condensed with a population of approximately 10^{13} . The clamping of molecules by modes $[0, 0]$ and $[0, 2]$ reduces the molecular excitation and causes the decondensation of mode $[0, 1]$. When starting the evolution from region ‘B’ this clamping occurs faster than when starting from region ‘A’ as the population in mode $[0, 0]$ is closer to the value required to clamp the molecules. Mode $[0, 1]$ is therefore clamped at an earlier time before it gains full macroscopic occupation.

The opposite effect is predicted for the evolution to a steady state in region ‘D’; evolution is faster when starting from regions ‘A’ and ‘C’ than when starting from ‘B’. The underlying cause is identical to the evolution to region ‘E’. In region ‘E’ the steady state of mode $[0, 1]$ is decondensed, so limiting its growth via clamping from a condensed mode $[0, 0]$ speeds up the evolution. In region ‘D’, however, the steady state of mode $[0, 1]$ is condensed, and limiting its growth slows down the evolution. When quenching from region ‘C’ to ‘D’ modes $[0, 0]$ and $[0, 1]$ both begin condensed, therefore mode $[0, 1]$ has a small relative population change during the evolution to ‘D’ which is not greatly slowed by the clamping of molecules by mode $[0, 0]$. It is only in starting regions ‘B’ and ‘E’ that mode $[0, 1]$ is not condensed *and* is rapidly clamped by a condensed mode $[0, 0]$.

The variation in equilibration time with starting pump power permits the optimisation of the system evolution to minimise the evolution time, given a desired steady state. Due to the exceptionally long evolution times and experimental limitations, this could be an essential requirement for experimentally observing particular multimode states. Fig. 4.7 shows the evolution of the system to a steady state in region ‘E’ for one, two, and three quenches in pump power. The initial mode population and pump power is zero in all cases, before the initial quench at time zero. For a single quench no optimisation is possible and the evolution takes approximately $10000/\kappa$. If a single intermediate quench is permitted then the optimal strategy is to first achieve the condensation of mode $[0, 0]$ and the decondensation of mode $[0, 1]$ and then quench to the final pump power. The middle plot shows this case, the intermediate pump power and the time of the quench were found via numerical optimization. This creates a reduction in equilibration time by 49.5%. If two intermediate quenches are permitted then the intermediate state in region ‘B’ may be obtained more quickly by first overpopulating modes $[0, 0]$ and mode $[0, 1]$. This may be done quickly due to the large pump power. The pump power is then quenched and the overpopulation in mode $[0, 0]$ strongly clamps the molecules and causes the rapid decondensation of mode $[0, 1]$. In contrast the smaller population of mode $[0, 0]$ shown in the middle clamps the molecules closer to the threshold of mode $[0, 1]$ causing its slow decondensation. As the additional quench only optimises the first section of evolution, which is far faster than the

second section of evolution, the evolution with two intermediate quenches shows a similar reduction in equilibration time of 50.0%.

4.3 Steady State Solutions For: Two Modes, Two Excitation Profiles

The simplification of a large number of molecules into collective excitations presented at the beginning of this chapter allows easier visualisation of the system state and a more intuitive understanding of the effects of clamping. This section shall present a graphical method for determining the steady state of a system with two modes and two spatial molecular bins, and discuss the generalisation of this method to a system with two modes and two collective excitation profiles.

Despite being a small system, it is difficult to plot the state of the system on 4 axes, two for the modes, and two for the molecules. Fortunately the steady state mode population may be derived from the molecular excitation f_j using

$$n_m^{(s)} = \frac{\Lambda_{\downarrow}^{(m)} \sum_j g_{m,j} M_j f_j}{\kappa - (\Lambda_{\downarrow}^{(m)} + \Lambda_{\uparrow}^{(m)}) \sum_j g_{m,j} M_j f_j + \Lambda_{\uparrow}^{(m)} \sum_j g_{m,j} M_j} \quad (4.13)$$

which may be derived by requiring that Eq. (4.1) equal zero and rearranging for n_m . Similarly to the analysis performed in chapter 3, the exact mode population is not required, only the phase of the system, determined by which modes are condensed. The steady state mode population is condensed if the denominator of Eq. (4.13) tends to zero, giving a threshold condition

$$\sum_j g_{m,j} M_j f_j = \frac{\Lambda_{\uparrow}^{(m)} \sum_j g_{m,j} M_j + \kappa}{\Lambda_{\downarrow}^{(m)} + \Lambda_{\uparrow}^{(m)}} \quad (4.14)$$

for mode m , in terms of the molecular excitation. If there are J molecular bins then the threshold condition is a $J - 1$ hyper-plane in J dimensional space. If the molecular excitation is on, or close to this plane, then the steady state of the mode is condensed. This eliminated the mode degree of freedom and allows the steady state phase to be calculated using only the molecular state.

In the case where there are only two molecular bins Eq. (4.14) describes a line, which shall be called a ‘condensation line’. Fig. 4.8 shows the condensation lines of two modes (0 and 1) labelled as ‘c0’ and ‘c1’. The angles of these lines are determined by the cavity shape, via the mode-molecule coupling. The distance of the lines from the origin is determined by the ratio of various gain and loss rates. The condensation lines divide the space of potential molecular excitation in two, on the origin side of the line the mode is uncondensed, the mode condenses at the line, and the system may not be in a state on the other side of the line as this causes stimulated emission to dominate and drain molecular excitation until the system reaches the condensation line¹¹. This creates the ‘forbidden’ region shown in Fig. 4.8.



In this section pump power shall always be assumed to be increasing, therefore ‘first’ means at the lowest pump power.

¹¹Alternatively the system cannot be on the other side of a condensation line as this results in an unphysical, negative mode population

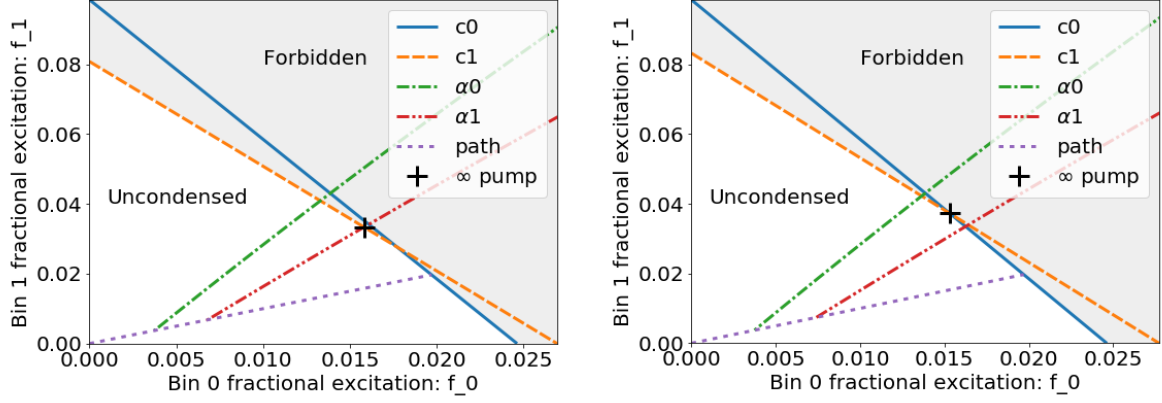


Figure 4.8: Plot for the graphical derivation of steady state, for a system exhibiting decondensation (Left) and multimode condensation (Right). Each axis is the excitation of a spatial molecular bin. If the state of the system lies on the ‘c0’/‘c1’ line then mode 0/1 is condensed. The ‘ $\alpha 0$ ’/‘ $\alpha 1$ ’ line is a potential state of the system at infinite pump power, assuming that only mode 0/1 is condensed. The ‘+’ is the state of the system at infinite pump power. The ‘path’ line shows the steady state of the system when no modes are condensed. $g = [[0.8, 0.2], [0.75, 0.25]]$ for both plots; Absorption is $\Lambda_{\uparrow}^{(m)} = [1.8, 3.9] \times 10^{-13} \kappa$ and $\Lambda_{\uparrow}^{(m)} = [1.8, 4.25] \times 10^{-13} \kappa$ for the decondensation and multimode plots respectively; Emission is $\Lambda_{\uparrow}^{(m)} = [4.8, 5.7] \times 10^{-11} \kappa$ both both figures. Molecular decay is $\Gamma_{\downarrow} = 10^{-2} \kappa$, and there are 1.3×10^{12} molecules per bin.

Given that the system steady state may be read off Fig. 4.8 using the molecular excitation, the molecular excitation must be determined. At low pump powers no modes are condensed, therefore pumping and loss dominate and the steady state molecular excitation

$$f_j^{(s)} = \frac{P_j}{P_j + \Gamma_{\downarrow j}} \quad (4.15)$$

may be derived from the steady state of Eq. (4.2). The path the molecular excitation takes as pump power is increased may be plotted parametrically on Fig. 4.8 as the dashed ‘path’ lines. Whichever condensation line this path intersects first will be the first mode to condense, in this case mode 0. This method is also applicable to higher dimensional systems however the rest of this section only applies to systems with two modes and two molecular bins.

Once a mode has condensed Eq. (4.15) is no longer valid and cannot be used to derive the system steady state. The state of the system at infinite pump power may be calculated, and the states of the system at intermediate pump powers may be deduced from the state at infinite pump power, and the first mode to condense. At infinite pump power the mode population becomes proportional to the pump power $n_m = \alpha_m P$, where α_m are constant with respect to pump power (proven in Box 4.3). In this regime the steady state of Eq. (4.2) becomes

$$f_j^{(s)} = \frac{1 + \sum_{m \in C} \alpha_m g_{m,j} \Lambda_{\uparrow}^{(m)}}{1 + \sum_{m \in C} \alpha_m (\Lambda_{\downarrow}^{(m)} + \Lambda_{\uparrow}^{(m)}) g_{m,j}}, \quad (4.16)$$

where C is the set of condensed modes. As α_m are constants the exact mode populations, and pump power are not required, however the values of the α_m must be determined. The state of the system at

Box 4.3: Constant Values of α_m

At infinite pump power the mode population becomes proportional to the pump power, with a proportionality constant α , which may be proven as follows. The steady state phase of the system at infinite pump power is constant (there are no changes in condensation as pump power is increased), therefore the derivative of the threshold condition Eq. (4.14) with respect to the pump power is zero. Taking this derivative and expressing $\frac{df}{dP}$ as $\frac{\partial f}{\partial \alpha} \frac{d\alpha}{dP}$ yields

$$\sum_{l,j} g_{m,j} M_j \frac{\partial f_j}{\partial \alpha_l} \frac{d\alpha_l}{dP} = 0 \quad (4.17)$$

This equation holds for each condensed mode $m \in C$ and may be rewritten in matrix form

$$\sum_{i \in C} Q_{m,i} \frac{d\alpha_i}{dP} = 0, \quad \forall m \in C, \quad (4.18)$$

where Q is constant with respect to pump power. As the determinant of Q is in general non-zero, α_i must be constant with respect to P .

infinite pump power is deduced from a set of possible solutions, only one of which is self consistent. Single mode condensation is a potential solution, and this assumption reduces Eq. (4.16) to a simple equation in terms of a single α . The potential infinite pump power values of f_j may be parametrically plotted in Fig. 4.8 by varying α . The line generated by assuming the condensation of mode m is labelled as ' αm ' and is called an 'alpha line'. There are now two conditions which must be satisfied for single mode condensation in mode m at infinite pump power: firstly the system must lie on the condensation m in order to support condensation. Secondly the system must lie on alpha line m in order to be a valid infinite pump power state. The intersection of the two lines is therefore a potential steady state of the system. There are two potential single mode condensation states, one for each mode. To be a valid state it must not be within the forbidden region of the other mode. In Fig. 4.8 (LEFT) the intersection of c_0 and α_0 is forbidden by mode 1, however the intersection of c_1 and α_1 is not, therefore single mode condensation in mode 1 is the state of the system at infinite pump power (marked by a black '+').

In Fig. 4.8 (RIGHT) both single mode solutions are within the forbidden region of the other mode, therefore the infinite pump power steady state is not single mode condensation. As the low power pump path intersects a condensation line the infinite pump power steady state is not uncondensed. By elimination the infinite pump power steady state must be multimode condensation. Multimode condensation leads to Eq. (4.16) containing two alpha variables. As the alpha lines require one alpha to equal zero and the other alpha to be greater than zero, the region between alpha lines is the set of potential values of molecular excitation at infinite pump power for multimode condensation. If the intersection of the condensation lines is within this region, then multimode condensation is a valid solution.

If the steady states of the system at zero and infinite pump power are known, then the intermediate steady states may be deduced. The steady state uncondensed molecular excitation is monotonic with

respect to pump power, therefore once a mode has condensed then all higher pump powers must cause the condensation of at least one mode. In a system with two modes and two molecular bins this restricts the state of the system to one dimension: the condensation line closest to the origin. Once the intersection of the low pump power path with a condensation line has been determined, increasing the pump power must cause the system to move along the condensation lines to the infinite pump power state. Fig. 4.8 (LEFT) describes a system which initially has condensation in mode 0, achieves multimode condensation as pump power is increased, and then decondenses mode 0 as pump power is increased further. Fig. 4.8 (LEFT), however, does not show decondensation as multimode condensation is the state at infinite pump power.

The steady state solutions predicted by the graphical solutions of Fig. 4.8 (LEFT) are confirmed by Fig. 4.9, which shows the steady state solution of the system presented in Fig. 4.8 (LEFT) as pump power is varied, as calculate using Eq. (4.1). The left plot shows the mode population. The right plot shows the excitation of the collective molecular profile associated with each mode. These saturate as the corresponding mode condenses, indicating that the system may not pass into the ‘forbidden’ region plotted in Fig. 4.8. The bottom plot shows the excitation of each spatial molecular bin, the excitation saturates in the multimode space as this corresponds to a single point in Fig. 4.8, however they are free to vary in the other phases provided the excitations remain on a condensation line.

4.3.1 Single Steady State

Plotting two condensation lines, two alpha lines, and a low pump power path is computationally very easy and gives an intuitive method of deducing the change in steady state as pump power is increased. To complete the method, the existence of only one infinite pump power solution must be demonstrated. Readers uninterested in this proof may skip to Sec. 4.4. To prove this the orientation of the alpha and condensation lines with respect to each other is required. As the coupling $g_{m,j}$ is always positive, Eq. (4.14) shows that the condensation lines always have a negative gradient. The derivative of molecular excitation with respect to α_m for a single condensed mode is

$$\frac{\partial f_j^{(s)}}{\partial \alpha_m} = \frac{-\Lambda_{\downarrow}^{(m)} g_{m,j}}{(1 + \alpha_m (\Lambda_{\downarrow}^{(m)} + \Lambda_{\uparrow}^{(m)}) g_{m,j})^2} , \quad (4.19)$$

therefore the alpha lines always have positive gradients¹² but are not straight lines. Each condensation line therefore crosses each alpha line exactly once.

Alpha Line Orientation

The alpha lines shall be said to be incorrectly oriented if a multiple steady state solutions may be simultaneously created by shifting the alpha lines along the condensation lines. If they are correctly orientated at the condensation lines then there is only a single solution. Fig. 4.8 (RIGHT) shows correctly oriented alpha lines, if the alpha lines were swapped then there would be three potential solutions

¹²Remember that the alpha lines are parametrically plotted so the derivative of $f_j^{(s)}$ with respect to α_m is not the gradient on Fig. 4.8.

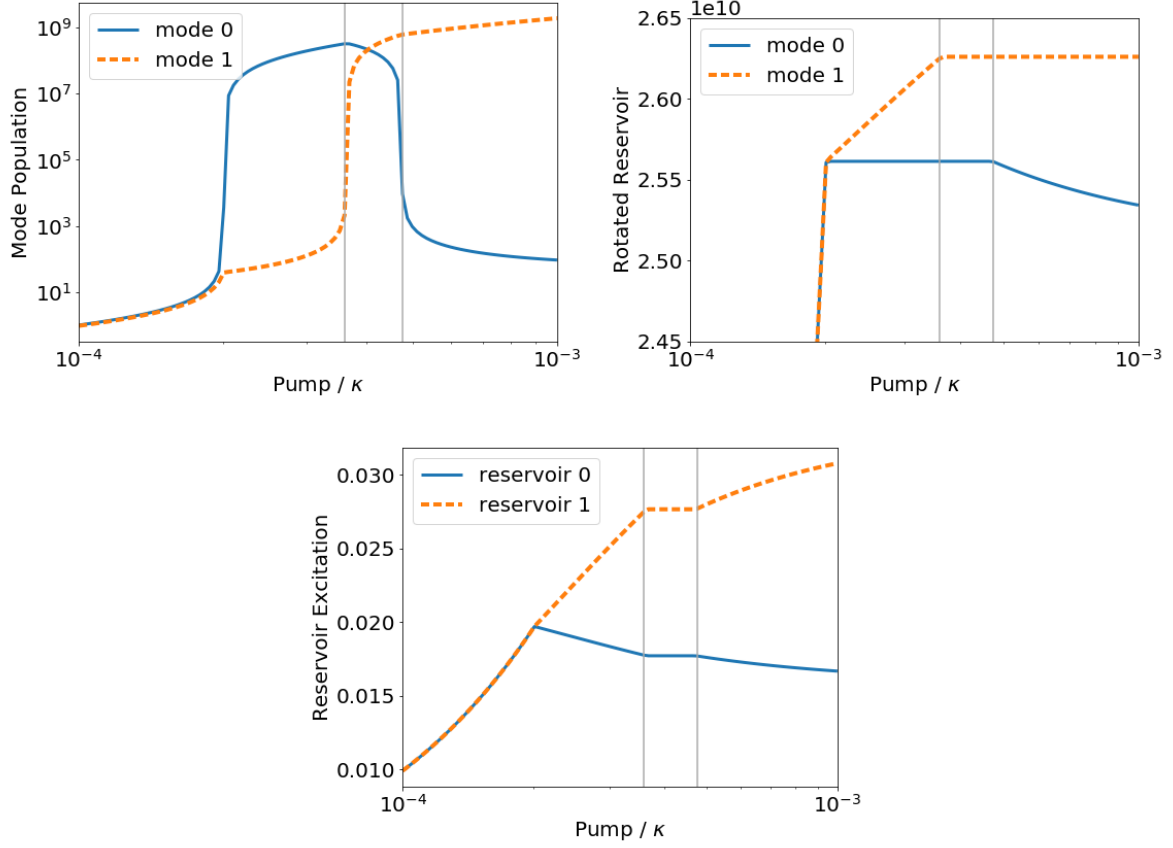


Figure 4.9: The steady state of the decondensation system shown in Fig 4.8 (LEFT) as pump power is varied. (LEFT) The population in each mode. (RIGHT) The excitation of the collective excitation profiles. (BOTTOM) The excitation of each molecular group. The vertical grey lines are plotted at the same pump power in each plot.

and the alpha lines would be incorrectly orientated. Swapping the alpha lines in Fig. 4.8 (LEFT) would still give a single valid solution, however shifting the alpha lines would result in the same three potential solutions as swapping the alpha lines in Fig. 4.8 (RIGHT). Swapping the alpha lines in Fig. 4.8 (LEFT) therefore also gives incorrectly orientated alpha lines. Orientation at r may be formally constructed as follows: define a line with gradient -1 which intersects both axes at r

$$f_0 + f_1 = r \quad (4.20)$$

Define $\alpha_m^{(i)}(r)$ as the value of α_m at which alpha line m intersects the line. The left-most intersection of alpha lines and the r-line may be tracked using

$$O_\alpha = \begin{cases} 1 & f_0(\alpha_0^{(i)}(r)) < f_0(\alpha_1^{(i)}(r)) \\ -1 & \text{otherwise} \end{cases} \quad (4.21)$$

The condensation line m has gradient

$$\left. \frac{\partial f_1}{\partial f_0} \right|_{c_m} = -\frac{g_{m,0}}{g_{m,1}} \quad (4.22)$$

Track which condensation line has the steeper gradient using

$$O_c = \begin{cases} 1 & \frac{g_{0,0}}{g_{0,1}} > \frac{g_{1,0}}{g_{1,1}} \\ -1 & \text{otherwise} . \end{cases} \quad (4.23)$$

If $O_\alpha O_c = 1$ then the alpha lines are correctly orientated.

Alpha Line Intersection

To determine the orientation of the alpha lines at a particular value of r the intersection of the alpha lines with each other is considered. Equating the steady state values of f_j given by Eq. (4.16) for α_0 to those for α_1 gives a quadratic equation for α_0 , there are therefore two potential intersection points. One intersection is $\alpha_0 = \alpha_1 = 0$ which gives $f_0 = f_1 = 1$. The orientation of the alpha lines at the point $f_0 = f_1 = 1$ is therefore purely determined by the gradient at that point. Eq. (4.19) gives the gradient of the alpha line

$$\left. \frac{df_1}{df_0} \right|_{\alpha_m=0} = \frac{g_{m,1}}{g_{m,0}} . \quad (4.24)$$

As the alpha lines are perpendicular to condensation lines at the point $f_0 = f_1 = 1$ they are correctly oriented at that point. If the second intersection of alpha lines is between the condensation lines and the point $f_0 = f_1 = 1$ then they will be incorrectly orientated at the condensation lines, otherwise they will be correctly orientated. Computational exploration of the limited parameter space shows that the second intersection lies above a condensation line only if one of the condensation lines is entirely within the forbidden region of the other condensation line, as shown in Fig. 4.10. As the condensation lines never cross there is still only one solution in this case. This demonstrates the existence of only one infinite pump power solution, however the proof has not been found.

4.4 Conclusion

The spatial coupling between molecules and modes may be used to identify collective modes which do not couple to the cavity modes¹³, allowing them to be eliminated. This provides an order of magnitude increase in the simulation speed with a minimal increase in error. This is particularly useful for simulating the mode population in irregular cavity shapes, where the many changes in mode profile dictate a fine sampling of the molecular excitation and large computational representations. The system size scales only with the number of modes and not the number of molecular bins thereby eliminating errors caused by under-sampling the molecules. A better measure of the simulation error would be useful; currently simulations with small errors in the time of condensation and decondensation display large errors in mode population due to their rapid changes over even short times. An improved method of quantifying the qualitative accuracy of simulations would allow qualitative studies of phenomena to be conducted using fewer molecular profiles, which produce large numerical, but small qualitative errors. The clamping of molecules by condensed modes occurs before steady state is reached. If the modes affected by this clamping are far from steady state, and the molecules are clamped close to their

¹³The derivation of which is described in Sec. 1.7

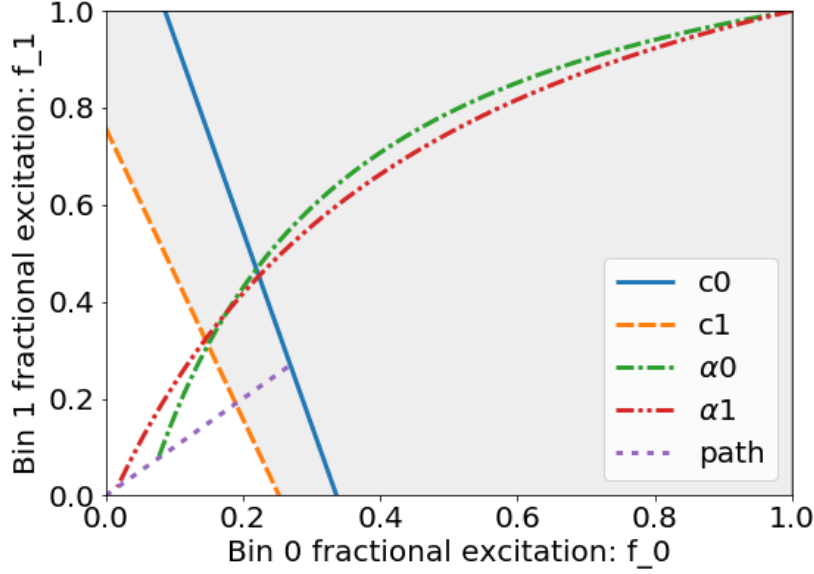


Figure 4.10: Plot constructed identically to Fig. 4.8, with identical coupling g , Absorption $\Lambda_{\uparrow}^{(m)} = [4, 1] \times 10^{-1}\kappa$, Emission $\Lambda_{\downarrow}^{(m)} = [4.8, 5.7]\kappa$, and one molecule per bin. These are not realistic parameters but produce a clear example figure. The red and green alpha lines cross above the orange ‘c1’ line, and the blue ‘c0’ line is entirely above the ‘c1’ line.

critical value then these mode experience extremely slow evolution towards steady state. This effect does *not* require the decondensation of the mode, region ‘D’ in Fig. 4.4 exhibits slower equilibration than regions ‘A’ to ‘C’. The clamping of molecules close to the threshold value is, in general, more consistent for decondensed modes and persists for a wider range of pump powers. The methods presented in this chapter provide a starting point for experimentalists attempting to efficiently create particular multimode phases of light.

Finally the excitation profiles themselves provide insight into the cavity dynamics. The unstructured model of many molecular bins effecting all modes may be simplified into a single excitation profile per mode. The coupling between these profiles may be studied to establish the effective coupling between modes. For example two excitation profiles may only be coupled via the third order when no modes are condensed, but are coupled via the second order after the condensation of the ground mode. This opens the way for studies of how condensation affects the flow of photons around cavities, which is especially interesting in cavities of usual shape, e.g. spirals.

Chapter 5

Higher Order Correlations

The mode populations and intensity do not provide a complete description of light inside the micro-cavity. As shown in the introduction 1.5.1 the correlation functions between different modes, and the correlation of a mode with itself also provide information about the state of light field. Correlation give insight into the coherence time and length of the condensate and allow it to be compared to other systems. For example a laser has a second order coherence of 1, and thermal light has a second order coherence of 2. Various experiments investigating the coherence of photon BECs are presented in the introduction. Additionally the rate of change of mode population is coupled to the second order correlation functions, and calculating it therefore increases the accuracy of the simulation. In Kirton and Keeling's derivation this coupling is removed using the semi-classical approximation, after Eq. (2.70). This chapter shows how the master equation (2.36) may be used to derive coupled rate equations for the mode populations, molecular excitations, and correlation functions. The rate equations are then simplified to improve simulation speed, using techniques similar to those discussed in Chapters 3 and 4. Finally the code used to perform the lengthy derivations of the rate equations is presented.

As discussed in 1.5.1 the second order correlation function

$$g_{p,q}^{(2)} = \frac{\langle a_p^\dagger a_q^\dagger a_p a_q \rangle}{\langle a_p^\dagger a_p \rangle \langle a_q^\dagger a_q \rangle} \quad (5.1)$$

between modes p and q may be expressed in terms of the mode-mode correlation $\langle a_p^\dagger a_q^\dagger a_p a_q \rangle$ and the mode populations $\langle a_p^\dagger a_p \rangle$, and $\langle a_q^\dagger a_q \rangle$. The evolution of the mode populations is already know and a rate equation for the mode-mode correlation must be found. As in Sec. 2.3 a rate equation may be constructed by performing a trace over the rate of change of the density matrix

$$\frac{d\langle a_p^\dagger a_q^\dagger a_p a_q \rangle}{dt} = \text{Tr} [a_p^\dagger a_q^\dagger a_p a_q \dot{\rho}] \quad (5.2)$$

This may be expanded by substituting in the value of the rate of change of the density matrix given by the master equation (2.36). The linearity of the trace may be used to expand the rate of change of

the correlation to

$$\begin{aligned}
\frac{d\langle a_p^\dagger a_q^\dagger a_p a_q \rangle}{dt} = & -i \text{Tr} \left\{ [\tilde{H}_0, \rho] a_p^\dagger a_q^\dagger a_p a_q \right\} - \sum_m \frac{\kappa}{2} \text{Tr} \left\{ \mathcal{L}[\hat{a}_m](\rho) a_p^\dagger a_q^\dagger a_p a_q \right\} \\
& + \sum_i \frac{\Gamma_{\uparrow,i}}{2} \text{Tr} \left\{ \mathcal{L}[\hat{\sigma}_i^+](\rho) a_p^\dagger a_q^\dagger a_p a_q \right\} + \sum_i \frac{\Gamma_{\downarrow}}{2} \text{Tr} \left\{ \mathcal{L}[\hat{\sigma}_i^-](\rho) a_p^\dagger a_q^\dagger a_p a_q \right\} \\
& + \sum_{m,i} \frac{\Lambda_{\downarrow}^{(m)}(\underline{r}_j)}{2} \text{Tr} \left\{ \mathcal{L}[\hat{a}_m^\dagger \hat{\sigma}_i^-](\rho) a_p^\dagger a_q^\dagger a_p a_q \right\} + \sum_{m,i} \frac{\Lambda_{\uparrow}^{(m)}(\underline{r}_j)}{2} \text{Tr} \left\{ \mathcal{L}[\hat{a}_m \hat{\sigma}_i^+](\rho) a_p^\dagger a_q^\dagger a_p a_q \right\} .
\end{aligned} \tag{5.3}$$

As in Sec. 2.3 each Lindblad term may be simplified by using the cyclicity of the trace to move the density matrix to the right hand side of each term. Commutation relations may then be used to write the first two terms of each Lindblad in the form of the last term of the Lindblad. The first two terms of each Lindblad then cancel the last term, leaving the terms produced by the commutation. Simplifying the Lindblad terms reduces Eq. (5.3) to

$$\begin{aligned}
\frac{d\langle a_p^\dagger a_q^\dagger a_p a_q \rangle}{dt} = & \sum_{j=0}^J \Lambda_{p,j}^\downarrow \text{Tr} \{ a_q^T a_q f_j \rho \} + \delta_{q,p} \sum_{j=0}^J \Lambda_{q,j}^\downarrow \text{Tr} \{ a_q^T a_q f_j \rho \} + \sum_{j=0}^J \Lambda_{q,j}^\downarrow \text{Tr} \{ a_p^T a_p f_j \rho \} \\
& + \delta_{p,q} \sum_{j=0}^J \Lambda_{p,j}^\downarrow \text{Tr} \{ a_p^T a_p f_j \rho \} - \sum_{j=0}^J \Lambda_{p,j}^\uparrow \text{Tr} \{ a_p^T a_q^T a_p a_q \rho \} - \sum_{j=0}^J \Lambda_{q,j}^\uparrow \text{Tr} \{ a_p^T a_q^T a_p a_q \rho \} \\
& - 2\kappa \text{Tr} \{ a_p^T a_q^T a_p a_q \rho \} + \sum_{j=0}^J \Lambda_{p,j}^\downarrow \text{Tr} \{ a_p^T a_q^T a_p a_q f_j \rho \} + \sum_{j=0}^J \Lambda_{q,j}^\downarrow \text{Tr} \{ a_p^T a_q^T a_p a_q f_j \rho \} \\
& + \sum_{j=0}^J \Lambda_{p,j}^\uparrow \text{Tr} \{ a_p^T a_q^T a_p a_q f_j \rho \} + \sum_{j=0}^J \Lambda_{q,j}^\uparrow \text{Tr} \{ a_p^T a_q^T a_p a_q f_j \rho \} ,
\end{aligned} \tag{5.4}$$

where, as in Chapter 2, the operator f_j is defined as $\sigma_j^+ \sigma_j^-$, and the absorption and emission rates $\Lambda_{\uparrow}^{(m)}(\underline{r}_j)$ have been replaced with $\Lambda_{m,j}^\uparrow$ for conciseness. Step by step derivations of these equations are given in appendix B. The rate of change of a mode-mode correlation is coupled to itself, the populations of the modes involved $\langle a_q^\dagger a_q \rangle$, the mode-molecule correlations $\langle a_p^\dagger a_p \sigma_j^z \rangle$, and the higher-order correlation $\langle a_p^\dagger a_q^\dagger a_p a_q \sigma_j^z \rangle$. These terms must either be explicitly calculated or approximated using known terms. In Sec. 2.3 the mode-molecule coupling $\langle a_p^\dagger a_p \sigma_j^z \rangle$ was treated as the product of the mode population $\langle a_p^\dagger a_p \rangle$ and the molecular excitation $\langle \sigma_j^z \rangle$. As the mode-mode correlation is mediated by absorption and emission from molecules, this is an inappropriate approximation for calculating the second order correlation. An expression for the rate of change of mode-molecule correlation must therefore be derived.

Similarly to the derivation of the rate equation for mode-mode coupling, the master equation may be used to write an expression for the rate of change of mode-molecule coupling

$$\begin{aligned}
\frac{d\langle a_p^\dagger a_p f_l \rangle}{dt} = & -i \text{Tr} \left\{ [\tilde{H}_0, \rho] a_p^\dagger a_p f_l \right\} - \sum_m \frac{\kappa}{2} \text{Tr} \left\{ \mathcal{L}[\hat{a}_m](\rho) a_p^\dagger a_p f_l \right\} \\
& + \sum_i \frac{\Gamma_{\uparrow,i}}{2} \text{Tr} \left\{ \mathcal{L}[\hat{\sigma}_i^+](\rho) a_p^\dagger a_p f_l \right\} + \sum_i \frac{\Gamma_{\downarrow}}{2} \text{Tr} \left\{ \mathcal{L}[\hat{\sigma}_i^-](\rho) a_p^\dagger a_p f_l \right\} \\
& + \sum_{m,i} \frac{\Lambda_{\downarrow}^{(m)}(\underline{r}_j)}{2} \text{Tr} \left\{ \mathcal{L}[\hat{a}_m^\dagger \hat{\sigma}_i^-](\rho) a_p^\dagger a_p f_l \right\} + \sum_{m,i} \frac{\Lambda_{\uparrow}^{(m)}(\underline{r}_j)}{2} \text{Tr} \left\{ \mathcal{L}[\hat{a}_m \hat{\sigma}_i^+](\rho) a_p^\dagger a_p f_l \right\} ,
\end{aligned} \tag{5.5}$$

which may be simplified to

$$\begin{aligned}
\frac{d\langle a_p^\dagger a_p f_l \rangle}{dt} = & -\Lambda_{p,l}^\downarrow \langle f_l \rangle + \sum_{j=0}^J \Lambda_{p,j}^\downarrow \text{Tr}\{f_j f_l \rho\} + \Gamma_l^\uparrow \langle n_p \rangle - \Gamma_l^\uparrow \text{Tr}\{a_p^T a_p f_l \rho\} - \Gamma_l^\downarrow \text{Tr}\{a_p^T a_p f_l \rho\} \\
& - \sum_{m=0}^M \Lambda_{m,l}^\downarrow \text{Tr}\{a_p^T a_p f_l \rho\} - \kappa \text{Tr}\{a_p^T a_p f_l \rho\} - \sum_{j=0}^J \Lambda_{p,j}^\uparrow \text{Tr}\{a_p^T a_p f_l \rho\} - 2\Lambda_{p,l}^\downarrow \text{Tr}\{a_p^T a_p f_l \rho\} \\
& + \sum_{j=0}^J \Lambda_{p,j}^\downarrow \text{Tr}\{a_p^T a_p f_j f_l \rho\} + \sum_{j=0}^J \Lambda_{p,j}^\uparrow \text{Tr}\{a_p^T a_p f_j f_l \rho\} + \sum_{m=0}^M \Lambda_{m,l}^\uparrow \text{Tr}\{a_m^T a_p^T a_m a_p \rho\} \\
& - \sum_{m=0}^M \Lambda_{m,l}^\downarrow \text{Tr}\{a_m^T a_p^T a_m a_p f_l \rho\} - \sum_{m=0}^M \Lambda_{m,l}^\uparrow \text{Tr}\{a_m^T a_p^T a_m a_p f_l \rho\} ,
\end{aligned} \tag{5.6}$$

a derivation of which is given in appendix B. The rate of change of mode molecule coupling is therefore coupled to itself, the mode population $\langle n_p \rangle$, the molecular excitation $\langle f_l \rangle$, the second order mode-mode correlation $\langle a_p^\dagger a_m^\dagger a_m a_p \rangle$, the molecule-molecule correlation $\langle f_j f_l \rangle$, and the higher order terms $\langle a_p^\dagger a_m^\dagger a_m a_p f_l \rangle$ and $\langle a_p^\dagger a_p f_j f_l \rangle$.

The rate equations for the correlations, Eqs. (5.5) and (5.6) are not closed as they contain as yet unknown correlations, which may be grouped into orders. A term of the r^{th} order may be defined as an expectation of r operators, where $a^\dagger a$ is counted as a single operator. The absorption and emission terms in the master equation couple the rate of change of order r terms to order $r+1$ terms. It is therefore impossible to form an exact closed set of rate equations. Some higher order terms must therefore be removed from the rate equations. The higher order terms may not be directly approximated as zero as they are often the largest terms in the equation; as the mode population is macroscopic $\langle (a_p^\dagger a_p)^3 \rangle \gg \langle (a_p^\dagger a_p)^2 \rangle$. Instead the higher order covariance is approximated as zero, as it is the correlations between operators not their absolute values which have negligible effects. The covariance of operators $\{z\}$ is defined as their joint deviations from their means

$$C(z_0 \dots z_N) = \langle (z_0 - \langle z_0 \rangle) \times \dots \times (z_N - \langle z_N \rangle) \rangle . \tag{5.7}$$

Terms containing three operators may therefore be written as

$$\langle z_0 z_1 z_2 \rangle = C(z_0, z_1, z_2) + z_0 C(z_1, z_2) + z_1 C(z_0, z_2) + z_2 C(z_0, z_1) + \langle z_0 \rangle \langle z_1 \rangle \langle z_2 \rangle , \tag{5.8}$$

and the three term covariance $C(z_0, z_1, z_2)$ may be approximated as zero. The remaining expression will contain only second order terms. Covariances between operators also give greater insight into the evolution of the system than the products of operators, and it is therefore convenient to convert second order terms into covariances and expectations of single operators

$$\begin{aligned}
\langle a_k^\dagger a_k f_j \rangle &= \langle n_k \rangle \langle f_j \rangle + C(n_k, f_j) \\
\langle a_k^\dagger a_l^\dagger a_k a_l \rangle &= \langle n_k \rangle \langle n_l \rangle + C(n_k, n_l) - \langle n_k \rangle \delta_{k,l} \\
\langle f_l f_j \rangle &= \langle f_l \rangle \langle f_j \rangle + C(f_l, f_j) \\
\langle a_k^\dagger a_l^\dagger a_k a_l f_j \rangle &= C(n_k, n_l, f_j) + \langle n_k \rangle C(n_l, f_j) + \langle n_l \rangle C(n_k, f_j) + \langle f_j \rangle C(n_k, n_l) + \langle n_k \rangle \langle n_l \rangle \langle f_j \rangle \\
&\quad - \delta_{k,l} \langle n_k \rangle \langle f_j \rangle + \delta_{k,l} C(n_k, f_j) \\
\langle a_k^\dagger a_k f_l f_j \rangle &= C(n_k, f_l, f_j) + \langle n_k \rangle C(f_l, f_j) + \langle f_l \rangle C(n_k, f_j) + \langle f_j \rangle C(n_k, f_l) + \langle n_k \rangle \langle f_l \rangle \langle f_j \rangle .
\end{aligned} \tag{5.9}$$

This allows the rate equations for mode population and molecular excitation (Eqs. (2.70) and (2.77) respectively) to be written in terms of covariances

$$\begin{aligned}
\frac{d\langle n_p \rangle}{dt} &= \sum_{j=0}^J C(n_p, f_j) \Lambda_{p,j}^\downarrow + \sum_{j=0}^J C(n_p, f_j) \Lambda_{p,j}^\uparrow + \sum_{j=0}^J \Lambda_{p,j}^\downarrow \langle f_j \rangle - \kappa \langle n_p \rangle - \sum_{j=0}^J \Lambda_{p,j}^\uparrow \langle n_p \rangle \\
&\quad + \sum_{j=0}^J \Lambda_{p,j}^\downarrow \langle f_j \rangle \langle n_p \rangle + \sum_{j=0}^J \Lambda_{p,j}^\uparrow \langle f_j \rangle \langle n_p \rangle \\
\frac{d\langle f_l \rangle}{dt} &= \Gamma_l^\uparrow - \sum_{m=0}^M C(n_m, f_l) \Lambda_{m,l}^\downarrow - \sum_{m=0}^M C(n_m, f_l) \Lambda_{m,l}^\uparrow - \Gamma_l^\uparrow \langle f_l \rangle - \Gamma_l^\downarrow \langle f_l \rangle - \sum_{m=0}^M \Lambda_{m,l}^\downarrow \langle f_l \rangle \\
&\quad + \sum_{m=0}^M \Lambda_{m,l}^\uparrow \langle n_m \rangle - \sum_{m=0}^M \Lambda_{m,l}^\downarrow \langle n_m \rangle \langle f_l \rangle - \sum_{m=0}^M \Lambda_{m,l}^\uparrow \langle n_m \rangle \langle f_l \rangle .
\end{aligned} \tag{5.10}$$

These rates require the covariance between modes and molecules which has the rate equation, derived from Eq. (5.6),

$$\begin{aligned}
\frac{dC(n_p, f_l)}{dt} &= -\Lambda_{p,l}^\downarrow \langle f_l \rangle + \sum_{j=0}^J C(f_j, f_l) \Lambda_{p,j}^\downarrow + \sum_{m=0}^M C(n_m, n_p) \Lambda_{m,l}^\uparrow - C(n_p, f_l) \Gamma_l^\uparrow - C(n_p, f_l) \Gamma_l^\downarrow \\
&\quad - C(n_p, f_l) \Lambda_{p,l}^\downarrow - C(n_p, f_l) \sum_{m=0}^M \Lambda_{m,l}^\downarrow - C(n_p, f_l) \kappa - C(n_p, f_l) \sum_{j=0}^J \Lambda_{p,j}^\uparrow + C(n_p, f_l) \Lambda_{p,l}^\uparrow \\
&\quad - \Lambda_{p,l}^\uparrow \langle n_p \rangle + \sum_{j=0}^J C(n_p, f_j, f_l) \Lambda_{p,j}^\downarrow + \sum_{j=0}^J C(n_p, f_j, f_l) \Lambda_{p,j}^\uparrow - \sum_{m=0}^M C(n_m, n_p, f_l) \Lambda_{m,l}^\downarrow \\
&\quad - \sum_{m=0}^M C(n_m, n_p, f_l) \Lambda_{m,l}^\uparrow - \sum_{m=0}^M C(n_m, n_p) \Lambda_{m,l}^\downarrow \langle f_l \rangle - \sum_{m=0}^M C(n_m, n_p) \Lambda_{m,l}^\uparrow \langle f_l \rangle - \Lambda_{p,l}^\downarrow \langle n_p \rangle \langle f_l \rangle \\
&\quad + \Lambda_{p,l}^\uparrow \langle n_p \rangle \langle f_l \rangle + C(n_p, f_l) \sum_{j=0}^J \Lambda_{p,j}^\downarrow \langle f_j \rangle + C(n_p, f_l) \sum_{j=0}^J \Lambda_{p,j}^\uparrow \langle f_j \rangle - C(n_p, f_l) \sum_{m=0}^M \Lambda_{m,l}^\downarrow \langle n_m \rangle \\
&\quad - C(n_p, f_l) \sum_{m=0}^M \Lambda_{m,l}^\uparrow \langle n_m \rangle + \sum_{j=0}^J C(f_j, f_l) \Lambda_{p,j}^\downarrow \langle n_p \rangle + \sum_{j=0}^J C(f_j, f_l) \Lambda_{p,j}^\uparrow \langle n_p \rangle ,
\end{aligned} \tag{5.11}$$

where the three term covariances $C(n_k, f_j, f_l)$ and $C(n_k, n_m, f_l)$ may be approximated as zero. The rate of mode molecule covariance depends on the mode populations, molecule excitations, all second order covariances, and two third order covariances. The covariance between modes has the rate equation,

derived from Eq. (5.4),

$$\begin{aligned}
\frac{dC(n_p, n_q)}{dt} = & \delta_{p,q} \sum_{j=0}^J \Lambda_{p,j}^\downarrow \langle f_j \rangle + \sum_{j=0}^J C(n_p, f_j) \Lambda_{q,j}^\downarrow - \delta_{p,q} \sum_{j=0}^J C(n_p, f_j) \Lambda_{p,j}^\uparrow + \sum_{j=0}^J C(n_q, f_j) \Lambda_{p,j}^\downarrow \\
& + \delta_{q,p} \sum_{j=0}^J C(n_q, f_j) \Lambda_{q,j}^\downarrow - C(n_p, n_q) \sum_{j=0}^J \Lambda_{p,j}^\uparrow - C(n_p, n_q) \sum_{j=0}^J \Lambda_{q,j}^\uparrow - 2C(n_p, n_q) \kappa \\
& + \delta_{p,q} \sum_{j=0}^J \Lambda_{p,j}^\uparrow \langle n_p \rangle + \kappa \delta_{p,q} \langle n_p \rangle + \sum_{j=0}^J C(n_p, n_q, f_j) \Lambda_{p,j}^\downarrow + \sum_{j=0}^J C(n_p, n_q, f_j) \Lambda_{q,j}^\downarrow \\
& + \sum_{j=0}^J C(n_p, n_q, f_j) \Lambda_{p,j}^\uparrow + \sum_{j=0}^J C(n_p, n_q, f_j) \Lambda_{q,j}^\uparrow - \delta_{p,q} \sum_{j=0}^J \Lambda_{p,j}^\uparrow \langle f_j \rangle \langle n_p \rangle \\
& + C(n_p, n_q) \sum_{j=0}^J \Lambda_{p,j}^\downarrow \langle f_j \rangle + C(n_p, n_q) \sum_{j=0}^J \Lambda_{q,j}^\downarrow \langle f_j \rangle + C(n_p, n_q) \sum_{j=0}^J \Lambda_{p,j}^\uparrow \langle f_j \rangle \\
& + C(n_p, n_q) \sum_{j=0}^J \Lambda_{q,j}^\uparrow \langle f_j \rangle + \delta_{q,p} \sum_{j=0}^J \Lambda_{q,j}^\downarrow \langle f_j \rangle \langle n_q \rangle + \sum_{j=0}^J C(n_p, f_j) \Lambda_{q,j}^\downarrow \langle n_q \rangle \\
& + \sum_{j=0}^J C(n_p, f_j) \Lambda_{q,j}^\uparrow \langle n_q \rangle + \sum_{j=0}^J C(n_q, f_j) \Lambda_{p,j}^\downarrow \langle n_p \rangle + \sum_{j=0}^J C(n_q, f_j) \Lambda_{p,j}^\uparrow \langle n_p \rangle .
\end{aligned} \tag{5.12}$$

Finally a rate equation for the molecule-molecule covariance may be derived in an identical manner to the other covariances and has the form

$$\begin{aligned}
\frac{dC(f_k, f_l)}{dt} = & \Gamma_k^\uparrow \delta_{k,l} - \Gamma_k^\uparrow \delta_{k,l} \langle f_k \rangle + \delta_{k,l} \sum_{m=0}^M \Lambda_{m,k}^\downarrow \langle f_k \rangle + \Gamma_k^\downarrow \delta_{k,l} \langle f_k \rangle + \sum_{m=0}^M C(n_m, f_k) \Lambda_{m,l}^\uparrow \\
& - \delta_{k,l} \sum_{m=0}^M C(n_m, f_k) \Lambda_{m,k}^\uparrow + \delta_{k,l} \sum_{m=0}^M C(n_m, f_k) \Lambda_{m,k}^\downarrow + \sum_{m=0}^M C(n_m, f_l) \Lambda_{m,k}^\uparrow - C(f_k, f_l) \Gamma_l^\uparrow \\
& - C(f_k, f_l) \Gamma_k^\uparrow - C(f_k, f_l) \Gamma_l^\downarrow - C(f_k, f_l) \Gamma_k^\downarrow - C(f_k, f_l) \sum_{m=0}^M \Lambda_{m,l}^\downarrow - C(f_k, f_l) \sum_{m=0}^M \Lambda_{m,k}^\downarrow \\
& + \delta_{k,l} \sum_{m=0}^M \Lambda_{m,k}^\uparrow \langle n_m \rangle - \sum_{m=0}^M C(n_m, f_k, f_l) \Lambda_{m,l}^\downarrow - \sum_{m=0}^M C(n_m, f_k, f_l) \Lambda_{m,k}^\downarrow \\
& - \sum_{m=0}^M C(n_m, f_k, f_l) \Lambda_{m,l}^\uparrow - \sum_{m=0}^M C(n_m, f_k, f_l) \Lambda_{m,k}^\uparrow - \sum_{m=0}^M C(n_m, f_l) \Lambda_{m,k}^\downarrow \langle f_k \rangle \\
& - \sum_{m=0}^M C(n_m, f_l) \Lambda_{m,k}^\uparrow \langle f_k \rangle - \sum_{m=0}^M C(n_m, f_k) \Lambda_{m,l}^\downarrow \langle f_l \rangle - \sum_{m=0}^M C(n_m, f_k) \Lambda_{m,l}^\uparrow \langle f_l \rangle \\
& - \delta_{k,l} \sum_{m=0}^M \Lambda_{m,k}^\uparrow \langle n_m \rangle \langle f_k \rangle + \delta_{k,l} \sum_{m=0}^M \Lambda_{m,k}^\downarrow \langle n_m \rangle \langle f_k \rangle - C(f_k, f_l) \sum_{m=0}^M \Lambda_{m,l}^\downarrow \langle n_m \rangle \\
& - C(f_k, f_l) \sum_{m=0}^M \Lambda_{m,k}^\downarrow \langle n_m \rangle - C(f_k, f_l) \sum_{m=0}^M \Lambda_{m,l}^\uparrow \langle n_m \rangle - C(f_k, f_l) \sum_{m=0}^M \Lambda_{m,k}^\uparrow \langle n_m \rangle
\end{aligned} \tag{5.13}$$

If the third order terms are approximated as zero, then Eqs. (5.10), (5.11), (5.12), and (5.13) form a closed set of rate equations which may be used to simulate the system. The results of this simulation

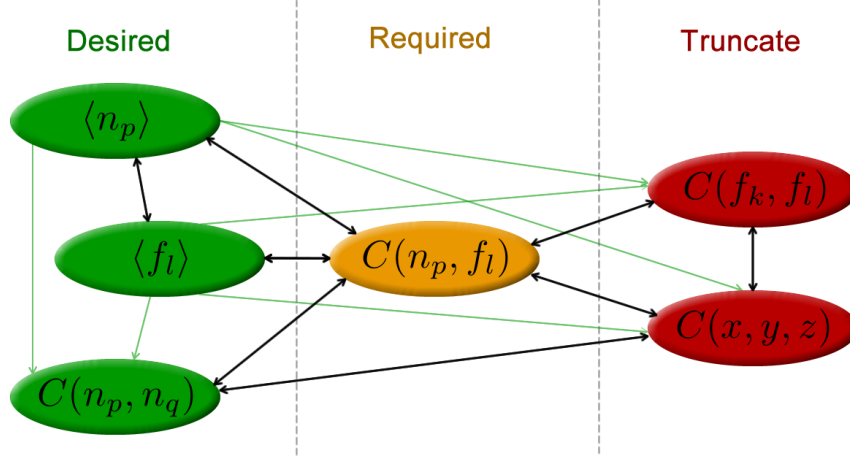


Figure 5.1: Diagram of the coupling between different expectations. The green expectations are the desired outputs of the simulation. The orange $C(n_p, f_l)$ is required to properly calculate the desired expectations. The red expectations may be discarded. $C(x, y, z)$ represents all the three operator covariances. Black arrows indicate important two way coupling, green arrows from A to B indicate that A affects B but B does not affect A .

give the mode and molecule populations, and all their coherences as functions of time. As discussed in Sec. 4, the biggest problem in the simulation is the number of molecules, or molecular bins: if there are J molecules then there are J^2 molecule-molecule covariance functions $C(f_k, f_l)$. As the mode populations, molecular excitations, and mode-mode covariances all depend on the molecule-molecule covariances $C(f_k, f_l)$ via the mode-molecule covariances $C(n_p, f_l)$ (shown in Fig. 5.1), the molecule-molecule covariances may be dropped as a first order approximation.

5.1 Second Order Coherence

The mode-mode covariance $C(n_k, n_l)$ allows the calculation of the second order coherence between modes

$$g_{k,l}^{(2)} = \frac{C(n_k, n_l)}{\langle n_k \rangle \langle n_l \rangle} - \frac{\delta_{k,l}}{\langle n_k \rangle} + 1. \quad (5.14)$$

The second order coherence may be simulated over time via the usual propagation of the rate equations (5.10), (5.11), and (5.12). If, however, only the steady state coherence is required then a further simplification may be made. In Sec. 2.3.1 the molecular degrees of freedom were eliminated when calculating the steady state because, given a mode population, the steady state molecular excitation could be calculated using Eq. (2.87). Similarly the property with the most degrees of freedom may be eliminated from the calculation of second order coherence (or any higher coherence). At the current level of approximation the mode-molecule covariance has the most degrees of freedom, therefore an

equation for the steady state of $C(n_k, \sigma_l^{(z)})$ is constructed by setting Eq. (5.11) to zero, yielding

$$\begin{aligned}
C^{(s)}(n_p, f_l) &= -\frac{\bar{N}}{\bar{D}} \\
\bar{N} &= -\Lambda_{p,l}^\downarrow \langle f_l \rangle + \sum_{m=0}^M C(n_m, n_p) \Lambda_{m,l}^\uparrow - \Lambda_{p,l}^\uparrow \langle n_p \rangle - \sum_{m=0}^M C(n_m, n_p) \Lambda_{m,l}^\downarrow \langle f_l \rangle \\
&\quad - \sum_{m=0}^M C(n_m, n_p) \Lambda_{m,l}^\uparrow \langle f_l \rangle - \Lambda_{p,l}^\downarrow \langle n_p \rangle \langle f_l \rangle + \Lambda_{p,l}^\uparrow \langle n_p \rangle \langle f_l \rangle \\
\bar{D} &= \Lambda_{p,l}^\uparrow - \Gamma_l^\uparrow - \Gamma_l^\downarrow - \Lambda_{p,l}^\downarrow - \sum_{m=0}^M \Lambda_{m,l}^\downarrow - \kappa - \sum_{j=0}^J \Lambda_{p,j}^\uparrow + \sum_{j=0}^J \Lambda_{p,j}^\downarrow \langle f_j \rangle + \sum_{j=0}^J \Lambda_{p,j}^\uparrow \langle f_j \rangle \\
&\quad - \sum_{m=0}^M \Lambda_{m,l}^\downarrow \langle n_m \rangle - \sum_{m=0}^M \Lambda_{m,l}^\uparrow \langle n_m \rangle .
\end{aligned} \tag{5.15}$$

This allows the mode-molecule covariance $C(n_p, f_l)$ in Eqs. (5.10), and (5.12) to be replaced with Eq. (5.15) for the purposes of calculating the steady state. In Sec. 2.3.1 this transformation allowed the mode populations to be calculated using the molecular excitations, without explicitly storing the mode populations during the simulation, which dramatically increases computational performance. The transformation permitted by Eq. (5.15) allows the mode populations and mode-mode coherences to be calculated using the mode-molecule covariance, but without explicitly storing the mode-molecule covariance, which again dramatically improves performance. A similar transformation may be made at any level of truncation: as the initial rate equation of variable x is linear in variable x , it may be easily rearranged to give the steady state of x in terms of the other variables. This allows x to be eliminated. After a single elimination the remaining rate equations are no longer linear so this transformation may not be repeated.

5.2 Collective Modes

The collective modes presented in chapter 4 may also be applied to this system. As in the secular approximation, each mode couples to a single collective excitation of molecules. Eq. (5.10) shows that each mode also couples to a superposition¹ of mode-molecule covariances. The mode-molecule covariances are linear in molecular terms, therefore the superposition of mode-molecule covariances may be combined into a single covariance between the mode and a collective excitation. For example the first term in Eq. (5.10) transforms as

$$\frac{d\langle n_p \rangle}{dt} = \sum_{j=0}^J C(n_p, f_j) \Lambda_{p,j}^\downarrow + \dots \rightarrow \frac{d\langle n_p \rangle}{dt} = W_p C_p^{(n,f)} + \dots , \tag{5.16}$$

where $C_p^{(n,f)}$ is the collective covariance coupled to mode p , and W_p is a constant. As in chapter 4, the sum over many covariances is replaced with a coupling to a single collective covariance. Furthermore the coupling between modes and molecules is identical to the coupling between modes and mode-molecule covariances, it is the mode wavefunction in both cases. Therefore the zeroth order collective covariances are the covariances between the modes and the zeroth order collective excitations.

¹Linear algebra superposition, not quantum superposition

The rate equations for the molecule excitation and mode-molecule covariances are structurally identical; the coupling between modes, molecules, and covariances is all mediated by either the absorption and emission, or is linear. As shown in chapter 4, the absorption and emission matrices have large null-spaces which prevent lower orders of collective excitations from being affected by higher orders of collective excitations. As the couplings, and therefore null spaces, in Eqs. (5.10), (5.11), and (5.12) are identical, the number and structure of collective covariances in each order will be similar to the number and structure of collective molecular excitations in that order. The difference between collective excitations and collective covariances is that each covariance contains information about which mode generated it. A collective covariance of mode p , in order r may couple to collective covariances in orders $r - 1$, r , and $r + 1$ only if those collective covariances also are of mode p . In contrast a collective excitation originating from mode p may couple to any other collective excitation. Therefore while the zeroth orders of collective excitations and collective covariances are identical the higher orders are not. The maximum number of collective excitations, of collective covariances in order r is M^r , where M is the number of modes. This is because each collective excitation in order r can in theory generate M independent vectors in order $r + 1$. As shown in chapter 4, this maximum is not reached as many of the generated vectors are dependent on each other. As the collective covariances generated by one mode may not interact with those of another mode, the reduction in the size of each order due to dependency begins one order later in collective covariances than in collective excitations. The number of collective covariances in order r is therefore approximately M times larger than the number of collective excitations in order r , for $r > 0$. The size of the system required to calculate the second order coherence over time is approximately $M + 1$ times larger than the systems required to calculate just the mode populations. As this calculation originally required MJ mode-molecule covariances (where J is the number of molecular bins) this is an excellent scaling of computational difficulty.

5.3 Computational Algebra

The rate equations used to calculate the second order coherence presented in this chapter are very lengthy, and evaluating them by hand is time consuming and will almost certainly result in error. This section presents the bespoke algorithms used to perform the operator algebra required to derive the rate equations (5.10), (5.11), (5.12), and (5.13). It is possible that packages exist which performing the required operator algebra, however the author was unimpressed by the capabilities of Mathematica and sympy, and found creating a bespoke system to be easier and more flexible. Readers uninterested in these details may skip to Sec. 5.4.

This section shall present how expressions are structured and stored, how they are rearranged and simplified, and how this allows the final form of the equations to be obtained. Any mathematical expression may be decomposed into terms, where each term may contain nested terms in a tree structure. For example $a + b + c \times (d + e)$ may be decomposed into the terms a , b , and $(c \times (d + e))$, where the final term may in turn be decomposed into c and $(d + e)$. Information about how these terms are to be combined i.e. addition or multiplication, allows the expression $a + b + c \times (d + e)$ to

be written as a computational function

$$a + b + c \times d = \text{add}(a, b, \text{mult}(c, \text{add}(d, e))) . \quad (5.17)$$

Due to the similar properties of many mathematical elements a object oriented structure is the best suited for programming the algebraic system. Each element in the equation is either an instance of one of the end classes: Number, Symbol, Operator, and Krönecker Delta, or is an instance of one of the structure classes: Trace, Summation, Addition, Multiplication, Fraction, Derivative, and Equation. The end classes contain information about the name of the symbol or operator along with any indices attached to it, or it contains the value of the number in the equation. The structure classes contain information about the terms nested within them. These classes allow the rate equations to be stored as a nested tree of objects, similar to Eq. (5.17).

Once an expression for the rate has been obtained it may be simplified using a series of basic rules. For example the product of two brackets $(a + b)(c + d)$ may be expanded into a sum of products $ac + ad + bc + bd$. The terms may also be rearranged, e.g. by bringing terms out of a summation if the do not contain the summed index. Various identities e.g. $\sum_{i=1}^N 1 = N$ are also used. Each rule need only be expressed as a short piece of code: if term matches pattern x , then change the term to pattern y . A simplification algorithm which uses these rules may then be applied recursively to each sub-term within a term. For example the simplification of $a + \text{Tr}(b)$ requires four simplification functions S , to cover all possible simplifications $S(S(a) + S(\text{Tr}(S(b))))$. This ensures that every level of an expression is in the most simple form. The simplification algorithm may be applied repeatedly to a term until that term does not change, at which point the simplification is complete. Due to the large number of terms it is important not to repeatedly simplify terms already in the simplified form, a flag is therefore added to each term when it is simplified to prevent further attempts at simplification.

Additional rules are required which are specific to the system in question and ensure that terms are represented systematically, which allows them to be easily combined. For example the expression $ab - ba$ is equal to zero if a and b are scalars, but this may only be computed if the symbols in the second term are rearranged to give $ab - ab$. The commutation rules are described by pairs of terms, and the commutator of each pair. Pairs of terms may then be looped through, and if any match a commutation rule they are commuted, and the commutator is added to the term. For example

$$b a a^\dagger c = b a^\dagger a c + b c . \quad (5.18)$$

Scalars which commute with everything are sorted alphabetically, which, along with commutation, ensures what two equal terms have the same form and may be easily combined. Replacement rules are identities which enable a group of terms to be replaced by an equivalent group, for example

$$\sigma_j^+ \sigma_j^- = f_j \quad (5.19)$$

eliminates the molecular raising and lowering operators introduced by the master equation. Finally the cyclicity of the trace is used to move the density matrix to the end of the trace.

The equations in terms of the absolute operators $\langle a_p^\dagger a_q^\dagger a_p a_q \rangle$ may be converted into equations of covariances using substitution code. This code searches the equations for terms matching a certain pattern

and replaces them with the appropriate covariances, ensuring that the indices are properly converted. The resulting equations may then be further simplified.

The final expressions may be easily converted into the latex code seen in this chapter, or into a variety of programming languages. This ensures that there are no mistakes in the derivations of the rate equations, and that there are no mistakes converting the equations between the programming language and latex. It also allows higher order covariances to be added to the system which would be exceedingly tedious to calculate by hand. The rate equations (5.4), and (5.6) have been independently calculated by hand to ensure that there are no bugs in the simplification program.

The simplification program along with the output equations as code are given in Appendix B.

5.4 Discussion

The equations presented in this chapter allow the efficient simulation of the second order coherence between modes both at steady state and over time. The steady state phase of the system discussed in Chapter 3 shows severe competition between modes which could dramatically enhance or suppress the inter-mode coherence. Due to the nature of mode competition it is expected that clamped modes are strongly anti-correlated with the clamping mode. Simulations investigating this could validate or advise ongoing experiments into inter-mode coherence.

The evolution of coherence may also be investigated to determine whether the dramatic retardation of mode population presented in Chapter 4 is also present in the coherence, and whether this adds an additional time scale to the evolution. It is unknown whether the change in coherence during condensation or decondensation is faster or slower than the change in mode population. For example, if a change in coherence between modes A and B requires changes in the populations of both A and B , then changes in coherence would be slower than changes in mode population. If, on the other hand, mode A affects the population in mode B via the inter-mode coherence, then a change in coherence would precede any change in the population of mode B .

The equations presented in this chapter represent an improvement in the accuracy of the equations used in the rest of this thesis. They will either verify the accuracy of existing models or uncover new, previously un-described phenomena which may be investigated. There are a variety of potential approximations which may be made, for example, if you are only interested in the correlations between two modes is it acceptable to discard the correlations between all other modes? Does the number of orders of collective covariances need to be identical to the number of orders of collective excitations in order to achieve satisfactory accuracy? The code provided in Appendix B also allows the addition of higher order correlations if the existing level of coherences is too unreliable.

Chapter 6

Transport

This chapter will study the steady state photon populations in different cavity shapes. The modes of these cavities will be localised and have limited spatial extent. In addition the cavities will be pumped with a narrow beam. The population of un-pumped modes may only be maintained by transport of photons across the cavity from pumped modes to un-pumped modes. The simple case of transport in a double square well will be analysed first before moving to a random potential. The clamping and thermalisation mechanisms discussed in the rest of this thesis have a significant effect on the degree of transport predicted for both cavity shapes. It is possible that photons may be transported across a cavity by the translation of molecules in between the absorption and emission steps, however this is not investigated here. This chapter contains important results but, due to time constraints, is an preliminary investigation only.

6.1 Double Well

The double potential well used is shown as a black line in Fig. 6.1 (left). The height and width of the potential was chosen so that only two modes were bound in each well, this reduces the complexity of the system, but maintain the potential for inter-mode coupling and clamping. The modes are shown overlapping in Fig. 6.1 (left) and shifted for clarity in Fig. 6.1 (right). The height of the left well was shifted relative to the right well by a factor of 1.2 to ensure that all modes have different frequencies, this is required by the derivation of the master equation in Chapter 2. The shift in height also ensures that the bound eigenstates are localised to a single well. The parameters used in the simulations presented in this section are given in Tab. 6.1. As frequencies of the cavity modes may be freely shifted and scaled by varying the length and width of the cavity, see Sec 1.7, the shape of the cavity is given in dimensionless units. The experimental practicality of creating the cavities in this section remains un-investigated. If creating the cavities is impractical then the insights gained from their theoretical study will still provide useful insight into the mechanism of photon transport.

The modes of a single harmonic potential Fig. 1.13, used in Chapters 3 and 4 have great spatial overlap. Given a sufficiently strong absorption and emission they will therefore thermalise and, in the BEC phase, the populations will follow a Bose-Einstein distribution. The modes localised to a single site in

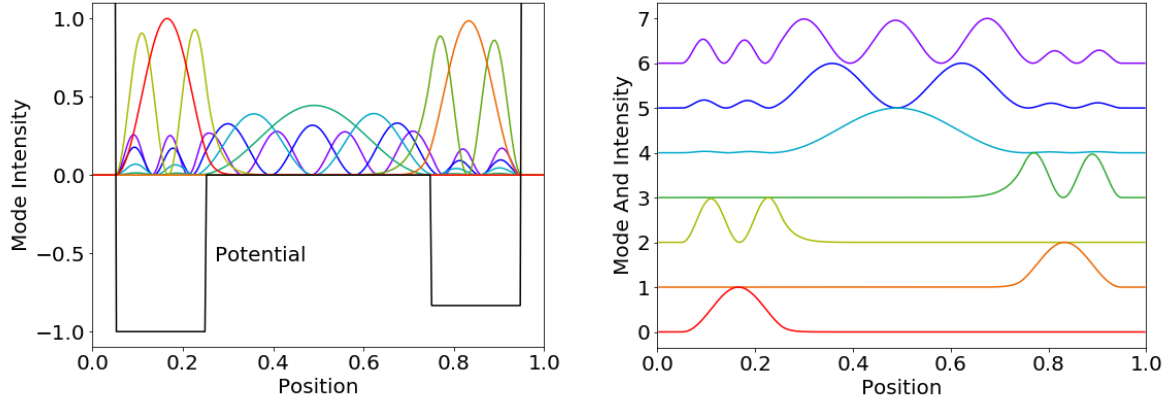


Figure 6.1: (LEFT) The normalised shape of the cavity and therefore the potential experienced by the photons is shown in black. The intensities of the lowest 7 modes of the cavity are shown coloured from red to purple in order of ascending frequency. Modes are normalised to the maximum mode intensity. (RIGHT) The individually normalised intensities of the modes, shifted for clarity.

Quantity	Symbol	Value
Cavity decay rate	κ	$1 \times \kappa$
Detuning of the lowest mode	δ_0	-39.8 THz
Spacing between the ground and 1st excited state in the left well	ϵ	4.77 THz
Free space emission	$\Gamma_{\downarrow}$	$\kappa/4$
1 dimensional density of molecules	ρ	$10^{12}/L$
Pump beam width	s	$0.1L$
Pump beam centre		$0.14L$
Number of modes		7
Cavity width	L	$1 \times L$
Well width		$L/5$
Absorption and Emission		Variable

Table 6.1: Default values used in double well simulations, unless otherwise specified.

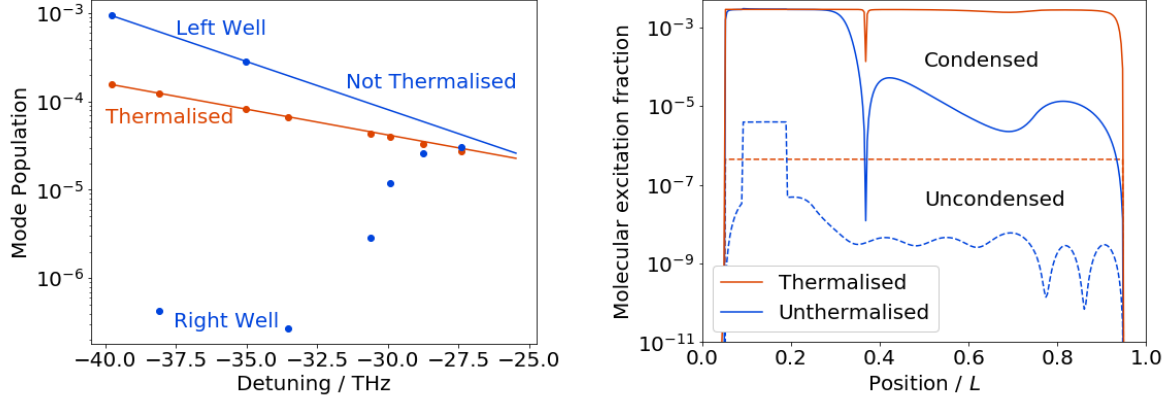


Figure 6.2: Dots show the steady state population in each mode as a function of mode frequency. The line shows a fit based on the modes of the left well. The system parameters are given in Tab. 6.1. (LEFT) An uncondensed system at low pump power, fits are generated from a Boltzmann distribution. The thermalised system has a thermalisation coefficient (see Chapter 3) $\gamma = \rho\Lambda_{\uparrow}^{[0,0]}/\kappa = 10^{12}$. The unthermalised system has a thermalisation coefficient $\gamma = 10^6$. Well labels indicate which well the nearby points belong in. (RIGHT) The molecular excitation fraction at steady state as a function of position in the cavity. The dashed lines correspond to the uncondensed system shown in Fig. 6.2 (left), and the solid lines correspond to the condensed system shown in Fig. 6.2 (right). The red/blue lines show the excitation of the thermalised/unthermalised system. The spikes in the condensed distributions are due to a minima of the condensed ground mode.

a double well potential do not overlap with the modes of the opposite well, and thermalisation is more complex. To test the degree of thermalisation the left well is pumped by a narrow square¹ beam of width $0.1L$ centred at $0.14L$, and the population of the right well is calculated. The populations produced by this simulation are shown in Fig. 6.2 (left) for two levels of thermalisation system parameters. The populations are produced by a weak pump $\Gamma_{\uparrow} = 4 \times 10^{-6}\Gamma_{\downarrow}$ which is insufficient to cause condensation. If the absorption and emission spectrum is stronger than losses from the system then the two wells will be thermalised and follow a single Bose-Einstein distribution, shown as the red lines in Fig. 6.2. Reduction of the absorption and emission spectrum causes losses to destroy the thermalisation between wells and the population in the right well does not follow the thermal distribution of population in the left well. The dashed lines in Fig. 6.2 (right) show the molecular excitation fraction as a function of position in the thermalised (red) and unthermalised cases (blue). The thermalised system exhibits a flat molecular excitation which provides a constant chemical potential to both wells, thereby generating a single Bose-Einstein distribution of mode population. In the unthermalised system the molecular excitation in the right well is reduced by losses, therefore a single Bose-Einstein of mode population is impossible.

The transport of an excitation from the left well to the right well may be tracked by defining a

¹Here a square distribution of x with width w and centre c is defined as $S(x) = \begin{cases} 1 & \text{if } |x - c| < w/2 \\ 0 & \text{otherwise} \end{cases}$

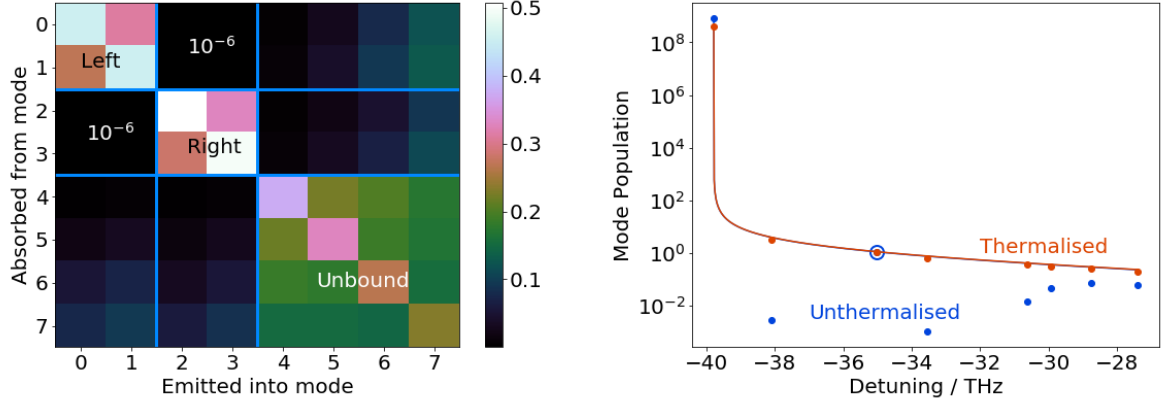


Figure 6.3: (LEFT) The coupling between modes, calculated using Eq. (6.2) for an uncondensed, thermalised system. The coupling is directional and the y axis indicates the mode giving photons to the mode indicated by the x axis. Blue lines delineate the modes bound to left and right wells, and the unbound modes of the cavity. The labels 10^{-6} indicate the approximate coupling between the left and right wells. The thermalisation coefficient is $\gamma = 10^{12}$, corresponding to the thermalised system shown in Fig. 6.2 (left). (RIGHT) a system just above threshold pump power, fits are generated from a Bose-Einstein distribution and overlap. The thermalised system has a thermalisation coefficient $\gamma = 10^6$ and the unthermalised system has a coefficient $\gamma = 10^2$. One of the points in the unthermalised system is drawn as a circle for clarity. Thermalisation is varied by directly changing the absorption and emission strength.

coupling between modes. The coupling $C_{i,l}$ from mode i to mode l may be defined as the probability that a molecule absorbing a photon from mode i will emit it into mode l . Given that a photon in mode i is absorbed, the probability that it was absorbed by a molecule between r and $r + dr$ is $P_i(r) = |\psi_i(r)|^2 dr$. The probability that this molecule will emit into mode l is

$$P_l(r) = \frac{|\psi_l(r)|^2 \Lambda_{\downarrow}^{(l)}(n_l + 1)}{\Gamma_{\downarrow} + \sum_m \Lambda_{\downarrow}^{(m)} |\psi_m(r)|^2 (n_m + 1)} . \quad (6.1)$$

Given a steady state with known mode populations the coupling from mode i to mode l may be calculated as

$$C_{i,l} = \int dr P_i(r) P_l(r) \quad (6.2)$$

$$C_{i,l} = \int dr |\psi_i(r)|^2 \frac{|\psi_l(r)|^2 \Lambda_{\downarrow}^{(l)}(n_l + 1)}{\Gamma_{\downarrow} + \sum_m \Lambda_{\downarrow}^{(m)} |\psi_m(r)|^2 (n_m + 1)} .$$

Note that this coupling is dependent on the mode population and will therefore change with the steady state of the system. The steady state population in the uncondensed system may be approximated as zero, and the coupling given in Eq. (6.2) will be dominated by stimulated emission. The uncondensed coupling matrix is plotted in Fig. 6.3 (left). The strong coupling on the block diagonal is expected as similar modes couple together. The probability of a photon in mode i travelling to the opposite well

²Assuming constant molecular density

via an unbound mode may be approximated as the sum over pairs of couplings multiplied together

$$P(\text{transfer}) \approx \sum_{u,b} C_{i,u} C_{u,b} , \quad (6.3)$$

where the sum is performed over unbound modes u , and the bound modes in the opposite well b . This is an approximation as there may be more than two transfers between modes, however probability these events decays exponentially with the number of transfers so they may be safely neglected. In the uncondensed system the probability of a transfer via the unbound modes is approximately 10^{-2} , which is far larger than the probability of direct re-emission into the opposite well. Transport in an uncondensed system is therefore facilitated by the unbound cavity modes. Including more unbound modes in the simulation will result in increased thermalisation between wells. Similarly, in an uncondensed system, experimentally increasing the number of unbound modes which have high intensities in both wells, and have strong absorption and emission coefficients will increase thermalisation.

The double well system also exhibits thermalised and un-thermalised condensed states, shown in Fig. 6.3 (right). As in the uncondensed case, strong thermalisation leads to a single Bose-Einstein distribution, whereas weak thermalisation allows losses to reduce the population in the right well. The spatial profile of molecular excitation Fig. 6.2 (right) in the condensed system shows the same pattern as the uncondensed system: the thermalised system exhibits a constant excitation, whereas the unthermalised system does not. The difference between the condensed and uncondensed systems lies in the mechanism of transporting photons. The coupling matrix Eq. (6.2) for a condensed system shows that the uncondensed modes mainly couple to the condensed mode, i.e.

$$C_{i,l} \approx \delta_{l,0} \quad \forall i \in \text{uncond} , \quad (6.4)$$

because the macroscopic population n_0 makes the fraction in Eq. (6.2) approximately one for $l = 0$ and zero otherwise. This dramatically reduces the coupling via the unbound modes (calculated using Eq. (6.3) and $i = 0$) from 0.023 in the uncondensed case to 6.0×10^{-12} in the condensed case. The direct transport of photons from the condensed mode to the right well is also reduced from 4.5×10^{-6} to 4.7×10^{-9} . The reduction in transport rates is offset by an increase in the number of photons in mode 0 which are available for transport, however the direct transport route has the smaller coupling in the uncondensed case and the larger coupling in the condensed case. Direct transport therefore dominates in the condensed case, and transport via unbound modes dominates in the uncondensed case. The enhanced direct transport alters the threshold absorption and emission strengths required for thermalisation: in the uncondensed system the thermalised and unthermalised plots in Fig. 6.2 (left) were generated with thermalisation coefficients $\gamma = \rho \Lambda_{\uparrow}^{[0,0]}/\kappa$ (see Chapter 3) of 10^{12} and 10^6 .³ The condensed system requires much smaller thermalisation coefficients to achieve the same degree of thermalisation: the plots of the condensed system in Fig. 6.3 (right) were generated with coefficients 10^2 and 10^6 . The relative occupation of the right well compared to the Bose-Einstein distribution generated by the left well is 7.2×10^{-4} in both the uncondensed unthermalised system and the condensed unthermalised system. The dramatic drop in thermalisation coefficient required to

³These rates are far higher than those in Chapter 3 because the modes in the left well do not spatially overlap the modes in the right well.

achieve the same level of thermalisation in the condensed system compared to the uncondensed system demonstrates that condensation greatly increases the rate of transport.

The frequency of the ground mode of the left well is lower than the ground mode of the right well. When the left well is pumped, thermalisation of the right well is straightforward. If the right well is pumped, however, then thermalisation would require the condensation in the left well and no condensation in the right, despite the lack of pumping in the left well. Which well or wells achieve condensation varies depending on the thermalisation, and it is therefore instructive to define a new thermalisation coefficient.

The thermalisation coefficient defined in Chapter 3 assumes that all modes approximately overlap and that a photon absorbed from one mode may be easily emitted into modes of a similar frequency. This is not the case for a double well which exhibits spatially separated bound modes linked by unbound modes. For the wells to be thermalised with each other, the chemical potential (excitation) of molecules in one well must equal the chemical potential in the other well. As one well is not pumped this only occurs at low pump powers if the unbound modes clamp the molecules in the un-pumped well and raise their excitation to approximately that of the pumped well. A transport coefficient of thermalisation between wells may therefore be defined as the ratio of molecular decay to emission into unbound (*unb.*) modes

$$\bar{\gamma} = \frac{\sum_{m \in \text{unb.}} \Lambda_{\downarrow}^{(m)} \langle |\psi_m(r)|^2 \rangle_r}{\Gamma_{\downarrow}}, \quad (6.5)$$

where spontaneous emission has been used due to the low occupancy of high frequency modes ($n_{\text{unb.}} \approx 0$), and $\langle |\psi_{\text{unb.}}(r)|^2 \rangle_r$ is the spatial average of the unbound mode profiles. If this ratio is large then molecules in the un-pumped well will be clamped, both wells will have a comparable chemical potential, and the wells will be thermalised. As the mode profiles are normalised and unbound modes span the entire cavity which has a length L , the average of the mode profiles is $\langle |\psi_{\text{unb.}}(r)|^2 \rangle_r = 1/L$, and the transport thermalisation coefficient may be written as

$$\bar{\gamma} = \frac{\sum_{m \in \text{unb.}} \Lambda_{\downarrow}^{(m)}}{\Gamma_{\downarrow} L}. \quad (6.6)$$

Fig. 6.4 (left) shows the phase of the double well system for a variety of transport thermalisation coefficients $\bar{\gamma}$ and a variety of pump rates where, as before, only the left well is pumped. When the wells are thermalised the left well condenses and not the right well, as the left well has a lower frequency. When the wells are not thermalised the right well condenses without the left well as the transport is insufficient to transfer the photons from the right well to the left well. At high pump powers and low thermalisation both wells condense because the population in the right well becomes large enough to start clamping the molecules in the left well, without the left well draining all the photons from the right well. The mode which condenses at the lowest pump power transitions from the ground mode of the right to the ground mode of the left well at a transport thermalisation coefficient of 1, which justifies the use of this measure at low pump powers. At higher pump powers it is less reliable due to the complex interactions of condensed modes. Fig. 6.4 (right) shows the population in each mode for the thermalised and unthermalised system. As expected the thermalised system shows a single Bose-Einstein distribution, whereas the unthermalised system shows two separate distributions.

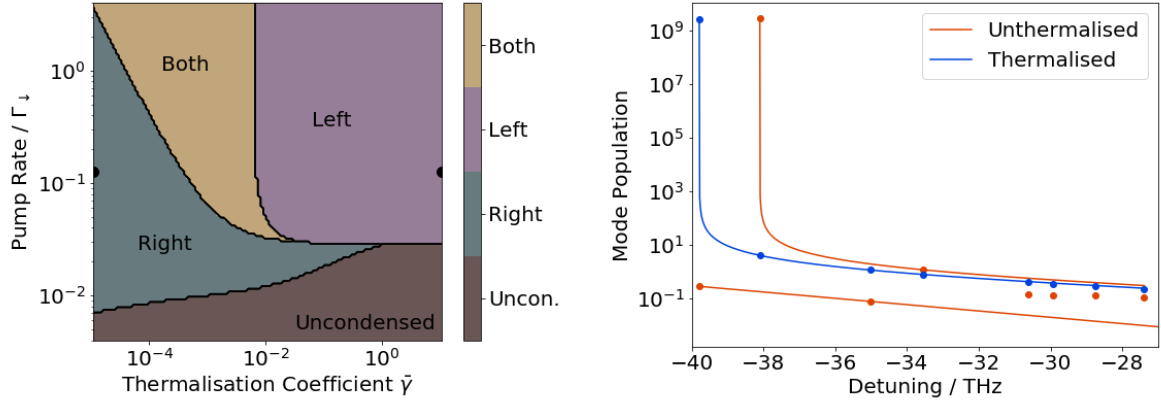


Figure 6.4: (LEFT) The phase of the double well system as the pump rate and absorption & emission strengths are varied. The transport thermalisation coefficient used is different to that used in Fig. 3.5, and is defined in Eq. (6.6). The right well is pumped, but the modes in the right well are higher in frequency than the left well. The labels indicate single mode condensation in the ground modes of either the ‘left’ or ‘right’ well, condensation in both ground modes ‘both’, or no condensation ‘uncondensed’. The black dots indicate the parameters used to generate the distributions shown in the right plot. Due to a similar but shifted distribution of mode populations to Fig. 3.4, the threshold condition for this system was chosen to be a mode population of $10^{3.5}$. The spectrum peaks used to generate this diagram ranged from $10^{-6}\kappa$ to 1κ . (RIGHT) The population in each mode as a function of detuning for a thermalised $\gamma = 10^9$ and unthermalised $\gamma = 10^3$ system. The lines are Bose-Einstein fits to the two modes in each well, the right well is not fitted in the thermalised case.

6.2 Random Potential

The previous section looked at the transport of photons via free, de-localised modes. Transport across a cavity is also possible through a chain of localised modes. The modes presented in this section are created from a potential with a random depth: the potential is defined at a series of points and the depth of each point is randomly drawn from an exponential distribution. This potential has been used to study Anderson localisation [121], however it is current unclear how relevant Anderson localisation will be in understanding this system, as the incoherent absorption and emission of photons by the dye is not a part of standard Anderson localisation theory. The lowest 100 modes created by this potential are shown in Fig 6.5.

Like the simulations of the double well, the pump used has a square profile centred on the left of the cavity, at position 0, with width 0.01. Photons in the majority of the cavity have therefore not been created by direct pumping, but have been transported from the left of the cavity via repeated absorption and emission. The largest width of a mode is approximately 0.1 cavity widths, therefore each photon which reaches the right side of the cavity must be absorbed and emitted at least 10 times. The steady state intensity and population in each mode is shown in Fig. 6.6. As the cavity loss rate is constant in position, the steady state intensity is directly proportional to the number of photons transported to that cavity position. There are a series of jumps in population as a function of position

which occur when by there are no modes spanning a spatial region.

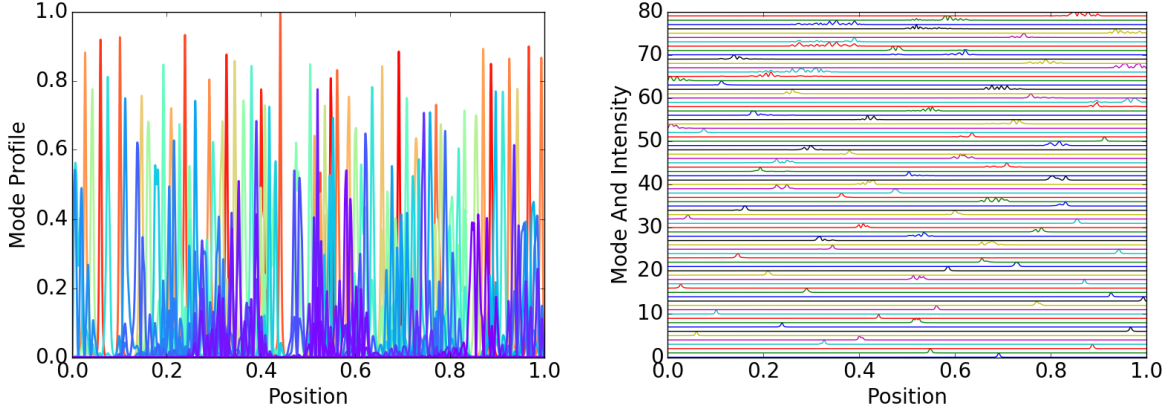


Figure 6.5: The modes used in the localisation simulations. (Left) The modes are plotted on the same axis and normalised to the maximum value. (Right) The modes are vertically shifted by $1 \times (\text{mode number})$, and independently normalised.

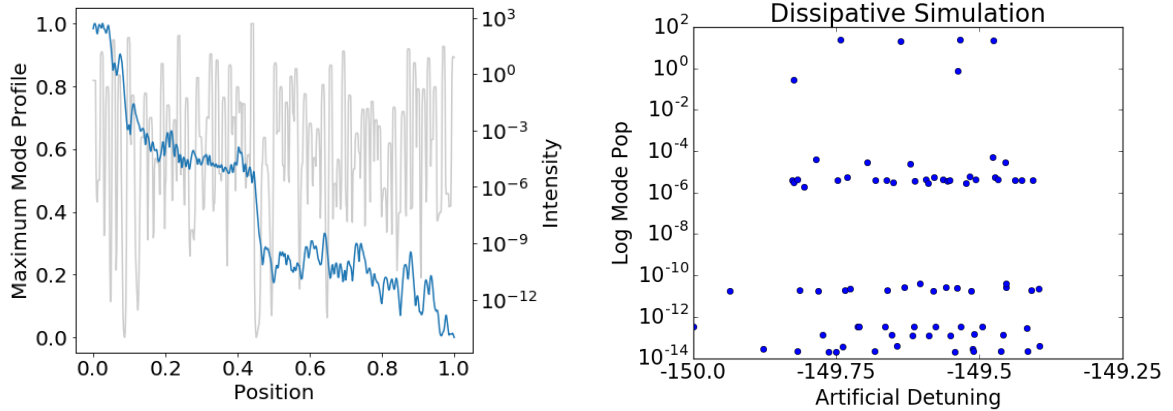


Figure 6.6: (Left) Blue line: the intensity as a function of position in the cavity. Grey line: the maximum mode profile at the cavity position. (Right) The population in each mode.

Transport occurs when a molecule on the right side of a mode absorbs a photon and re-emits it into a mode to the right⁴ of the original mode. Therefore if there is a spatial region not spanned by any modes then transport across this region is impossible. Sparsely populated regions always contain the tails of modes, however emission from these modes is reduced by the intensity of the mode on the far side of the region. As the tails of a mode typically reduce exponentially with distance, empty regions cause a large reduction in the transport of photons. Fig. 6.6(right) shows bands containing modes of similar population, and large empty gaps between bands. Each band corresponds to a spatial region of overlapping modes, leading to a well thermalised mode population. The gaps between bands suggest that any reduction in intensity across the cavity occurs due to low transport between spatial regions, and not transport within regions.

⁴On average, the modes must have some overlap.

As a toy model of the random potential cavity consider well thermalised groups of modes separated by gaps in space. Within a group there is enough spatial overlap that the rates of absorption and emission dominate loss, and the population is given by a thermal distribution. The spatial gaps are sufficiently large that loss dominates absorption and emission, therefore adjacent groups are not thermalised with each other. The population of a group may be modelled with a rate equation:

$$\frac{dn_i}{dt} = -\alpha_i n_i + R_i n_{i-1} + R_{i+1} n_{i+1} . \quad (6.7)$$

where α_i is the rate of loss from group i , R_i is the rate of transport into group i from group $i-1$, and n_i is the total population in group i . The loss rate α contains contributions from the transport rates R_i and R_{i+1} as photons are lost when transported to adjacent groups. As transport occurs from left to right, and the spatial gaps induce large decreases in population, the approximation $n_i \ll n_{i-1}$ may be made. The last term may therefore be neglected and the steady state population found:

$$n_i = \frac{R_i}{\alpha_i} n_{i-1} . \quad (6.8)$$

This equation may be substituted into itself recursively to give an equation for group population in terms of the population in the left-most group

$$n_i = \prod_{j=1}^i \frac{R_j}{\alpha_j} n_0 . \quad (6.9)$$

If the cavity is sufficiently large relative to the widths of the modes, and there are a large number of gaps, then transport across the cavity requires transport across many gaps. The gaps may be approximated by an average distribution of gaps without knowing the exact mode structure of the cavity. To calculate the number and the size of the gaps between group, the shape of a mode centred at x_0 with a constant width w is approximated as:

$$|\psi(x - x_0)|^2 = \begin{cases} B & |x| < w/2 \\ B e^{-||x-x_0|-w/2|/\lambda} & |x| > w/2 , \end{cases} \quad (6.10)$$

where λ is an average exponential rate of mode intensity decay, and B is a normalisation constant. A gap is defined to be a position in the cavity more than $w/2$ distant from the centre of any mode. The size of the gap between two modes is $g = x_0 - x_1 - w$ where x_0 and x_1 are the centres of each mode. As the cavity potential is randomly generated, the size and frequency of each g is unknown, but will follow a frequency distribution for a sufficiently large cavity. This distribution has yet to be derived, however many different cavities have been simulated to approximate the distribution. The frequency density of gaps between g and $g + dg$ wide is approximately exponential

$$f(g) dg = A e^{-ag} , \quad (6.11)$$

where the constants a and A may be expanded to give

$$f(g) dg = \frac{0.444M^2 + 11.01M}{8.08 \times 10^{-6}} e^{-0.436w/W} e^{-(0.444M+11.01)g/W} , \quad (6.12)$$

where M is the number of modes, and W is the width of the cavity. This distribution of gaps may be used to find the average rate of transport across the cavity. First Eq. (6.8) is written as

$$\log n_{end} = \log n_0 + \sum_j [\log R_j - \log \alpha_j] . \quad (6.13)$$

This allows the conversion of the sum over rates into an integral over the distribution of rates

$$\log n_{end} = \log n_0 - \sum_j \log \alpha_j + \int_0^\infty dg f(g) \log(R(g)) . \quad (6.14)$$

As the coupling between modes and molecules depends on the intensity of the mode, the transport rate may be related to the gap size via $R = R_0 e^{-g/\lambda}$, where R_0 is a base rate of coupling and λ is the decay of mode intensity profiles across gaps. Eq. (6.14) may therefore be written as

$$\log n_{end} = \log n_0 - \sum_j \log \alpha_j + R_0 N_g - \int_0^\infty dg f(g) \frac{g}{\lambda} , \quad (6.15)$$

where N_g is the total number of groups. The distribution of gap size, Eq. (6.12), may be substituted into Eq. (6.15) to give

$$\log n_{end} = \log n_0 - \sum_j \log \alpha_j + R_0 N_g - A \int_0^\infty dg e^{-ag} \frac{g}{\lambda} , \quad (6.16)$$

which may be simplified to

$$\log n_{end} = \log n_0 - \sum_j \log \alpha_j + R_0 N_g - \frac{A}{a^2 \lambda} . \quad (6.17)$$

As the transport between groups is slow, the loss rate α_j may be approximated as a constant cavity loss rate κ to give

$$\log n_{end} = \log n_0 - N_g \log \kappa + R_0 N_g - \frac{A}{a^2 \lambda} . \quad (6.18)$$

The logs may be removed leaving

$$n_{end} = \frac{n_0}{\kappa^{N_g}} e^{\left(R_0 N_g - \frac{A}{a^2 \lambda}\right)} . \quad (6.19)$$

This formula predicts a well defined spatial decay of population across the cavity, and has yet to be tested.

6.3 Optical Gate

Whether a mode is condensed is a convenient binary property of the mode. As shown in Fig. 3.4 it is easy to engineer a system where modes are either clearly condensed, or clearly uncondensed. This, in theory, allows optical circuits to be constructed. It is well established that any logic gate may be constructed from multiple NAND gates, which are defined as giving the output 1 unless both inputs are one. If, therefore, a reliable and scalable NAND gate may be produced, an optical processor may be made. Using condensation as a logical state requires a potential NAND gate to output a condensed system unless both inputs to the system are condensed. This requirement has already been seen in Chapter 3, where mode $[0, 1]$ decondensed under the combined clamping of modes $[0, 0]$ and $[0, 2]$. The

reader is advised to re-familiarise themselves with the clamping mechanism discussed in Sec. 3.1 before continuing.

The parabolic cavity used in Chapter 3 is unsuitable as a logic gate as the output light at a cavity position is a mixture of many modes. To function as a logic gate a cavity must independently allow the coupling of light into each of the input modes, and the independent coupling of light out of the output mode. An ideal mode structure for these requirements is shown in Fig. 6.7. External pumping of the output mode will, without interference, cause it to condense. If either input mode condenses then it will clamp one of the regions labelled C. If the input modes are a lower frequency than the output mode then the molecules in region C will be clamped to a value below the condensation threshold of the output mode, potentially causing it's decondensation. As shown in Chapter 3, it is possible to tune the mode frequencies and pumping to cause the decondensation of the output mode only if both input modes are condensed, thereby creating a NAND gate. A cavity shape which produces a similar mode structure to that shown in Fig. 6.7 is the double well shown in Fig. 6.1. The bound modes do not extend outside their respective wells, however each overlaps with the free modes. The free modes contain nodes in each well which may be used to pump the bound input modes without affecting the free output mode. The cavity shape may be adjusted to eliminate the other modes.

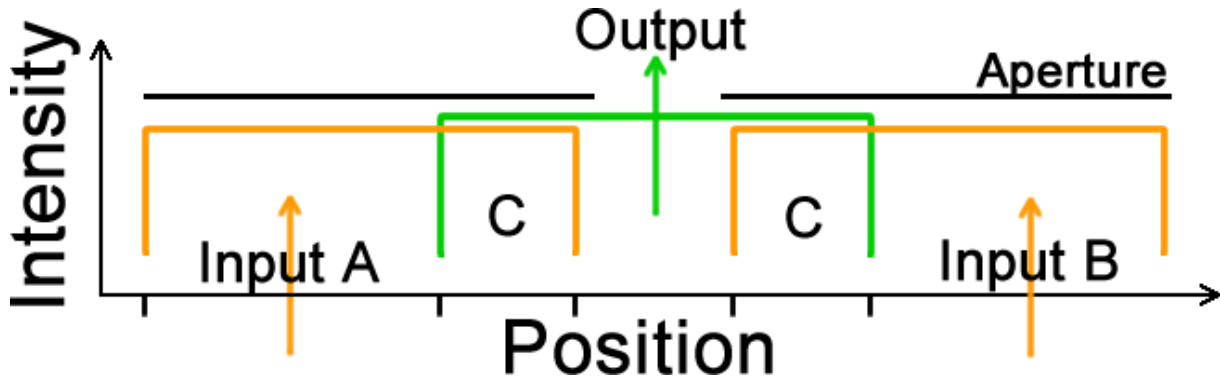


Figure 6.7: Idealised mode profiles used to create a NAND gate. Positions outside the central green mode are used as inputs. In regions labelled ‘C’ the input modes clamp the central mode. An aperture ensures that only light from the central mode leaves the cavity.

A logic gate constructed in this manner is almost certainly less useful than a silicon chip, however it serves as an example of the ways in which photon transport and novel cavity shapes may be used to create powerful effects.

6.4 Conclusion

The high degree of accuracy with which the transport thermalisation coefficient predicts the transition from right well condensation to left well condensation at low pump powers supports using coupling and clamping to model transport. The theory developed for a double well should be extended to more complex systems with complex interactions between multiple groups of modes. The exchange of condensation between wells as thermalisation is changed will become even more interesting as more groups of modes are included, and could yield many useful applications.

The analysis of transport across a cavity with a randomly shaped potential shows that transport across complex cavities may be treated using approximate models. The key features of the cavity may be identified by grouping modes together, and potentially incorporating the collective excitation profiles discussed in Chapter 4. The behaviour of these features allows properties of the cavity to be determined without having to simulate the large number of modes and groups of molecules. This allows larger and more complex cavities to be studied.

Chapter 7

Conclusion

7.1 Summary

This thesis has presented a detailed analysis of the theory behind photonic condensates and provided multiple insights into the creation and manipulation of different non-equilibrium phases of the light. The theory is built from the microscopic model presented in Chapter 2 and is thoroughly justified by its simple origins and excellent agreement with experimental results. The different presentations of the model are derived in detail, from equations which give the full evolution of a density matrix, to a model describing the probability distributions of its diagonal elements, and finally deriving rate equations for mode population and molecular excitation. Chapter 3 investigates the continuous transition from thermalised to un-thermalised condensates, and the effects this has on the condensate phase. The steady state decondensation phenomena is identified, and fully explained using the microscopic model. The evolution of the system towards these novel steady state phases is discussed in Chapter 4, which identifies a severe retardation of system evolution both close to, but also far from decondensation phase boundaries. The simulations presented in this chapter were only made possible by the transformation of the microscopic model into a basis of collective molecular modes, which may be used to reduce the system size by orders of magnitude. The derivation of this transformation is presented in full, and it is used to provide insight into multimode condensation via a graphical method of solving a system of two modes and two groups of molecules. Chapter 5 shows how the collective molecular excitations may also be applied to rate equations of correlation functions. The full derivation of these rate equations is provided in appendix B to allow the reader to compare their own derivations. The custom computer code used to generate these length equations is provided to allow higher order correlations to be studied in the future. Finally the transport of photons across double well, and random potential cavities is discussed. These examples demonstrate the ability of condensation in one cavity region to have dramatic effects on other cavity regions, even if the coupling between regions is weak, or only possible via intermediate modes.

7.2 Outlook

Many of the topics presented in this thesis reveal more questions than they have answered. The novel decondensation phenomena discussed in Chapter 3 has interesting implications when applied to more complex cavity shapes. Additionally decondensation may occur in a similar form in other types of condensates, in particular plasmonic condensates. The rich landscape of multimode phases may be experimentally explored to either justify the theory, or provide interesting deviations for further study. The multimode phase may also be simulated further by varying parameters other than the thermalisation rate, to find unusual parameter regimes leading to, for example, decondensation at low pump power, many different phases which are tightly packed in parameter space, or regions of high stability. The inter-mode and mode-molecule correlations may be investigated in all of the situations previously discussed, as its behaviour is mostly unknown. Additionally variation over time of both coherence and mode populations may be studied. Finally, different cavity shapes provide endless possibilities for creating new and unusual phenomena which may provide insight into the interaction of condensed modes, and may potentially yield useful applications.

Appendices

Appendix A

Analytic Boundaries

A.1 Analytic expressions for molecular overlap f_m within the BEC phase

When the system is in the BEC phase the steady state fraction of excited molecules overlapping a mode may be analytically calculated, as described in Sec. 3.2.1. The explicit forms of the Hermite-Gauss wavefunctions are required, see Sec. 1.7:

$$\begin{aligned}
 |\psi_{[0,0]}|^2 &= \frac{1}{\pi} \frac{1}{L^2} e^{-(x^2 + y^2)/L^2} \\
 |\psi_{[0,1]}|^2 &= 2 |\psi_{[0,0]}|^2 \frac{x^2}{L^2} \\
 |\psi_{[0,2]}|^2 &= \frac{1}{2} |\psi_{[0,0]}|^2 \left[4 \left(\frac{x}{L} \right)^4 - 4 \left(\frac{x}{L} \right)^2 + 1 \right] \\
 |\psi_{[0,3]}|^2 &= \frac{1}{3} |\psi_{[0,0]}|^2 \left[4 \left(\frac{x}{L} \right)^6 - 12 \left(\frac{x}{L} \right)^4 + 9 \left(\frac{x}{L} \right)^2 \right] .
 \end{aligned} \tag{A.1}$$

The molecular overlap for each mode, Eq. (3.11) may then be written as

$$\begin{aligned}
 f_{[0,0]} &= 2I_0 \\
 f_{[0,1]} &= 2I_2 \\
 f_{[0,2]} &= \frac{3}{2}I_4 - 2I_2 + I_0 \\
 f_{[0,3]} &= \frac{5}{6}I_6 - 3I_4 + 3I_2 ,
 \end{aligned} \tag{A.2}$$

where I_k is defined as

$$I_k = \frac{\Gamma_{\uparrow}}{\Gamma_{\downarrow}} \int dr \frac{1 + \sigma e^{-r^2}}{1 + \eta e^{-r^2}} r^{(k+1)} e^{-r^2} , \tag{A.3}$$

and

$$\begin{aligned}
 \sigma &= \frac{\Lambda_{\uparrow}^{[0,0]}}{\Gamma_{\uparrow}} \frac{n_{[0,0]}}{\pi L^2} , \\
 \eta &= \frac{\Lambda_{\downarrow}^{(0)}}{\Gamma_{\downarrow}} \frac{n_{[0,0]}}{\pi L^2} , \\
 r &= \frac{-(x^2 + y^2)}{L^2} .
 \end{aligned} \tag{A.4}$$

The integrals in Eq. (A.3) may be performed to give

$$\begin{aligned}
I_0 &= \frac{\Gamma_{\uparrow}}{2\eta\Gamma_{\downarrow}} \left[\sigma + \left(1 - \frac{\sigma}{\eta}\right) \log(1 + \eta) \right] \\
I_2 &= \frac{\Gamma_{\uparrow}}{2\eta\Gamma_{\downarrow}} \left(\sigma \left(1 - \frac{\pi^2}{6\eta}\right) - \text{Li}_2(-\eta) + \right. \\
&\quad \left. \frac{\sigma}{\eta} \left(\frac{\log(1 + \eta)}{2} \log \left(\frac{1 + \eta}{\eta^2} \right) + \text{Li}_2 \left(\frac{1}{1 + \eta} \right) \right) \right) \\
I_4 &= \frac{\Gamma_{\uparrow}}{\eta\Gamma_{\downarrow}} \left(\sigma - \frac{1 - \sigma}{\eta} \text{Li}_3(-\eta) \right) \\
I_6 &= \frac{3\Gamma_{\uparrow}}{\eta\Gamma_{\downarrow}} \left(\sigma - \frac{1 - \sigma}{\eta} \text{Li}_4(-\eta) \right) ,
\end{aligned} \tag{A.5}$$

where the polylogarithm function is defined as

$$\text{Li}_j(x) = \sum_{i=1}^{\infty} \frac{x^i}{i^j} . \tag{A.6}$$

As described in section 3.2.1, the Eqs. (A.5) may be transcendently solved to find the population in the ground mode, and thence the population in the other modes. Attempts to approximate Eqs. (A.5) have failed because the relative magnitudes of the variables σ and η change considerably along the phase boundary.

Appendix B

Higher Order Correlation Code

This appendix contains lengthy derivations of the equations presented in Chapter 5, the code used to generate the equations Sec. B.2, and the equations themselves in a form a computer can interpret.

B.1 Human Derivation

The rate equations are best derived term by term to keep the size manageable. Hopefully these equations are equivalent to those presented in chapter 5, if there are any discrepancies then the equations derived by the computer should be assumed correct. The notation $A =^x B$ indicates that B is equal to the terms in A proportional to x . Equivalently $B = x \frac{dA}{dx}$. The method of solving the equation is identical for each rate equation, and for each term:

1. Insert the master equation into $\frac{d\langle O \rangle}{dt} = \text{Tr}[O\dot{\rho}]$, where O is the desired operator.
2. Pick a Lindblad term and ignore the others.
3. Expand the Lindblad.
4. Use the cyclicity of the trace to order the terms identically according to their types: photon operators, density matrix, and molecule operators.
5. Use commutation relations to change the form of the first two terms into the form of the last term.
6. Cancel these terms and simplify the remainder.

The rate equation for mode population is therefore

$$\frac{d\langle a_k^\dagger a_k \rangle}{dt} =^\delta -i \sum_m \delta_m \text{Tr} \left[a_k^\dagger a_k a_m^\dagger a_m \rho - a_k^\dagger a_k \rho a_m^\dagger a_m \right] = 0 \quad (\text{B.1})$$

$$\begin{aligned} \frac{d\langle a_k^\dagger a_k \rangle}{dt} &=^\kappa -\frac{\kappa}{2} \sum_m \text{Tr} \left[a_k^\dagger a_k a_m^\dagger a_m \rho + a_k^\dagger a_k \rho a_m^\dagger a_m - 2a_k^\dagger a_k a_m \rho a_m^\dagger \right] \\ &=^\kappa -\frac{\kappa}{2} \sum_{m \neq k} \text{Tr} \left[a_k^\dagger a_k a_m^\dagger a_m \rho + a_k^\dagger a_k a_m^\dagger a_m \rho - 2a_k^\dagger a_k a_m^\dagger a_m \rho \right] - \frac{\kappa}{2} \text{Tr} \left[a_k^\dagger a_k a_k^\dagger a_k \rho + a_k^\dagger a_k a_k^\dagger a_k \rho - 2a_k^\dagger a_k^\dagger a_k a_k \rho \right] \\ &=^\kappa -\kappa \text{Tr} \left[a_k^\dagger [a_k, a_k^\dagger] a_k \rho \right] \\ &=^\kappa -\kappa \text{Tr} \left[a_k^\dagger a_k \rho \right] = -\kappa \langle a_k^\dagger a_k \rangle \end{aligned} \quad (\text{B.2})$$

$$\begin{aligned}
\frac{d\langle a_k^\dagger a_k \rangle}{dt} &= \Lambda_\uparrow - \sum_{m,j} \frac{\Lambda_\uparrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_k a_m^\dagger a_m \sigma_j^- \sigma_j^+ \rho + a_k^\dagger a_k \rho a_m^\dagger a_m \sigma_j^- \sigma_j^+ - 2a_k^\dagger a_k a_m \sigma_j^+ \rho a_m^\dagger \sigma_j^- \right] \\
&= \Lambda_\uparrow - \sum_{m,j} \frac{\Lambda_\uparrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_k a_m^\dagger a_m \rho \sigma_j^- \sigma_j^+ + a_m^\dagger a_m a_k^\dagger a_k \rho \sigma_j^- \sigma_j^+ - 2a_m^\dagger a_k^\dagger a_k a_m \rho \sigma_j^- \sigma_j^+ \right] \\
&= \Lambda_\uparrow - \sum_j \frac{\Lambda_\uparrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_k a_k^\dagger a_k \rho \sigma_j^- \sigma_j^+ + a_k^\dagger a_k a_k^\dagger a_k \rho \sigma_j^- \sigma_j^+ - 2a_k^\dagger a_k^\dagger a_k a_k \rho \sigma_j^- \sigma_j^+ \right] \\
&= \Lambda_\uparrow - \sum_j \Lambda_\uparrow^{(m)} \text{Tr} \left[a_k^\dagger a_k \sigma_j^- \sigma_j^+ \rho \right], \quad \sigma_j^- \sigma_j^+ = \frac{1 - \sigma_j^z}{2} \\
&= \Lambda_\uparrow - \sum_j \frac{\Lambda_\uparrow^{(m)}}{2} \langle a_k^\dagger a_k (1 - \sigma_j^z) \rangle
\end{aligned} \tag{B.3}$$

$$\begin{aligned}
\frac{d\langle a_k^\dagger a_k \rangle}{dt} &= \Lambda_\downarrow - \sum_{m,j} \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_k a_m a_m^\dagger \sigma_j^+ \sigma_j^- \rho + a_k^\dagger a_k \rho a_m a_m^\dagger \sigma_j^+ \sigma_j^- - 2a_k^\dagger a_k a_m^\dagger \sigma_j^- \rho a_m \sigma_j^+ \right] \\
&= \Lambda_\downarrow - \sum_j \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_k a_k a_k^\dagger \rho \sigma_j^+ \sigma_j^- + a_k a_k^\dagger a_k^\dagger a_k \rho \sigma_j^+ \sigma_j^- - 2a_k a_k^\dagger a_k a_k^\dagger \rho \sigma_j^+ \sigma_j^- \right] \\
&= \Lambda_\downarrow - \sum_j \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[[a_k^\dagger, a_k] a_k a_k^\dagger \rho \sigma_j^+ \sigma_j^- + a_k a_k^\dagger [a_k^\dagger, a_k] \rho \sigma_j^+ \sigma_j^- \right] \\
&= \Lambda_\downarrow \sum_j \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[2a_k a_k^\dagger \rho \sigma_j^+ \sigma_j^- \right] \\
&= \Lambda_\downarrow \sum_j \frac{\Lambda_\downarrow^{(m)}}{2} \langle (a_k^\dagger a_k + 1)(1 + \sigma_j^z) \rangle
\end{aligned} \tag{B.4}$$

which may be combined into

$$\frac{d\langle n_k \rangle}{dt} = -\kappa \langle n_k \rangle - \sum_j \frac{\Lambda_\uparrow^{(k)}}{2} \langle n_k (1 - \sigma_j^z) \rangle + \sum_j \frac{\Lambda_\downarrow^{(k)}}{2} \langle (n_k + 1)(1 + \sigma_j^z) \rangle \tag{B.5}$$

The equation for molecular excitation may be treated identically. Note that sums are omitted and j is used because any term which commutes with the argument of a Lindblad gives zero when traced over.

$$\begin{aligned}
\frac{d\sigma_j^z}{dt} &= \Gamma_\uparrow - \frac{\Gamma_\uparrow}{2} \text{Tr} \left[\sigma_j^z \sigma_j^- \sigma_j^+ \rho + \sigma_j^z \rho \sigma_j^- \sigma_j^+ - 2\sigma_j^z \sigma_j^+ \rho \sigma_j^- \right] \\
&= \Gamma_\uparrow - \frac{\Gamma_\uparrow}{2} \text{Tr} \left[\sigma_j^z \sigma_j^- \sigma_j^+ \rho + \sigma_j^- \sigma_j^+ \sigma_j^z \rho - 2\sigma_j^- \sigma_j^z \sigma_j^+ \rho \right] \\
&= \Gamma_\uparrow - \frac{\Gamma_\uparrow}{2} \text{Tr} \left[[\sigma_j^z, \sigma_j^-] \sigma_j^+ \rho + \sigma_j^- [\sigma_j^+, \sigma_j^z] \rho \right] \\
&= \Gamma_\uparrow - \Gamma_\uparrow \text{Tr} \left[-\sigma_j^- \sigma_j^+ \rho - \sigma_j^- \sigma_j^+ \rho \right] \\
&= \Gamma_\uparrow 2\Gamma_\uparrow \langle \sigma_j^- \sigma_j^+ \rangle \\
&= \Gamma_\uparrow \Gamma_\uparrow (1 - \langle \sigma_j^z \rangle)
\end{aligned} \tag{B.6}$$

$$\begin{aligned}
\frac{d\langle\sigma_j^z\rangle}{dt} &= \Gamma_\downarrow - \frac{\Gamma_\downarrow}{2} \text{Tr} [\sigma_j^z \sigma_j^+ \sigma_j^- \rho + \sigma_j^z \rho \sigma_j^+ \sigma_j^- - 2\sigma_j^z \sigma_j^- \rho \sigma_j^+] \\
&= \Gamma_\downarrow - \frac{\Gamma_\downarrow}{2} \text{Tr} [\sigma_j^z \sigma_j^+ \sigma_j^- \rho + \sigma_j^+ \sigma_j^- \sigma_j^z \rho - 2\sigma_j^+ \sigma_j^z \sigma_j^- \rho] \\
&= \Gamma_\downarrow - \frac{\Gamma_\downarrow}{2} \text{Tr} [[\sigma_j^z, \sigma_j^+] \sigma_j^- \rho + \sigma_j^+ [\sigma_j^-, \sigma_j^z] \rho] \\
&= \Gamma_\downarrow - \frac{\Gamma_\downarrow}{2} \text{Tr} [\sigma_j^+ \sigma_j^- \rho + \sigma_j^+ \sigma_j^- \rho] \\
&= \Gamma_\downarrow - \Gamma_\downarrow \text{Tr} [\sigma_j^+ \sigma_j^- \rho + \sigma_j^+ \sigma_j^- \rho] \\
&= \Gamma_\downarrow - \Gamma_\downarrow (1 + \langle\sigma_j^z\rangle)
\end{aligned} \tag{B.7}$$

$$\begin{aligned}
\frac{d\langle\sigma_j^z\rangle}{dt} &= \Lambda_\uparrow - \sum_m \frac{\Lambda_\uparrow^{(m)}}{2} \text{Tr} [\sigma_j^z a_m^\dagger \sigma_j^- a_m \sigma_j^+ \rho + \sigma_j^z \rho a_m^\dagger \sigma_j^- a_m \sigma_j^+ - 2\sigma_j^z a_m \sigma_j^+ \rho a_m^\dagger \sigma_j^-] \\
&= \Lambda_\uparrow \sum_m \Lambda_\uparrow^{(m)} \langle a_m^\dagger a_m (1 - \sigma_j^z) \rangle
\end{aligned} \tag{B.8}$$

$$\begin{aligned}
\frac{d\langle\sigma_j^z\rangle}{dt} &= \Lambda_\downarrow - \sum_m \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} [\sigma_j^z a_m \sigma_j^+ a_m^\dagger \sigma_j^- \rho + \sigma_j^z \rho a_m \sigma_j^+ a_m^\dagger \sigma_j^- - 2\sigma_j^z a_m^\dagger \sigma_j^- \rho a_m \sigma_j^+] \\
&= \Lambda_\downarrow - \sum_m \Lambda_\downarrow^{(m)} \langle (a_m^\dagger a_m + 1)(1 + \sigma_j^z) \rangle
\end{aligned} \tag{B.9}$$

$$\frac{d\langle\sigma_j^z\rangle}{dt} = \Gamma_\uparrow (1 - \langle\sigma_j^z\rangle) - \Gamma_\downarrow (1 + \langle\sigma_j^z\rangle) + \sum_m \Lambda_\uparrow^{(m)} \langle n_m (1 - \sigma_j^z) \rangle - \sum_m \Lambda_\downarrow^{(m)} \langle (n_m + 1)(1 + \sigma_j^z) \rangle \tag{B.10}$$

The equation for $\langle a_k^\dagger a_l^\dagger a_l a_k \rangle$ is:

$$\begin{aligned}
\frac{d\langle a_k^\dagger a_l^\dagger a_l a_k \rangle}{dt} &=^\delta - i \sum_m \delta_m \left(\text{Tr} [a_k^\dagger a_l^\dagger a_l a_k a_m^\dagger a_m \rho] - \text{Tr} [a_k^\dagger a_l^\dagger a_l a_k \rho a_m^\dagger a_m] \right) \\
&=^\delta - i \sum_m \delta_m \left(\text{Tr} [a_k^\dagger a_l^\dagger a_l a_k a_m^\dagger a_m \rho] - \text{Tr} [a_m^\dagger a_m a_k^\dagger a_l^\dagger a_l a_k \rho] \right)
\end{aligned} \tag{B.11}$$

If $k = l = m$

$$\begin{aligned}
\frac{d\langle a_k^\dagger a_l^\dagger a_l a_k \rangle}{dt} &=^\delta - i \sum_m \delta_m \left(\text{Tr} [a_k^\dagger a_k^\dagger a_k a_k a_k^\dagger a_k \rho] - \text{Tr} [a_k^\dagger a_k a_k^\dagger a_k^\dagger a_k a_k \rho] \right) \\
&=^\delta - i \sum_m \delta_m \left(\text{Tr} [a_k^\dagger a_k^\dagger a_k a_k a_k^\dagger a_k \rho] + \text{Tr} [a_k^\dagger a_k^\dagger a_k a_k \rho] - \text{Tr} [a_k^\dagger a_k^\dagger a_k a_k^\dagger a_k a_k \rho] - \text{Tr} [a_k^\dagger a_k^\dagger a_k a_k \rho] \right) = 0
\end{aligned} \tag{B.12}$$

If $k = m \neq l$

$$\frac{d\langle a_k^\dagger a_l^\dagger a_l a_k \rangle}{dt} =^\delta - i \sum_m \delta_m \left(\text{Tr} [a_k^\dagger a_l^\dagger a_l a_k a_k^\dagger a_k \rho] - \text{Tr} [a_k^\dagger a_k a_k^\dagger a_l^\dagger a_l a_k \rho] \right) = 0 \tag{B.13}$$

If $k \neq m = l$

$$\frac{d\langle a_k^\dagger a_l^\dagger a_l a_k \rangle}{dt} =^\delta - i \sum_m \delta_m \left(\text{Tr} [a_k^\dagger a_l^\dagger a_l a_k a_l^\dagger a_l \rho] - \text{Tr} [a_l^\dagger a_l a_k^\dagger a_l^\dagger a_l a_k \rho] \right) = 0 \tag{B.14}$$

$$\begin{aligned}
\frac{d\langle a_k^\dagger a_l^\dagger a_l a_k \rangle}{dt} &=^\kappa -\frac{\kappa}{2} \sum_m \text{Tr} \left[a_k^\dagger a_l^\dagger a_l a_k a_m^\dagger a_m \rho + a_k^\dagger a_l^\dagger a_l a_k \rho a_m^\dagger a_m - 2a_k^\dagger a_l^\dagger a_l a_k a_m \rho a_m^\dagger \right] \\
&=^\kappa -\frac{\kappa}{2} \sum_m \text{Tr} \left[a_k^\dagger a_l^\dagger a_l a_k a_m^\dagger a_m \rho + a_m^\dagger a_m a_k^\dagger a_l^\dagger a_l a_k \rho - 2a_m^\dagger a_k^\dagger a_l^\dagger a_l a_k a_m \rho \right] \\
&=^\kappa -\frac{\kappa}{2} \sum_m \text{Tr} \left[a_k^\dagger a_l^\dagger a_l a_m^\dagger a_k a_m \rho + \delta_{m,k} a_k^\dagger a_l^\dagger a_l a_m \rho + a_m^\dagger a_k^\dagger a_m a_l^\dagger a_l a_k \rho + \delta_{m,k} a_m^\dagger a_l^\dagger a_l a_k \rho \right. \\
&\quad \left. + -2a_m^\dagger a_k^\dagger a_l^\dagger a_l a_k a_m \rho \right] \\
&=^\kappa -\frac{\kappa}{2} \sum_m \text{Tr} \left[a_k^\dagger a_l^\dagger a_m^\dagger a_l a_k a_m \rho + \delta_{l,m} a_k^\dagger a_l^\dagger a_k a_m \rho + \delta_{m,k} a_k^\dagger a_l^\dagger a_l a_m \rho + a_m^\dagger a_k^\dagger a_l^\dagger a_m a_l a_k \rho \right. \\
&\quad \left. + \delta_{m,l} a_m^\dagger a_k^\dagger a_l a_k \rho + \delta_{m,k} a_m^\dagger a_l^\dagger a_l a_k \rho - 2a_m^\dagger a_k^\dagger a_l^\dagger a_l a_k a_m \rho \right] \\
&=^\kappa -\frac{\kappa}{2} \text{Tr} \left[a_k^\dagger a_l^\dagger a_k a_l \rho + a_k^\dagger a_l^\dagger a_l a_k \rho + a_l^\dagger a_k^\dagger a_l a_k \rho + a_k^\dagger a_l^\dagger a_l a_k \rho \right] \\
&=^\kappa -2\kappa \text{Tr} \left[a_k^\dagger a_l^\dagger a_l a_k \rho \right]
\end{aligned} \tag{B.15}$$

$$\frac{d\langle a_k^\dagger a_l^\dagger a_l a_k \rangle}{dt} =^{\Lambda_\uparrow} -\sum_{m,j} \frac{\Lambda_\uparrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_l^\dagger a_l a_k a_m^\dagger a_m \sigma_j^- \sigma_j^+ \rho + a_k^\dagger a_l^\dagger a_l a_k \rho a_m^\dagger a_m \sigma_j^- \sigma_j^+ - 2a_k^\dagger a_l^\dagger a_l a_k a_m \sigma_j^+ \rho a_m^\dagger \sigma_j^- \right] \tag{B.16}$$

This is similar to the κ term, therefore

$$\begin{aligned}
\frac{d\langle a_k^\dagger a_l^\dagger a_l a_k \rangle}{dt} &=^{\Lambda_\uparrow} -\sum_j (\Lambda_\uparrow^{(k)} + \Lambda_\uparrow^{(l)}) \text{Tr} \left[a_k^\dagger a_l^\dagger a_l a_k \sigma_j^- \sigma_j^+ \rho \right] \quad ; \quad \sigma_j^- \sigma_j^+ = \frac{1 - \sigma_j^z}{2} \\
&=^{\Lambda_\uparrow} -\sum_j (\Lambda_\uparrow^{(k)} + \Lambda_\uparrow^{(l)}) \text{Tr} \left[a_k^\dagger a_l^\dagger a_l a_k \frac{1 - \sigma_j^z}{2} \rho \right]
\end{aligned} \tag{B.17}$$

$$\begin{aligned}
\frac{d\langle a_k^\dagger a_l^\dagger a_l a_k \rangle}{dt} &= \Lambda_\downarrow - \sum_{m,j} \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_l^\dagger a_l a_k a_m a_m^\dagger \sigma_j^+ \sigma_j^- \rho + a_k^\dagger a_l^\dagger a_l a_k \rho a_m a_m^\dagger \sigma_j^+ \sigma_j^- - 2a_k^\dagger a_l^\dagger a_l a_k a_m^\dagger \sigma_j^- \rho a_m \sigma_j^+ \right] \\
&= \Lambda_\downarrow - \sum_{m,j} \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_l^\dagger a_l a_k a_m a_m^\dagger \rho \sigma_j^+ \sigma_j^- + a_m a_m^\dagger a_k^\dagger a_l^\dagger a_l a_k \rho \sigma_j^+ \sigma_j^- - 2a_m a_k^\dagger a_l^\dagger a_l a_k a_m^\dagger \rho \sigma_j^+ \sigma_j^- \right] \\
&= \Lambda_\downarrow - \sum_{m,j} \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_m a_l^\dagger a_l a_k a_m^\dagger \rho \sigma_j^+ \sigma_j^- - \delta_{m,l} a_k^\dagger a_l a_k a_m^\dagger \rho \sigma_j^+ \sigma_j^- + a_m a_k^\dagger a_l^\dagger a_l a_m^\dagger a_k \rho \sigma_j^+ \sigma_j^- \right. \\
&\quad \left. + -\delta_{m,l} a_m a_k^\dagger a_l^\dagger a_k \rho \sigma_j^+ \sigma_j^- - 2a_m a_k^\dagger a_l^\dagger a_l a_k a_m^\dagger \rho \sigma_j^+ \sigma_j^- \right] \\
&= \Lambda_\downarrow - \sum_{m,j} \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[a_m a_k^\dagger a_l^\dagger a_l a_k a_m^\dagger \rho \sigma_j^+ \sigma_j^- - \delta_{m,k} a_l^\dagger a_l a_k a_m^\dagger \rho \sigma_j^+ \sigma_j^- \right. \\
&\quad \left. + -\delta_{m,l} a_k^\dagger a_l a_k a_m^\dagger \rho \sigma_j^+ \sigma_j^- + a_m a_k^\dagger a_l^\dagger a_l a_k a_m^\dagger \rho \sigma_j^+ \sigma_j^- - \delta_{m,k} a_m a_k^\dagger a_l^\dagger a_l \rho \sigma_j^+ \sigma_j^- - \delta_{m,l} a_m a_k^\dagger a_l^\dagger a_k \rho \sigma_j^+ \sigma_j^- \right. \\
&\quad \left. + -2a_m a_k^\dagger a_l^\dagger a_l a_k a_m^\dagger \rho \sigma_j^+ \sigma_j^- \right] \\
&= \Lambda_\downarrow - \sum_j \frac{1}{2} \text{Tr} \left[-\Lambda_\downarrow^{(k)} a_l^\dagger a_l a_k a_k^\dagger \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(l)} a_k^\dagger a_l a_k a_l^\dagger \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(k)} a_k a_k^\dagger a_l^\dagger a_l \rho \sigma_j^+ \sigma_j^- \right. \\
&\quad \left. + -\Lambda_\downarrow^{(l)} a_l a_k^\dagger a_l^\dagger a_k \rho \sigma_j^+ \sigma_j^- \right] \\
&= \Lambda_\downarrow - \sum_j \frac{1}{2} \text{Tr} \left[-\Lambda_\downarrow^{(k)} a_l^\dagger a_l a_k^\dagger a_k \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(k)} a_l^\dagger a_l \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(l)} a_k^\dagger a_l a_l^\dagger a_k \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(l)} \delta_{k,l} a_k^\dagger a_l \rho \sigma_j^+ \sigma_j^- \right. \\
&\quad \left. + -\Lambda_\downarrow^{(k)} a_k^\dagger a_k a_l^\dagger a_l \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(k)} a_l^\dagger a_l \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(l)} a_k^\dagger a_l a_l^\dagger a_k \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(l)} \delta_{k,l} a_l^\dagger a_k \rho \sigma_j^+ \sigma_j^- \right] \\
&= \Lambda_\downarrow - \sum_j \frac{1}{2} \text{Tr} \left[-\Lambda_\downarrow^{(k)} a_l^\dagger a_k^\dagger a_l a_k \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(k)} \delta_{k,l} a_l^\dagger a_k \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(l)} a_k^\dagger a_l^\dagger a_l a_k \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(l)} a_k^\dagger a_k \rho \sigma_j^+ \sigma_j^- \right. \\
&\quad \left. + -\Lambda_\downarrow^{(k)} a_k^\dagger a_l^\dagger a_k a_l \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(k)} \delta_{k,l} a_k^\dagger a_l \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(l)} a_k^\dagger a_l^\dagger a_l a_k \rho \sigma_j^+ \sigma_j^- - \Lambda_\downarrow^{(l)} a_k^\dagger a_k \rho \sigma_j^+ \sigma_j^- \right. \\
&\quad \left. + -2\delta_{k,l} \Lambda_\downarrow^{(l)} a_l^\dagger a_k \rho \sigma_j^+ \sigma_j^- - 2\Lambda_\downarrow^{(k)} a_l^\dagger a_l \rho \sigma_j^+ \sigma_j^- \right] \\
&= \Lambda_\downarrow - \sum_j \frac{1}{2} \text{Tr} \left[-2(\Lambda_\downarrow^{(k)} + \Lambda_\downarrow^{(l)}) a_k^\dagger a_l^\dagger a_l a_k \rho \sigma_j^+ \sigma_j^- - 2(\Lambda_\downarrow^{(k)} + \Lambda_\downarrow^{(l)}) \delta_{k,l} a_l^\dagger a_k \rho \sigma_j^+ \sigma_j^- \right. \\
&\quad \left. + -2\Lambda_\downarrow^{(l)} a_k^\dagger a_k \rho \sigma_j^+ \sigma_j^- - 2\Lambda_\downarrow^{(k)} a_l^\dagger a_l \rho \sigma_j^+ \sigma_j^- \right] ; \sigma_j^+ \sigma_j^- = \frac{1 + \sigma_j^z}{2} \\
&= \Lambda_\downarrow \sum_j \text{Tr} \left[(\Lambda_\downarrow^{(k)} + \Lambda_\downarrow^{(l)}) a_k^\dagger a_l^\dagger a_l a_k \rho \frac{1 + \sigma_j^z}{2} + (\Lambda_\downarrow^{(k)} + \Lambda_\downarrow^{(l)}) \delta_{l,k} a_k^\dagger a_k \rho \frac{1 + \sigma_j^z}{2} \right. \\
&\quad \left. + +\Lambda_\downarrow^{(l)} a_k^\dagger a_k \rho \frac{1 + \sigma_j^z}{2} + \Lambda_\downarrow^{(k)} a_l^\dagger a_l \rho \frac{1 + \sigma_j^z}{2} \right]
\end{aligned} \tag{B.18}$$

If $k = l$

$$\frac{d\langle a_k^\dagger a_k^\dagger a_k a_k \rangle}{dt} = \Lambda_\downarrow J \Lambda_\downarrow^{(k)} \langle a_k^\dagger a_l^\dagger a_l a_k \rangle + \sum_j \Lambda_\downarrow^{(k)} \langle a_k^\dagger a_l^\dagger a_l a_k \sigma_j^z \rangle + 2J \Lambda_\downarrow^{(k)} \langle a_k^\dagger a_k \rangle + \sum_j 2\Lambda_\downarrow^{(k)} \langle a_k^\dagger a_k \sigma_j^z \rangle \tag{B.19}$$

If $k \neq l$

$$\begin{aligned} \frac{d\langle a_k^\dagger a_l^\dagger a_l a_k \rangle}{dt} = & \Lambda_\downarrow \frac{J(\Lambda_\downarrow^{(k)} + \Lambda_\downarrow^{(l)})}{2} \langle a_k^\dagger a_l^\dagger a_l a_k \rangle + \sum_j \frac{(\Lambda_\downarrow^{(k)} + \Lambda_\downarrow^{(l)})}{2} \langle a_k^\dagger a_l^\dagger a_l a_k \sigma_j^z \rangle + \frac{J\Lambda_\downarrow^{(k)}}{2} \langle a_k^\dagger a_k \rangle \\ & + \frac{J\Lambda_\downarrow^{(l)}}{2} \langle a_l^\dagger a_l \rangle + \sum_j \frac{\Lambda_\downarrow^{(k)}}{2} \langle a_k^\dagger a_k \sigma_j^z \rangle + \sum_j \frac{\Lambda_\downarrow^{(l)}}{2} \langle a_l^\dagger a_l \sigma_j^z \rangle \end{aligned} \quad (\text{B.20})$$

In total, if $k \neq l$

$$\begin{aligned} \frac{d\langle a_k^\dagger a_l^\dagger a_l a_k \rangle}{dt} = & -2\kappa \langle a_k^\dagger a_l^\dagger a_l a_k \rangle - \sum_j \frac{1}{2} (\Lambda_\uparrow^{(k)} + \Lambda_\uparrow^{(l)}) \langle a_k^\dagger a_l^\dagger a_l a_k (1 - \sigma_j^z) \rangle + \frac{J(\Lambda_\downarrow^{(k)} + \Lambda_\downarrow^{(l)})}{2} \langle a_k^\dagger a_l^\dagger a_l a_k \rangle \\ & + \sum_j \frac{(\Lambda_\downarrow^{(k)} + \Lambda_\downarrow^{(l)})}{2} \langle a_k^\dagger a_l^\dagger a_l a_k \sigma_j^z \rangle + \frac{J\Lambda_\downarrow^{(k)}}{2} \langle a_k^\dagger a_k \rangle + \frac{J\Lambda_\downarrow^{(l)}}{2} \langle a_l^\dagger a_l \rangle \\ & + \sum_j \frac{\Lambda_\downarrow^{(k)}}{2} \langle a_k^\dagger a_k \sigma_j^z \rangle + \sum_j \frac{\Lambda_\downarrow^{(l)}}{2} \langle a_l^\dagger a_l \sigma_j^z \rangle, \end{aligned} \quad (\text{B.21})$$

and if $k = l$

$$\begin{aligned} \frac{d\langle a_k^\dagger a_k^\dagger a_k a_k \rangle}{dt} = & -2\kappa \langle a_k^\dagger a_l^\dagger a_l a_k \rangle - \sum_j \frac{1}{2} (\Lambda_\uparrow^{(k)} + \Lambda_\downarrow^{(l)}) \langle a_k^\dagger a_l^\dagger a_l a_k (1 - \sigma_j^z) \rangle \\ & + J\Lambda_\downarrow^{(k)} \langle a_k^\dagger a_l^\dagger a_l a_k \rangle + \sum_j \Lambda_\downarrow^{(k)} \langle a_k^\dagger a_l^\dagger a_l a_k \sigma_j^z \rangle + 2J\Lambda_\downarrow^{(k)} \langle a_k^\dagger a_k \rangle + \sum_j 2\Lambda_\downarrow^{(k)} \langle a_k^\dagger a_k \sigma_j^z \rangle \end{aligned} \quad (\text{B.22})$$

The equation for $\langle a_k^\dagger a_k \sigma_j^z \rangle$ follows. Some terms are the same as for $\langle a_k^\dagger a_k \rangle$ as the addition of the σ makes no difference.

$$\begin{aligned} \frac{d\langle a_k^\dagger a_k \sigma_l^z \rangle}{dt} = & \delta - i \text{Tr} a_k^\dagger a_k \sigma_l^z \left[\sum_m \delta_m a_m^\dagger a_m, \rho \right] \\ = & \delta - i \sum_m \delta_m \text{Tr} \left[a_k^\dagger a_k \sigma_l^z a_m^\dagger a_m \rho - a_k^\dagger a_k \sigma_l^z \rho a_m^\dagger a_m \right] = 0 \end{aligned} \quad (\text{B.23})$$

$$\begin{aligned} \frac{d\langle a_k^\dagger a_k \sigma_l^z \rangle}{dt} = & \kappa - \sum_j \frac{\kappa}{2} \text{Tr} \left[a_k^\dagger a_k \sigma_l^z a_m^\dagger a_m \rho + a_k^\dagger a_k \sigma_l^z \rho a_m^\dagger a_m - 2a_k^\dagger a_k \sigma_l^z a_m \rho a_m^\dagger \right] \\ = & \kappa - \kappa \langle a_k^\dagger a_k \sigma_l^z \rangle \end{aligned} \quad (\text{B.24})$$

$$\frac{d\langle a_k^\dagger a_k \sigma_l^z \rangle}{dt} = \Gamma_\uparrow - \sum_j \frac{\Gamma_\uparrow}{2} \text{Tr} \left[a_k^\dagger a_k \sigma_l^z \sigma_j^- \sigma_j^+ \rho + a_k^\dagger a_k \sigma_l^z \rho \sigma_j^- \sigma_j^+ - 2a_k^\dagger a_k \sigma_l^z \sigma_j^+ \rho \sigma_j^- \right] \quad (\text{B.25})$$

$$\begin{aligned} = & \Gamma_\uparrow - \frac{\Gamma_\uparrow}{2} \text{Tr} \left[a_k^\dagger a_k \sigma_l^z \sigma_l^- \sigma_l^+ \rho + a_k^\dagger a_k \sigma_l^z \rho \sigma_l^- \sigma_l^+ - 2a_k^\dagger a_k \sigma_l^z \sigma_l^+ \rho \sigma_l^- \right] \\ = & \Gamma_\uparrow \Gamma_\uparrow (\langle a_k^\dagger a_k \rangle - \langle a_k^\dagger a_k \sigma_l^z \rangle) \end{aligned} \quad (\text{B.26})$$

$$\frac{d\langle a_k^\dagger a_k \sigma_l^z \rangle}{dt} = \Gamma_\downarrow - \Gamma_\downarrow (\langle a_k^\dagger a_k \rangle + \langle a_k^\dagger a_k \sigma_l^z \rangle) \quad (\text{B.27})$$

$$\begin{aligned}
\frac{d\langle a_k^\dagger a_k \sigma_l^z \rangle}{dt} &= \Lambda_\uparrow - \sum_{m,j} \frac{\Lambda_\uparrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_k \sigma_l^z a_m^\dagger a_m \sigma_j^- \sigma_j^+ \rho + a_k^\dagger a_k \sigma_l^z \rho a_m^\dagger a_m \sigma_j^- \sigma_j^+ - 2a_k^\dagger a_k \sigma_l^z a_m \sigma_j^+ \rho a_m^\dagger \sigma_j^- \right] \\
&= \Lambda_\uparrow - \sum_{m,j} \frac{\Lambda_\uparrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_k a_m^\dagger a_m \sigma_l^z \sigma_j^- \sigma_j^+ \rho + a_m^\dagger a_m a_k^\dagger a_k \sigma_j^- \sigma_j^+ \sigma_l^z \rho - 2a_m^\dagger a_k^\dagger a_k a_m \sigma_j^- \sigma_l^z \sigma_j^+ \rho \right] \\
&= \Lambda_\uparrow - \sum_{m,j} \frac{\Lambda_\uparrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_m^\dagger a_k a_m \sigma_l^z \sigma_j^- \sigma_j^+ \rho + a_k^\dagger [a_k, a_m^\dagger] a_m \sigma_l^z \sigma_j^- \sigma_j^+ \rho + a_m^\dagger a_k^\dagger a_m a_k \sigma_j^- \sigma_j^+ \sigma_l^z \rho \right. \\
&\quad \left. + a_m^\dagger [a_m, a_k^\dagger] a_k \sigma_j^- \sigma_j^+ \sigma_l^z \rho - 2a_m^\dagger a_k^\dagger a_k a_m \sigma_j^- \sigma_l^z \sigma_j^+ \rho \right] \\
&= \Lambda_\uparrow - \sum_{m,j} \frac{\Lambda_\uparrow^{(m)}}{2} \text{Tr} \left[a_m^\dagger a_k^\dagger a_k a_m \sigma_l^z \sigma_j^- \sigma_j^+ \rho + a_m^\dagger a_k^\dagger a_k a_m \sigma_j^- \sigma_j^+ \sigma_l^z \rho - 2a_m^\dagger a_k^\dagger a_k a_m \sigma_j^- \sigma_l^z \sigma_j^+ \rho \right] \\
&\quad - \sum_j \frac{\Lambda_\uparrow^{(k)}}{2} \text{Tr} \left[a_k^\dagger a_k [\sigma_l^z \sigma_j^- \sigma_j^+ \rho + \sigma_j^- \sigma_j^+ \sigma_l^z \rho] \right] \\
&= \Lambda_\uparrow - \sum_{m,j} \frac{\Lambda_\uparrow^{(m)}}{2} \text{Tr} \left[a_m^\dagger a_k^\dagger a_k a_m \sigma_j^- \sigma_l^z \sigma_j^+ \rho + a_m^\dagger a_k^\dagger a_k a_m [\sigma_l^z, \sigma_j^-] \sigma_j^+ \rho + a_m^\dagger a_k^\dagger a_k a_m \sigma_j^- \sigma_l^z \sigma_j^+ \rho \right. \\
&\quad \left. + a_m^\dagger a_k^\dagger a_k a_m \sigma_j^- [\sigma_j^+, \sigma_l^z] \rho - 2a_m^\dagger a_k^\dagger a_k a_m \sigma_j^- \sigma_l^z \sigma_j^+ \rho \right] - \sum_j \frac{\Lambda_\uparrow^{(k)}}{2} \text{Tr} \left[a_k^\dagger a_k [\sigma_l^z \sigma_j^- \sigma_j^+ \rho + \sigma_j^- \sigma_j^+ \sigma_l^z \rho] \right] \\
&= \Lambda_\uparrow - \sum_{m,j} \frac{\Lambda_\uparrow^{(m)}}{2} \text{Tr} \left[a_m^\dagger a_k^\dagger a_k a_m [\sigma_l^z, \sigma_j^-] \sigma_j^+ \rho + a_m^\dagger a_k^\dagger a_k a_m \sigma_j^- [\sigma_j^+, \sigma_l^z] \rho \right] \\
&\quad - \sum_j \frac{\Lambda_\uparrow^{(k)}}{2} \text{Tr} a_k^\dagger a_k [\sigma_l^z \sigma_j^- \sigma_j^+ \rho + \sigma_j^- \sigma_j^+ \sigma_l^z \rho] \\
&= \Lambda_\uparrow - \sum_{m,j} \Lambda_\uparrow^{(m)} \delta_{j,l} \text{Tr} \left[-a_m^\dagger a_k^\dagger a_k a_m \sigma_j^- \sigma_j^+ \rho - a_m^\dagger a_k^\dagger a_k a_m \sigma_j^- \sigma_j^+ \rho \right] \\
&\quad - \sum_j \frac{\Lambda_\uparrow^{(k)}}{2} \text{Tr} a_k^\dagger a_k \left[\sigma_l^z \frac{1 - \sigma_j^z}{2} \rho + \frac{1 - \sigma_j^z}{2} \sigma_l^z \rho \right] \\
&= \Lambda_\uparrow \sum_m 2\Lambda_\uparrow^{(m)} \text{Tr} \left[a_m^\dagger a_k^\dagger a_k a_m \frac{1 - \sigma_l^z}{2} \rho \right] + \sum_j \frac{\Lambda_\uparrow^{(k)}}{2} \left[-\langle a_k^\dagger a_k \sigma_l^z \rangle + \langle a_k^\dagger a_k \sigma_l^z \sigma_j^z \rangle \right] \\
&= \Lambda_\uparrow \sum_m 2\Lambda_\uparrow^{(m)} \text{Tr} \left[a_m^\dagger a_k^\dagger a_k a_m \frac{1 - \sigma_l^z}{2} \rho \right] - \frac{J \Lambda_\uparrow^{(k)}}{2} \langle a_k^\dagger a_k \sigma_l^z \rangle + \sum_j \frac{\Lambda_\uparrow^{(k)}}{2} \langle a_k^\dagger a_k \sigma_l^z \sigma_j^z \rangle \\
&= \Lambda_\uparrow \sum_m \Lambda_\uparrow^{(m)} \langle a_m^\dagger a_k^\dagger a_k a_m \rangle - \sum_m \Lambda_\uparrow^{(m)} \langle a_m^\dagger a_k^\dagger a_k a_m \sigma_l^z \rangle - \frac{J \Lambda_\uparrow^{(k)}}{2} \langle a_k^\dagger a_k \sigma_l^z \rangle + \sum_j \frac{\Lambda_\uparrow^{(k)}}{2} \langle a_k^\dagger a_k \sigma_l^z \sigma_j^z \rangle
\end{aligned}
\tag{B.28}$$

$$\begin{aligned}
\frac{d\langle a_k^\dagger a_k \sigma_l^z \rangle}{dt} &= \Lambda_\downarrow - \sum_{m,j} \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_k \sigma_l^z a_m a_m^\dagger \sigma_j^+ \sigma_j^- \rho + a_k^\dagger a_k \sigma_l^z \rho a_m a_m^\dagger \sigma_j^+ \sigma_j^- - 2a_k^\dagger a_k \sigma_l^z a_m^\dagger \sigma_j^- \rho a_m \sigma_j^+ \right] \\
&= \Lambda_\downarrow - \sum_{m,j} \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[a_k^\dagger a_m a_k a_m^\dagger \sigma_l^z \sigma_j^+ \sigma_j^- \rho + a_m a_k^\dagger a_m^\dagger a_k \sigma_j^+ \sigma_j^- \sigma_l^z \rho - 2a_m a_k^\dagger a_k a_m^\dagger \sigma_j^+ \sigma_l^z \sigma_j^- \rho \right] \\
&= \Lambda_\downarrow - \sum_{m,j} \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[a_m a_k^\dagger a_k a_m^\dagger \sigma_l^z \sigma_j^+ \sigma_j^- \rho + [a_k^\dagger, a_m] a_k a_m^\dagger \sigma_l^z \sigma_j^+ \sigma_j^- \rho + a_m a_k^\dagger a_k a_m^\dagger \sigma_j^+ \sigma_j^- \sigma_l^z \rho \right. \\
&\quad \left. + a_m a_k^\dagger [a_m^\dagger, a_k] \sigma_j^+ \sigma_j^- \sigma_l^z \rho - 2a_m a_k^\dagger a_k a_m^\dagger \sigma_j^+ \sigma_l^z \sigma_j^- \rho \right] \\
&= \Lambda_\downarrow - \sum_{m,j} \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[a_m a_k^\dagger a_k a_m^\dagger \sigma_l^z \sigma_j^+ \sigma_j^- \rho + a_m a_k^\dagger a_k a_m^\dagger \sigma_j^+ \sigma_j^- \sigma_l^z \rho - 2a_m a_k^\dagger a_k a_m^\dagger \sigma_j^+ \sigma_l^z \sigma_j^- \rho \right] \\
&\quad + \frac{\Lambda_\downarrow^{(k)}}{2} \sum_j \text{Tr} \left[a_k a_k^\dagger \sigma_l^z \sigma_j^+ \sigma_j^- \rho + a_k a_k^\dagger \sigma_j^+ \sigma_j^- \sigma_l^z \rho \right] \\
&= \Lambda_\downarrow - \sum_{m,j} \frac{\Lambda_\downarrow^{(m)}}{2} \text{Tr} \left[a_m a_k^\dagger a_k a_m^\dagger \sigma_j^+ \sigma_l^z \sigma_j^- \rho + a_m a_k^\dagger a_k a_m^\dagger [\sigma_l^z, \sigma_j^+] \sigma_j^- \rho + a_m a_k^\dagger a_k a_m^\dagger \sigma_j^+ \sigma_l^z \sigma_j^- \rho \right. \\
&\quad \left. + a_m a_k^\dagger a_k a_m^\dagger \sigma_j^+ [\sigma_j^-, \sigma_l^z] \rho - 2a_m a_k^\dagger a_k a_m^\dagger \sigma_j^+ \sigma_l^z \sigma_j^- \rho \right] + \frac{\Lambda_\downarrow^{(k)}}{2} \sum_j \text{Tr} \left[a_k a_k^\dagger \sigma_l^z \frac{1 + \sigma_j^z}{2} \rho + a_k a_k^\dagger \frac{1 + \sigma_j^z}{2} \sigma_l^z \rho \right] \\
&= \Lambda_\downarrow - \sum_m \Lambda_\downarrow^{(m)} \text{Tr} \left[a_m a_k^\dagger a_k a_m^\dagger (\sigma_l^z + 1) \rho \right] + \frac{J \Lambda_\downarrow^{(k)}}{2} \langle a_k a_k^\dagger \sigma_l^z \rangle + \frac{\Lambda_\downarrow^{(k)}}{2} \sum_j \langle a_k a_k^\dagger \sigma_l^z \sigma_j^z \rangle
\end{aligned}
\tag{B.29}$$

[illegible]

In total

$$\begin{aligned}
\frac{d\langle a_k^\dagger a_k \sigma_l^z \rangle}{dt} = & -\kappa \langle a_k^\dagger a_k \sigma_l^z \rangle + \Gamma_\uparrow (\langle a_k^\dagger a_k \rangle - \langle a_k^\dagger a_k \sigma_l^z \rangle) - \Gamma_\downarrow (\langle a_k^\dagger a_k \rangle + \langle a_k^\dagger a_k \sigma_l^z \rangle) + \sum_m \Lambda_\uparrow^{(m)} \langle a_m^\dagger a_k^\dagger a_k a_m \rangle \\
& - \sum_m \Lambda_\uparrow^{(m)} \langle a_m^\dagger a_k^\dagger a_k a_m \sigma_l^z \rangle - \frac{J \Lambda_\uparrow^{(k)}}{2} \langle a_k^\dagger a_k \sigma_l^z \rangle + \sum_j \frac{\Lambda_\uparrow^{(k)}}{2} \langle a_k^\dagger a_k \sigma_l^z \sigma_j^z \rangle - \sum_m \Lambda_\downarrow^{(m)} \langle a_k^\dagger a_m^\dagger a_m a_k \rangle \\
& - \sum_m \Lambda_\downarrow^{(m)} \langle a_k^\dagger a_k \rangle - 2\Lambda_\downarrow^{(k)} \langle a_k^\dagger a_k \rangle - \Lambda_\downarrow^{(k)} - \sum_m \Lambda_\downarrow^{(m)} \langle a_k^\dagger a_m^\dagger a_m a_k \sigma_l^z \rangle - \sum_m \Lambda_\downarrow^{(m)} \langle a_k^\dagger a_k \sigma_l^z \rangle \\
& - \frac{(J-4) \Lambda_\downarrow^{(k)}}{2} \langle a_k^\dagger a_k \sigma_l^z \rangle + \frac{(J-2) \Lambda_\downarrow^{(k)}}{2} \langle \sigma_l^z \rangle + \frac{\Lambda_\downarrow^{(k)}}{2} \sum_j \langle a_k^\dagger a_k \sigma_l^z \sigma_j^z \rangle + \frac{\Lambda_\downarrow^{(k)}}{2} \sum_j \langle \sigma_l^z \sigma_j^z \rangle
\end{aligned} \tag{B.31}$$

B.2 Computer Readable Equations

As discussed in Sec. 5.3, any equation may be broken into a nested tree of terms. Each term may be written as a computational function using the following convention:

Description	Math	Code
Number	1	numb(1)
Symbol	$x_{i,j}$	sym('x', ['i','j'])
Operator	$a_{i,j}$	op('a', ['i','j'])
Kronecker Delta	$\delta_{i,j}$	delta(['i','j'])
Summation	$\sum_{m=0}^M Q$	summ(Q, ['M', numb(0), sym('M')])
Trace	$\text{Tr} \{Q\}$	trac(Q)
Addition	$Q + W + R$	addi([Q,W,R])
Multiplication	$Q \times W \times R$	mult([Q,W,R])
Fraction	$\frac{Q}{W}$	frac(Q,W)
Derivative	$\frac{dQ}{dt}$	deriv(Q, sym('t'))
Equation	$Q = W$	equation(Q,W)

where Q , W , and R are dummy terms.

B.3 Master Equation

The master equation may be produced with the following python code:

```
## The density matrix
rr = rho()

## mode operators
am = op("a",["m"])
aTm = op("a^T",["m"])
ap = op("a",["p"])
aTp = op("a^T",["p"])
aq = op("a",["q"])
aTq = op("a^T",["q"])

##molecule operators
spj = op("sp",["j"])
smj = op("sp^T",["j"])
spl = op("sp",["l"])
sml = op("sp^T",["l"])
spk = op("sp",["k"])
smk = op("sp^T",["k"])
fl = mult([spl,sml])
fk = mult([spk,smk])

## Defines the lindblad operator
def lind(opp):
    return addi([
        mult([opp.HermConj(),opp,rr]),
        mult([rr,opp.HermConj(),opp]),
        mult([numb(-2),opp,rr,opp.HermConj()]),
    ])

masterA = [
    summ(mult([numb(-0.5),sym("kap"), lind(am)]),["m",numb(0),sym("M")]),
    summ(mult([numb(-0.5),sym("gu",["j"]), lind(spj)]),["j",numb(0),sym("J")]),
    summ(mult([numb(-0.5),sym("gd",["j"]), lind(smj)]),["j",numb(0),sym("J")]),
    summ(summ(mult([numb(-0.5),sym("ld",["m","j"]),lind(mult([aTm,smj]))]),["j",numb(0),sym(
        ↪ ("J")]),["m",numb(0),sym("M")]),
    summ(summ(mult([numb(-0.5),sym("lu",["m","j"]),lind(mult([am,spj]))]),["j",numb(0),sym(
        ↪ "J")]),["m",numb(0),sym("M")]),
]

master = addi(masterA)
```

The output of this code is:

```
addi([summ(mult([numb(-0.5),sym('kap',[ ]),addi([mult([op('a^T',[ 'm'])],op('a',[ 'm']),rho())],
    mult([rho(),op('a^T',[ 'm']),op('a',[ 'm'])]),mult([numb(-2),op('a',[ 'm']),rho(),op('a^T',[ 'm'
    ''])])),[ 'm',numb(0),sym('M',[ ])]),summ(mult([numb(-0.5),sym('gu',[ 'j']),addi([mult([op('
    sp^T',[ 'j']),op('sp',[ 'j']),rho())],mult([rho(),op('sp^T',[ 'j']),op('sp',[ 'j'])]),mult([
    numb(-2),op('sp',[ 'j']),rho(),op('sp^T',[ 'j'])])),[ 'j',numb(0),sym('J',[ ])]),summ(mult([
    numb(-0.5),sym('gd',[ 'j']),addi([mult([op('sp',[ 'j']),op('sp^T',[ 'j']),rho())],mult([rho(),
    op('sp',[ 'j']),op('sp^T',[ 'j'])]),mult([numb(-2),op('sp^T',[ 'j']),rho(),op('sp',[ 'j'])])),
    ]),[ 'j',numb(0),sym('J',[ ])]),summ(summ(mult([numb(-0.5),sym('ld',[ 'm', 'j']),addi([mult([
    mult([op('sp',[ 'j']),op('a',[ 'm'])]),mult([op('a^T',[ 'm']),op('sp^T',[ 'j'])]),rho())],mult
    ([rho(),mult([op('sp',[ 'j']),op('a',[ 'm'])]),mult([op('a^T',[ 'm']),op('sp^T',[ 'j'])])),
    mult([numb(-2),mult([op('a^T',[ 'm']),op('sp^T',[ 'j'])]),rho(),mult([op('sp',[ 'j']),op('a
    ',[ 'm'])])),[ 'j',numb(0),sym('J',[ ])]),[ 'm',numb(0),sym('M',[ ])]),summ(summ(mult([numb
    (-0.5),sym('lu',[ 'm', 'j']),addi([mult([mult([op('sp^T',[ 'j']),op('a^T',[ 'm'])]),mult([op('
    a',[ 'm']),op('sp',[ 'j'])]),rho())],mult([rho(),mult([op('sp^T',[ 'j']),op('a^T',[ 'm'])]),
    mult([op('a',[ 'm']),op('sp',[ 'j'])])),mult([numb(-2),mult([op('a',[ 'm']),op('sp',[ 'j'])]),
    rho(),mult([op('sp^T',[ 'j']),op('a^T',[ 'm'])])),[ 'j',numb(0),sym('J',[ ])]),[ 'm',numb
    (0),sym('M',[ ])]))
```

B.4 Rate Equations

The equation for the rate of change of mode population, Eq. (5.10)(1), in code form is

```
equality(deriv(trac(mult([op('a^T',[ 'p']),op('a',[ 'p']),rho())]),sym('t',[ ])),addi([summ(mult
    ([sym('Cnf',[ 'p', 'j']),sym('ld',[ 'p', 'j'])]),[ 'j',numb(0),sym('J',[ ])]),summ(mult([sym('
    Cnf',[ 'p', 'j']),sym('lu',[ 'p', 'j'])]),[ 'j',numb(0),sym('J',[ ])]),summ(mult([sym('ld',[ 'p
    ', 'j']),trac(mult([op('f',[ 'j']),rho())])),[ 'j',numb(0),sym('J',[ ])]),mult([numb(-1.0),
    sym('kap',[ ]),trac(mult([op('a^T',[ 'p']),op('a',[ 'p']),rho())]),mult([numb(-1.0),summ(sym
    ('lu',[ 'p', 'j']),[ 'j',numb(0),sym('J',[ ])]),trac(mult([op('a^T',[ 'p']),op('a',[ 'p']),rho()
    ]))),mult([summ(mult([sym('ld',[ 'p', 'j']),trac(mult([op('f',[ 'j']),rho())])),[ 'j',numb
    (0),sym('J',[ ])]),trac(mult([op('a^T',[ 'p']),op('a',[ 'p']),rho())]),mult([summ(mult([sym
    ('lu',[ 'p', 'j']),trac(mult([op('f',[ 'j']),rho())])),[ 'j',numb(0),sym('J',[ ])]),trac(mult
    ([op('a^T',[ 'p']),op('a',[ 'p']),rho())]))))
```

The equation for the rate of change of molecular excitation, Eq. (5.10)(2), in code form is

```
equality(deriv(trac(mult([op('f',[ 'l']),rho())]),sym('t',[ ])),addi([sym('gu',[ 'l']),mult([numb
    (-1),summ(mult([sym('Cnf',[ 'm', 'l']),sym('ld',[ 'm', 'l'])]),[ 'm',numb(0),sym('M',[ ])])),
    mult([numb(-1),summ(mult([sym('Cnf',[ 'm', 'l']),sym('lu',[ 'm', 'l'])]),[ 'm',numb(0),sym('M
    ',[ ])])),mult([numb(-1),sym('gu',[ 'l']),trac(mult([op('f',[ 'l']),rho())])),mult([numb(-1)
    ,sym('gd',[ 'l']),trac(mult([op('f',[ 'l']),rho())])),mult([numb(-1),summ(sym('ld',[ 'm', 'l
    '']),[ 'm',numb(0),sym('M',[ ])]),trac(mult([op('f',[ 'l']),rho())])),summ(mult([sym('lu',[ 'm
```

```

', 'l']), trac(mult([op('a^T', ['m']), op('a', ['m']), rho()])))], ['m', numb(0), sym('M', [])]),
mult([numb(-1), summ(mult([sym('ld', ['m', 'l']), trac(mult([op('a^T', ['m']), op('a', ['m']), rho
()])))], ['m', numb(0), sym('M', [])]), trac(mult([op('f', ['l']), rho()])))], mult([numb(-1), summ(
mult([sym('lu', ['m', 'l']), trac(mult([op('a^T', ['m']), op('a', ['m']), rho()])))], ['m', numb(0)
, sym('M', [])]), trac(mult([op('f', ['l']), rho()])))])])

```

The equation for the rate of change of mode-mode covariance, Eq. (5.12), in code form is

```

equality(deriv(sym('Cnn', ['p', 'q']), sym('t', [])), addi([mult([delta(['p', 'q']), summ(mult([sym
('ld', ['p', 'j']), trac(mult([op('f', ['j']), rho()])))], ['j', numb(0), sym('J', [])])]), summ(
mult([sym('Cnf', ['p', 'j']), sym('ld', ['q', 'j'])]), ['j', numb(0), sym('J', [])]), mult([numb
(-1), delta(['p', 'q']), summ(mult([sym('Cnf', ['p', 'j']), sym('lu', ['p', 'j'])]), ['j', numb(0)
, sym('J', [])])]), summ(mult([sym('Cnf', ['q', 'j']), sym('ld', ['p', 'j'])]), ['j', numb(0), sym('
J', [])]), mult([delta(['q', 'p']), summ(mult([sym('Cnf', ['q', 'j']), sym('ld', ['q', 'j'])]), ['
j', numb(0), sym('J', [])])]), mult([numb(-1.0), sym('Cnn', ['p', 'q']), summ(sym('lu', ['p', 'j']
), ['j', numb(0), sym('J', [])])]), mult([numb(-1.0), sym('Cnn', ['p', 'q']), summ(sym('lu', ['q', 'j
']), ['j', numb(0), sym('J', [])])]), mult([numb(-2.0), sym('Cnn', ['p', 'q']), sym('kap', [])]),
mult([delta(['p', 'q']), summ(sym('lu', ['p', 'j']), ['j', numb(0), sym('J', [])]), trac(mult([op
('a^T', ['p']), op('a', ['p']), rho()])))], mult([sym('kap', []), delta(['p', 'q']), trac(mult([op
('a^T', ['p']), op('a', ['p']), rho()])))], summ(mult([sym('Cnnf', ['p', 'q', 'j']), sym('ld', ['p
', 'j'])]), ['j', numb(0), sym('J', [])]), summ(mult([sym('Cnnf', ['p', 'q', 'j']), sym('ld', ['q',
', 'j'])]), ['j', numb(0), sym('J', [])]), summ(mult([sym('Cnnf', ['p', 'q', 'j']), sym('lu', ['p', '
j'])]), ['j', numb(0), sym('J', [])]), summ(mult([sym('Cnnf', ['p', 'q', 'j']), sym('lu', ['q', 'j
']), ['j', numb(0), sym('J', [])]), mult([numb(-1), delta(['p', 'q']), summ(mult([sym('lu', ['p',
', 'j']), trac(mult([op('f', ['j']), rho()])))], ['j', numb(0), sym('J', [])]), trac(mult([op('a^T
', ['p']), op('a', ['p']), rho()])))], mult([sym('Cnn', ['p', 'q']), summ(mult([sym('ld', ['p', 'j
']), trac(mult([op('f', ['j']), rho()])))], ['j', numb(0), sym('J', [])])]), mult([sym('Cnn', ['p',
', 'q']), summ(mult([sym('ld', ['q', 'j']), trac(mult([op('f', ['j']), rho()])))], ['j', numb(0), sym
('J', [])])]), mult([sym('Cnn', ['p', 'q']), summ(mult([sym('lu', ['p', 'j']), trac(mult([op('f
', ['j']), rho()])))], ['j', numb(0), sym('J', [])])]), mult([sym('Cnn', ['p', 'q']), summ(mult([sym
('lu', ['q', 'j']), trac(mult([op('f', ['j']), rho()])))], ['j', numb(0), sym('J', [])])]), mult([
delta(['q', 'p']), summ(mult([sym('ld', ['q', 'j']), trac(mult([op('f', ['j']), rho()])))], ['j',
numb(0), sym('J', [])]), trac(mult([op('a^T', ['q']), op('a', ['q']), rho()])))], mult([summ(mult([
sym('Cnf', ['p', 'j']), sym('ld', ['q', 'j'])]), ['j', numb(0), sym('J', [])]), trac(mult([op('a^T
', ['q']), op('a', ['q']), rho()])))], mult([summ(mult([sym('Cnf', ['p', 'j']), sym('lu', ['q', 'j
']), ['j', numb(0), sym('J', [])]), trac(mult([op('a^T', ['q']), op('a', ['q']), rho()])))], mult([
summ(mult([sym('Cnf', ['q', 'j']), sym('ld', ['p', 'j'])]), ['j', numb(0), sym('J', [])]), trac(
mult([op('a^T', ['p']), op('a', ['p']), rho()])))], mult([summ(mult([sym('Cnf', ['q', 'j']), sym('
lu', ['p', 'j'])]), ['j', numb(0), sym('J', [])]), trac(mult([op('a^T', ['p']), op('a', ['p']), rho(
)]]))])])

```

The equation for the rate of change of mode-molecule covariance, Eq. (5.11), in code form is

```

equality(deriv(sym('Cnf',[p', 'l']),sym('t',[])),addi([mult([numb(-1),sym('ld',[p', 'l']),
trac(mult([op('f',[l']),rho()))])),summ(mult([sym('Cff',[j', 'l']),sym('ld',[p', 'j'])]),
[j',numb(0),sym('J',[])]),summ(mult([sym('Cnn',[m', 'p']),sym('lu',[m', 'l'])]),[m',
numb(0),sym('M',[])]),mult([numb(-1),sym('Cnf',[p', 'l']),sym('gu',[l'])]),mult([numb(-1),
sym('Cnf',[p', 'l']),sym('gd',[l'])]),mult([numb(-1),sym('Cnf',[p', 'l']),sym('ld',[p',
'l'])]),mult([numb(-1),sym('Cnf',[p', 'l']),summ(sym('ld',[m', 'l']),[m',numb(0),sym
('M',[])])),mult([numb(-1.0),sym('Cnf',[p', 'l']),sym('kap',[])]),mult([numb(-1.0),sym('
Cnf',[p', 'l']),summ(sym('lu',[p', 'j']),[j',numb(0),sym('J',[])])),mult([sym('Cnf',[p',
'l']),sym('lu',[p', 'l'])]),mult([numb(-1),sym('lu',[p', 'l']),trac(mult([op('a^T',[p',
p']),op('a',[p']),rho()))])),summ(mult([sym('Cnff',[p', 'j', 'l']),sym('ld',[p', 'j'])]),
[j',numb(0),sym('J',[])]),summ(mult([sym('Cnff',[p', 'j', 'l']),sym('lu',[p', 'j'])]),
[j',numb(0),sym('J',[])]),mult([numb(-1),summ(mult([sym('Cnnf',[m', 'p', 'l']),sym('ld',
[m', 'l'])]),[m',numb(0),sym('M',[])])),mult([numb(-1),summ(mult([sym('Cnnf',[m', 'p',
'l']),sym('lu',[m', 'l'])]),[m',numb(0),sym('M',[])])),mult([numb(-1),summ(mult([sym
('Cnn',[m', 'p']),sym('ld',[m', 'l'])]),[m',numb(0),sym('M',[])]),trac(mult([op('f',[l',
l']),rho()))])),mult([numb(-1),summ(mult([sym('Cnn',[m', 'p']),sym('lu',[m', 'l'])]),[m',
numb(0),sym('M',[])]),trac(mult([op('f',[l']),rho()))])),mult([numb(-1),sym('ld',[p', 'l',
l']),trac(mult([op('a^T',[p']),op('a',[p']),rho()))]),trac(mult([op('f',[l']),rho()))]),
mult([sym('lu',[p', 'l']),trac(mult([op('a^T',[p']),op('a',[p']),rho()))]),trac(mult([op
('f',[l']),rho()))]),mult([sym('Cnf',[p', 'l']),summ(mult([sym('ld',[p', 'j']),trac(
mult([op('f',[j']),rho()))])),[j',numb(0),sym('J',[])])),mult([sym('Cnf',[p', 'l']),
summ(mult([sym('lu',[p', 'j']),trac(mult([op('f',[j']),rho()))])),[j',numb(0),sym('J',
[])])),mult([numb(-1),sym('Cnf',[p', 'l']),summ(mult([sym('ld',[m', 'l']),trac(mult([
op('a^T',[m']),op('a',[m']),rho()))])),[m',numb(0),sym('M',[])])),mult([numb(-1),sym('
Cnf',[p', 'l']),summ(mult([sym('lu',[m', 'l']),trac(mult([op('a^T',[m']),op('a',[m']),
rho()))])),[m',numb(0),sym('M',[])])),mult([summ(mult([sym('Cff',[j', 'l']),sym('ld',[p',
j']),[j',numb(0),sym('J',[])]),trac(mult([op('a^T',[p']),op('a',[p']),rho()))])),
mult([summ(mult([sym('Cff',[j', 'l']),sym('lu',[p', 'j']),[j',numb(0),sym('J',[])]),
trac(mult([op('a^T',[p']),op('a',[p']),rho()))]))))

```

Finally the equation for the rate of change of molecule-molecule covariance, Eq. (5.13), in code form is

```

equality(deriv(sym('Cff',[k', 'l']),sym('t',[])),addi([mult([sym('gu',[k']),delta(['k', 'l',
l']),mult([numb(-1),sym('gu',[k']),delta(['k', 'l']),trac(mult([op('f',[k']),rho()))])),
mult([delta(['k', 'l']),summ(sym('ld',[m', 'k']),[m',numb(0),sym('M',[])]),trac(mult([op
('f',[k']),rho()))])),mult([sym('gd',[k']),delta(['k', 'l']),trac(mult([op('f',[k']),rho
()))])),summ(mult([sym('Cnf',[m', 'k']),sym('lu',[m', 'l'])]),[m',numb(0),sym('M',[])]),
mult([numb(-1),delta(['k', 'l']),summ(mult([sym('Cnf',[m', 'k']),sym('lu',[m', 'k'])]),[m',
numb(0),sym('M',[])])),mult([delta(['k', 'l']),summ(mult([sym('Cnf',[m', 'k']),sym('ld',
[m', 'k'])]),[m',numb(0),sym('M',[])])),summ(mult([sym('Cnf',[m', 'l']),sym('lu',[m',
k']),[m',numb(0),sym('M',[])]),mult([numb(-1),sym('Cff',[k', 'l']),sym('gu',[l'])]),
mult([numb(-1),sym('Cff',[k', 'l']),sym('gu',[k'])]),mult([numb(-1),sym('Cff',[k', 'l',

```

```

'']),sym('gd',[ 'l'])]),mult([numb(-1),sym('Cff',[ 'k', 'l']),sym('gd',[ 'k'])]),mult([numb(-1)
,sym('Cff',[ 'k', 'l']),summ(sym('ld',[ 'm', 'l']),[ 'm',numb(0),sym('M',[ ])])]),mult([numb
(-1),sym('Cff',[ 'k', 'l']),summ(sym('ld',[ 'm', 'k']),[ 'm',numb(0),sym('M',[ ])])]),mult([
delta([ 'k', 'l']),summ(mult([sym('lu',[ 'm', 'k']),trac(mult([op('a^T',[ 'm']),op('a',[ 'm']),
rho()))]),[ 'm',numb(0),sym('M',[ ])])]),mult([numb(-1),summ(mult([sym('Cnff',[ 'm', 'k', 'l
']),sym('ld',[ 'm', 'l'])]),[ 'm',numb(0),sym('M',[ ])])]),mult([numb(-1),summ(mult([sym('Cnff
',[ 'm', 'k', 'l']),sym('ld',[ 'm', 'k'])]),[ 'm',numb(0),sym('M',[ ])])]),mult([numb(-1),summ(
mult([sym('Cnff',[ 'm', 'k', 'l']),sym('lu',[ 'm', 'l'])]),[ 'm',numb(0),sym('M',[ ])])]),mult
([numb(-1),summ(mult([sym('Cnff',[ 'm', 'k', 'l']),sym('lu',[ 'm', 'k'])]),[ 'm',numb(0),sym('
M',[ ])])]),mult([numb(-1),summ(mult([sym('Cnf',[ 'm', 'l']),sym('ld',[ 'm', 'k'])]),[ 'm',numb
(0),sym('M',[ ])]),trac(mult([op('f',[ 'k']),rho()))]), ...

```

```

... mult([numb(-1),summ(mult([sym('Cnf',[ 'm', 'l']),sym('lu',[ 'm', 'k'])]),[ 'm',numb(0),sym('M
',[ ])]),trac(mult([op('f',[ 'k']),rho()))]),mult([numb(-1),summ(mult([sym('Cnf',[ 'm', 'k'])
,sym('ld',[ 'm', 'l'])]),[ 'm',numb(0),sym('M',[ ])]),trac(mult([op('f',[ 'l']),rho()))]),mult
([numb(-1),summ(mult([sym('Cnf',[ 'm', 'k']),sym('lu',[ 'm', 'l'])]),[ 'm',numb(0),sym('M',[ ])
]),trac(mult([op('f',[ 'l']),rho()))]),mult([numb(-1),delta([ 'k', 'l']),summ(mult([sym('lu
',[ 'm', 'k']),trac(mult([op('a^T',[ 'm']),op('a',[ 'm']),rho()))]),[ 'm',numb(0),sym('M',[ ])
]),trac(mult([op('f',[ 'k']),rho()))]),mult([delta([ 'k', 'l']),summ(mult([sym('ld',[ 'm', 'k
']),trac(mult([op('a^T',[ 'm']),op('a',[ 'm']),rho()))]),[ 'm',numb(0),sym('M',[ ])]),trac(
mult([op('f',[ 'k']),rho()))]),mult([numb(-1),sym('Cff',[ 'k', 'l']),summ(mult([sym('ld',[ 'm
', 'l']),trac(mult([op('a^T',[ 'm']),op('a',[ 'm']),rho()))]),[ 'm',numb(0),sym('M',[ ])])]),
mult([numb(-1),sym('Cff',[ 'k', 'l']),summ(mult([sym('ld',[ 'm', 'k']),trac(mult([op('a^T',[ '
m']),op('a',[ 'm']),rho()))]),[ 'm',numb(0),sym('M',[ ])])]),mult([numb(-1),sym('Cff',[ 'k', '
l']),summ(mult([sym('lu',[ 'm', 'l']),trac(mult([op('a^T',[ 'm']),op('a',[ 'm']),rho()))]),[ '
m',numb(0),sym('M',[ ])])]),mult([numb(-1),sym('Cff',[ 'k', 'l']),summ(mult([sym('lu',[ 'm', '
k']),trac(mult([op('a^T',[ 'm']),op('a',[ 'm']),rho()))]),[ 'm',numb(0),sym('M',[ ])])])])])

```

B.5 Generating Code

The code used to generate these equations may be found at:

https://github.com/henryhesten/computational_algebra

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