

Energy Transport in Open Quantum Systems



Felix Alexander Pollock

St Anne's College

University of Oxford

A thesis submitted for the degree of

Doctor of Philosophy

Trinity 2014

For Kasia

Acknowledgements

First of all, I would like to sincerely thank my supervisor Vlatko Vedral — whose unending optimism and enthusiasm has kept me constantly inspired — as well as my unofficial co-supervisors Simon Benjamin and Brendon Lovett, for all their support over the last three years. I can't emphasise enough how appreciative I am of the opportunity they have given me to do research in such a relaxed and enjoyable environment, and I couldn't imagine having a better set of people to oversee my degree!

I am also indebted to all the other researchers with whom I've worked over the course of my D. Phil, especially those who contributed to the papers on which this thesis is based. In alphabetical order these are: Agata Chęcińska, Megan Edwards, Adam Esmail, Andrew Ferguson, Erik Gauger, Libby Heaney, Nick Lambert, Brendon Lovett, Dara McCutcheon and Ahsan Nazir. Working with them has been a pleasure, and I sincerely hope that we will continue our collaborations in the future. I would like to thank Erik and Brendon in particular for commenting on parts of this thesis and for all the valuable discussions we've shared!

All the members of Vlatko's and Simon's research groups, as well as the Leverhulme group — too many names to list here individually — have my gratitude for making my time in Oxford stimulating, sociable and more than anything fun! Andrew Garner and Oscar Dahlsten deserve special mention for distracting me with fascinating discussions of the foundations of quantum theory, which have kept me dipping my toes into more fundamental physics.

Financially, I couldn't have undertaken this degree without the support of the Leverhulme Trust, whom I would like to thank deeply for allowing me to continue my studies here in Oxford. In a similar vein, I am eternally grateful to St. Anne's College and the tutors there, Neville Harnew and Patrick Irwin, for not only encouraging me through my earlier undergraduate degree, but also supporting me with travel grants and providing

opportunities for paid teaching work. The Oxford Physics department likewise deserves my thanks for their help over the years.

Finally, I'm not sure I'd have made it to the end if I hadn't had the love and support of all my friends and family, especially my parents and my parents-in-law. Without their kindness and encouragement (and excellent cooking!) I may have given up along the way. Above all, I would like to express my gratitude to my wife Kasia; though she might not understand all that much of it, the completion of this thesis owes almost as much to her as it does to me. Ta praca doktorska jest dla Ciebie!

Abstract

This thesis is concerned with modelling the dynamics of open quantum systems in several different contexts. Of principal interest is the manner in which the environment can modify, or even dominate, a system's quantum behaviour in order to facilitate the transport of energetic excitations.

In the first research chapter, a time-local, non-Markovian quantum master equation is derived in a variationally defined reference frame, for networks of two-level systems coupled to bosonic environments. The predictions of this master equation are then compared with those derived using both weak-coupling and polaron approximations. The variational master equation is found to agree with these standard approaches in their regimes of validity, whilst interpolating between them in intermediate parameter regimes.

The second research chapter focusses on the dynamics of a superconducting double quantum dot embedded in a resonant circuit. The device is considered in a regime where the ground state consists of a coherent spatial superposition of a single Cooper pair, which can be excited by a variety of interactions with the environment. The relevant transition rates are calculated and the processes responsible are identified. A numerical simulation of the system is then used to explain experimental data, and show that for certain parameters a significant fraction of excitations occur via absorption of photons from the environment.

The final chapter considers a model for an olfactory receptor, in which odorant molecules are recognised by their vibrational modes. Electron transfer occurs in the receptor, dependent on the presence of a vibrational mode of the right frequency. A quantum master equation for the system is derived, and the resulting dynamics is compared to earlier semi-classical treatments. The behaviour of the receptor is found to be sensitive not only to the frequency of the vibrational mode, but also to the character of the surrounding environment. Increased dissipation on the odorant mode, as well as the presence of higher frequencies in the environment is found to improve the frequency resolution of the receptor.

Contents

1	Motivation and outline	1
1.1	Motivation	1
1.2	Outline	2
2	Open quantum systems theory	4
2.1	Background	4
2.2	The mathematical representation of open systems	6
2.2.1	Pure and mixed states	6
2.2.2	Composite systems and dynamical maps	8
2.2.3	The Schrödinger, Heisenberg and interaction pictures	9
2.3	The Born-Markov master equation	10
2.4	The time-convolutionless projection operator master equation	13
2.5	A model for energy transport	17
3	Variational polaron transformations for multi-site exciton transport models	20
3.1	Introduction	20
3.2	Local and global environments in the transport model	21
3.3	The variational polaron transformation	24
3.3.1	The variational transformation for systems with local environments	24
3.3.2	Extending the transformation to spatially-correlated environments	27
3.4	The time-local projection operator Master Equation in the variational frame	29
3.5	Example dynamics	32
3.5.1	A three-site comparison	32
3.5.2	The Fenna-Matthews-Olsen complex	34

3.6	Conclusions	37
4	Excitation and relaxation in a superconducting double quantum dot	41
4.1	Introduction	41
4.2	BCS model and tunnelling across a barrier	42
4.2.1	Tunnelling across a barrier in the normal state	46
4.2.2	The Josephson effect	48
4.2.3	Lifetime broadening and the Dynes density of states	49
4.3	The energy eigenstates of the superconducting double dot	50
4.4	Quantum capacitance and measurement	52
4.5	Dynamical processes in the double dot	54
4.5.1	Single-quasiparticle tunnelling	55
4.5.2	Andreev reflection	57
4.5.3	Cooper-pair splitting and photon absorption	61
4.6	Results and comparison with experimental data	62
4.6.1	Breaking pathways	64
4.6.2	Recombination pathways	64
4.6.3	Comparison with experimental data	67
4.7	Conclusions	68
5	Olfaction as a vibrationally-activated molecular switch	71
5.1	Introduction	71
5.2	The vibrationally-assisted electron transfer model for olfaction	74
5.3	Incoherent electron transfer rates from a polaron master equation . .	76
5.3.1	Odorant absent	78
5.3.2	Odorant present	79
5.4	Treating the odorant mode non-perturbatively	81
5.4.1	Master equation dynamics	84
5.4.2	Damping the odorant mode	86
5.5	The dependence of transfer rates on environmental structure	88
5.6	Conclusions	92
	Bibliography	94

List of Figures

3.1	A schematic representation of the exciton transport network.	23
3.2	A comparison of the variational master equation dynamics with those of weak coupling and polaron master equations for a three-site system.	33
3.3	Population dynamics of sites 1 and 3 of the FMO complex with a range of environment parameters.	35
3.4	Full population dynamics for the FMO complex predicted by the variational master equation.	37
4.1	The superconducting double dot.	43
4.2	The energy structure of the SDD.	53
4.3	Theoretically calculated breaking rates.	63
4.4	Theoretically calculated recombination rates.	65
4.5	A comparison with experimental rates.	67
5.1	Population dynamics of the donor-acceptor system in different environments.	83
5.2	Odorant mode population dynamics.	85
5.3	Donor-acceptor population dynamics with dissipation on the odorant mode.	87
5.4	Frequency selectivity for different environmental parameters.	89
5.5	Sensitivity to the presence of the odorant as a function of reorganisation energy.	90
5.6	The effect of odorant mode dissipation on frequency selectivity.	91

Chapter 1

Motivation and outline

1.1 Motivation

The early formulation of quantum mechanics by Heisenberg, Schrödinger *et al* was principally concerned with the physics of isolated or *closed* quantum systems, whose behaviour is self-contained and unitary. However, in reality it is incredibly difficult to isolate a system from its environment; all physical systems, with the possible exception of the universe as a whole, are actually *open*. That is, they are not self-contained and their behaviour is influenced by their environment. It is this interaction with the environment — which manifests itself as noise — that has provided the major obstacle to the experimental realisation of many of the phenomena predicted by basic quantum theory, such as entanglement and macroscopic quantum coherence. Only on the very smallest length and temperature scales can pure quantum dynamical effects be studied cleanly.

However, modern quantum technologies — that is to say those that rely on quantum effects beyond those described by equilibrium chemistry and condensed matter theory — are increasingly reaching the point where they cannot avoid significant interactions with their environments. In order to control these interactions, and even potentially harness them for the benefit of the aforementioned technologies, it is important that we have a firm theoretical understanding of the way in which they can affect dynamics.

In particular, quantifying the effects of noise in quantum computing has been a principal goal of both theoretical and experimental research in recent years. Solid-state implementations based on superconducting circuits are no exception, and the precise behaviour of quasiparticle excitations in their component devices, created through environmental interactions, can have direct consequences for their functionality.

Moreover, it has emerged that some biological energy transport processes involve relatively long-lived quantum coherence and other non-classical effects, which they could potentially be utilising to improve their efficiency. These processes usually occur in what are — to the quantum physicist — incredibly messy and disruptive circumstances. Not only is it of fundamental scientific interest to model these processes accurately, and hence determine the functional purpose of the pertinent quantum phenomena, it is also of great practical relevance; the principles underlying the biological transport could influence the design of artificial nano-scale technologies.

One such potential biological source of inspiration is the olfactory receptor, which, it has been suggested, could work on a principle of electron transfer — mediated by the vibrational environment that candidate odorant molecules provide. There is currently no commercially-available, artificial analogue of this system and a better understanding of the fundamental physics involved in olfaction could lead to the development of such a general-purpose chemical sensor.

The unifying theme of this thesis is the study of out-of-equilibrium energetic excitations in small, open quantum systems and how their dynamics is influenced by the environment to which they are coupled. Whether in the context of biological molecular networks or of low-temperature superconducting devices, understanding the transport of these energy quanta is of paramount importance to their respective systems' function.

1.2 Outline

This thesis begins, in chapter 2, with a review of some of the mathematical techniques of open quantum systems theory on which later chapters depend. After briefly setting the scene with an outline of the broader theory, and introducing the basic mathematical formalism, we focus on the derivation of two successively more sophisticated quantum master equations. We then conclude with a discussion of energy transport, in which we construct the spin-boson model used in later chapters.

The first of the subsequent research chapters (chapter 3), develops a master equation technique in which the dynamics of an open system is computed in a variationally constrained reference frame. This allows for potentially more accurate simulation of certain important energy transfer models in parameter regimes which are not only physically relevant, but also problematic for more pedestrian methods. After extending the technique to systems with multiple excitation sites and with a broad class of environments, we present example simulations comparing the variational master

equation with the more commonly used weak-coupling and polaron master equations. The work presented is based primarily on ref. [1].

Chapter 4, including and extending calculations performed for refs. [2, 3], concerns itself with modelling the excitation behaviour of a pair of coupled, nano-scale superconducting islands (the ‘superconducting double quantum dot’) connected to an external circuit. After describing the device in detail, we use results from BCS theory to derive rates for each of the environmentally driven transitions in the system, before predicting the average dynamical behaviour that would be observed in an experiment. We then go on to compare these predictions with actual experimental data and discuss the possibility of the device as a microwave photon detector. In contrast to other chapters of this thesis, the environment contains a fermionic component and thus the mathematics involved differs considerably; the techniques used come more often from condensed matter physics than from quantum chemistry or quantum optics — the two fields most relevant to the other chapters. However, the end goal is the same — we are interested in the dynamics of non-equilibrium excitations in an open system and how the energy they carry is dissipated to the environment.

Finally, in chapter 5, we investigate a model for olfaction (the sense of smell) in which molecules’ vibrational modes promote the tunnelling of electrons in a receptor, thus facilitating their recognition. A master equation is used to simulate the olfactory receptor in the presence of an odorant molecule, and the resulting dynamics is found to differ considerably from that predicted by earlier semi-classical models, which do not take into account certain details of the environment. We show in which regimes the earlier results can be recovered and go on to describe how, outside of these cases, the environment can be used to facilitate higher frequency resolution in the receptor. This chapter is mainly based on ref. [4].

Since the research chapters contend with a rather wide selection of research problems, they each contain their own introduction and conclusions. These are intended to respectively motivate and provide context for the particular questions involved, and provide a summary of both the chapters’ key results and potential avenues of further research.

Chapter 2

Open quantum systems theory

We begin this thesis with an introduction to the theory of open quantum systems, much of which will be useful for later chapters. After briefly providing context for the later derivations within the broader theory, we move on to describe some of the basic mathematical concepts of quantum mechanics which may not be taught in a first course on the subject (a great deal of this material can be found in textbooks such as refs. [5–7]). Subsequently, we cover two standard master equation derivations, for which we closely follow chapters 3 & 9 (for secs. 2.3 & 2.4 respectively) of the excellent book by Breuer & Petruccione (ref. [7]) Finally, in sec. 2.5 we briefly discuss one of the most commonly used models for energy transfer in open systems, which we will go on to use later in the thesis.

2.1 Background

Open quantum systems theory can trace its origins to early models of spontaneous emission in the 1930’s [8]. Since then — partly due to the necessity of accurately modelling environmental noise in realistic scenarios — extensive research effort has gone into describing the properties and behaviour of open quantum systems, and the field has developed to the point where there are now several comprehensive textbooks covering standard results and techniques [7–9].

The principal utility of the theory is in taking into account the influence of the environment without having to explicitly track its behaviour. By definition, the environment contains all the degrees of freedom which are not of direct interest or are otherwise inaccessible, and it is therefore of great benefit not to have to waste computational resources modelling it in detail. Open quantum systems theory has found especial use in simulating the effects of noise in quantum computing, for example in

optical [10], solid-state [11] and superconducting circuit based [12–14] implementations. Quantum computing schemes have even been suggested in which noise plays a beneficial role [15, 16]. Furthermore, and most relevant to this thesis, open systems theory is vital for studying environment-assisted energy transport, which will be discussed further in sec. 2.5.

Probably the most commonly used and conceptually straightforward approach to modelling open quantum systems is that using master equations — approximate equations of motion for the statistical state of an open system [7]. The interaction with the environment is encoded in the increasingly complicated terms of a perturbation series, which is eventually cut off at some finite order. One of the primary advantages of master equations over other methods is their comparatively simple form — interactions with the environment appear order by order and it is usually clear which terms in the system-environment Hamiltonian are contributing to the dynamics. Their solutions also tend to scale well, in terms of computability, with the dimension of the system in question and do not depend on the presence of particular symmetries.

In sec. 2.3 we derive a master equation from the equation of motion of the joint system-environment state by averaging over, or *tracing out*, the state of the environment. Along the way, we make several approximations, including the Markovian approximation, in which we neglect the backflow of information from the environment to the system. This allows us to greatly simplify the resulting equations of motion and to bring them into a form commonly applied to energy transport problems.

However, it is often impossible to neglect the consequences of correlations built up with the environment. So-called non-Markovian effects are present whenever the environment does not relax quickly, or when the system experiences rapid evolution, and have been the subject of much recent research [17, 18]. Whilst the aforementioned method of simply tracing out the environment can be used to produce a non-Markovian master equation, there exist several more powerful techniques which can be used to systematically derive master equations that do not make the same assumptions about the state of the environment as in the former case. In sec. 2.4 we use a projection super-operator approach to derive a comparatively straightforward master equation which, nevertheless, makes no approximations regarding the rate of relaxation of the environment. Other methods for deriving non-Markovian master equations include those based on quantum state diffusion [19–21], where the effect of the environment is encoded in a stochastic differential equation for the quantum state vector, which is then used to define an equation of motion for the density operator.

Several other techniques have been developed to calculate the explicit time-domain dynamics of open quantum systems which do not rely on the formulation of master equations. Some are approximate, such as a recent proposal which uses a perturbative phase-space representation of the density operator to analytically solve for dynamics [22]. Other approaches are numerically exact, meaning that given sufficient computational resources, they will converge to the correct dynamics under some well-controlled approximations. Such techniques include those based on Feynman path integrals [23–26], hierarchical equations of motion [27–29] and density matrix renormalization group methods [30]. Though powerful, these approaches typically place restrictions on the kind of system that can be modelled, and they may also scale badly (in terms of computing resources) with the size and complexity of said system. Therefore, for large scale simulations across a range of parameters they are often impractical, and it is the master equation approach that must be taken.

2.2 The mathematical representation of open systems

2.2.1 Pure and mixed states

A quantum system’s state can be described by a vector $|\psi\rangle$ in a complex Hilbert space $\mathcal{H}$. $|\psi\rangle$ contains all the information about the system that one could hope to extract through measurement of physical observables — represented by Hermitian operators on $\mathcal{H}$. The dynamical behaviour of an isolated, *closed* quantum system is determined by its Hamiltonian H which generates time evolution through the Schrödinger equation:

$$\frac{d}{dt}|\psi(t)\rangle = -\frac{i}{\hbar}H|\psi(t)\rangle. \quad (2.1)$$

The solution to this equation is always of the form $|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle$, where $U(t, t_0)$ is a unitary time-evolution operator satisfying $U^\dagger U = \mathbb{1}$. Furthermore, the time evolution operator is composable $U(t, t_1)U(t_1, t_0) = U(t, t_0)$ and is time reversible, in the sense that the time reversed operator $U(t_0, t)$ is also a legitimate time-evolution operator, and is simply related to its forward-time counterpart by Hermitian conjugation: $U(t_0, t) = U^\dagger(t, t_0)$. For a Hamiltonian which is constant in time, the evolution operator is simply $U(t, t_0) = \exp[-\frac{i}{\hbar}H(t - t_0)]$.

When there is some uncertainty about the exact quantum state of a system, or equivalently, when one wants to describe the average state of an ensemble of identical systems, the description in terms of a single ‘pure’ quantum state $|\psi\rangle$ is insufficient

to account for the measurement statistics of physical observables. In this case, a statistical mixture of pure states $\{|\psi_j\rangle\}$ with associated classical probabilities $\{p_j\}$ is encoded in the density operator

$$\rho = \sum_j p_j |\psi_j\rangle\langle\psi_j|. \quad (2.2)$$

Although often (including in this thesis) referred to as the state of the system, it is worth remembering that the density operator is actually the statistical state of an (actual or hypothetical) ensemble of such systems. Measurements of an individual system will always be consistent with it being in a particular pure quantum state at any given time, the probability of which can be determined from the corresponding density operator. Chapters 5-8 of ref. [7] provide a detailed account of the quantum trajectory (or quantum jump) formalism, which describes the stochastic, pure-state evolution of an individual system in the presence of an environment.

The density operator has several characteristic properties which follow directly from its definition in eq. (2.2):

- ρ is Hermitian: $\rho^\dagger = \rho$.
- Due to the normalisation of its constituent pure states and the fact that $\sum_j p_j = 1$, $\text{tr}(\rho) = 1$.
- ρ is a positive operator: $\langle\phi|\rho|\phi\rangle \geq 0 \quad \forall \quad |\phi\rangle \in \mathcal{H}$. In fact, the diagonal elements of ρ are the probabilities to be found in the corresponding basis states.
- $\text{tr}(\rho^2) \leq 1$, with equality for pure states; this is known as the purity of the state.
- For any operator Q , $\text{tr}(\rho Q) = \sum_j p_j \langle\psi_j|\rho|\psi_j\rangle = \langle Q \rangle$. In this way, ρ encodes the measurement statistics of the system.

Since the pure quantum states appearing in the definition of ρ evolve under the Schrödinger equation, the density operator itself evolves in time according to the corresponding von Neumann equation

$$\frac{d}{dt}\rho(t) = -\frac{i}{\hbar}[H, \rho(t)], \quad (2.3)$$

which follows directly from eqs. (2.1) & (2.2). For a closed quantum system, this again leads to a unitary evolution

$$\rho(t) = U(t, t_0)\rho(t_0)U^\dagger(t, t_0). \quad (2.4)$$

2.2.2 Composite systems and dynamical maps

In quantum theory, the (pure) state of a system with multiple degrees of freedom — each with its corresponding Hilbert space $\mathcal{H}_j$ — is an element of the tensor product space $\bigotimes_j \mathcal{H}_j = \mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \cdots$. This is the way in which subsystems are composed in quantum mechanics. Considered individually, these subsystems are *open*, in the sense that they are interacting with the external environment formed by the remaining subsystems. Density operators describing the statistical state of the individual subsystems can be obtained from the overall density operator by means of a partial trace, which involves averaging over the degrees of freedom belonging to the other subsystems. Mathematically, the operation is defined as follows: For a partition of the total system into subsystems A and B , the *reduced state* of subsystem A is

$$\rho_A = \text{tr}_B(\rho_{AB}) = \sum_j \langle j_B | \rho_{AB} | j_B \rangle, \quad (2.5)$$

where $\{|j_B\rangle\}$ is a complete basis for subsystem B . This is, in essence, the quantum analogue of finding the marginals of a joint probability distribution.

One important difference between open and closed quantum systems is that open systems are no longer restricted to unitary evolution. This can be seen by taking the partial trace over B in the evolution equation for ρ_{AB} (eq. (2.4))

$$\begin{aligned} \rho_A(t) &= \text{tr}_B \{ \rho_{AB}(t) \} \\ &= \text{tr}_B \{ U(t, t_0) \rho_{AB}(t_0) U^\dagger(t, t_0) \} \\ &\neq U_A(t, t_0) \text{tr}_B \{ \rho_{AB}(t_0) \} U_A^\dagger(t, t_0), \end{aligned} \quad (2.6)$$

where the last line becomes an equality if and only if the two systems are initially uncorrelated ($\rho_{AB}(t_0) = \rho_A(t_0) \otimes \rho_B(t_0)$) and are non-interacting ($H_{AB} = H_A + H_B$) such that $U(t, t_0) = U_A(t, t_0) \otimes U_B(t, t_0)$. In general, the dynamical evolution is non-linear with respect to the reduced system initial state $\rho_A(t_0)$ [31, 32], but if one is restricted to uncorrelated initial states the resulting dynamical maps are ensured to be linear and completely positive [33].

Completely positive (CP) transformations are those that take density operators to other density operators (they preserve their positivity and trace properties) and also have the property that, if applied to a subsystem in some joint state, they preserve the positivity — and hence physicality — of the overall density operator. It thus makes sense that dynamical evolution arising from interactions with some external, physical environment should be CP. This evolution can be written as a linear operator

acting on the reduced system state — a CP map — with the important caveat that the particular state of the reduced system initially cannot depend on that of the environment (as mentioned above, they must be uncorrelated). One can write a CP map in terms of a set of *Kraus operators* [34] $\{K_i(t, t_0)\}$ which evolve the reduced density matrix in the following way

$$\rho_A(t) = \sum_j K_j(t, t_0) \rho_A(t_0) K_j^\dagger(t, t_0). \quad (2.7)$$

These operators can be derived from the evolution of the overall system; taking the partial trace over subsystem B in eq. (2.4), for $\rho_{AB}(t_0) = \rho_A(t_0) \otimes \rho_B(t_0)$, leads to the following expression for the transformed reduced density matrix:

$$\begin{aligned} \rho_A(t) &= \text{tr}_B \{ U(t, t_0) \rho_A(t_0) \otimes \rho_B(t_0) U^\dagger(t, t_0) \} \\ &= \sum_{jk} \langle j_B | U(t, t_0) | k_B \rangle \rho_A(t_0) \langle k_B | \rho_B(t_0) | k_B \rangle \langle k_B | U^\dagger(t, t_0) | j_B \rangle \\ &= \sum_{jk} (\sqrt{p_{Bk}} \langle j_B | U(t, t_0) | k_B \rangle) \rho_A(t_0) (\sqrt{p_{Bk}} \langle j_B | U(t, t_0) | k_B \rangle)^\dagger, \end{aligned} \quad (2.8)$$

where $p_{Bk} = \langle k_B | \rho_B(t_0) | k_B \rangle$. By equating the final line to eq. (2.7), it follows that $\sum_j \hat{K}_j^\dagger(t, t_0) \hat{K}_j(t, t_0) = \mathbb{1}$. However, it is not necessarily true that the Kraus operators satisfy $\sum_j \hat{K}_j(t, t_0) \hat{K}_j^\dagger(t, t_0) = \mathbb{1}$ (when they do, the overall map is called *unital*).

2.2.3 The Schrödinger, Heisenberg and interaction pictures

One of the useful properties of quantum mechanics is that its predictions are invariant under changes of reference frame, described mathematically by unitary transformations (we will use this symmetry extensively in chapter 3). In particular, one of the great early results of quantum theory was the proof of equivalence between what have now become known as the Schrödinger and Heisenberg pictures of quantum mechanics. The former describes the evolution of time-dependent states $|\psi_S(t)\rangle$ under the Schrödinger equation, which are acted upon by time-independent operators Q_S , whilst in the latter it is the operators $Q_H(t)$ which evolve in time and the states $|\psi_H\rangle$ which remain constant. States and operators in the two pictures are related by the time evolution operator generated by the system's Hamiltonian H :

$$\begin{aligned} |\psi_H\rangle &= e^{iHt/\hbar} |\psi_S(t)\rangle, \\ Q_H(t) &= e^{iHt/\hbar} Q_S e^{-iHt/\hbar}. \end{aligned} \quad (2.9)$$

Throughout this thesis, we will primarily work within the Schrödinger picture (and will indicate when this is not the case). However, it will often prove convenient

to move into the Heisenberg picture with respect to *part* of the Hamiltonian. If we partition a composite Hamiltonian into parts local to each subsystem and a remaining interaction term, $H = H_A + H_B + H_{AB}$, we can move into a new reference frame in which new states $|\psi^I(t)\rangle$ are related to the old ones $|\psi(t)\rangle$ (where we have dropped the subscript for the Schrödinger picture) by

$$|\psi^I(t)\rangle = e^{i(H_A+H_B)t/\hbar}|\psi(t)\rangle. \quad (2.10)$$

This intermediate picture is known as the interaction picture, in which the time evolution of states is governed solely by the (now time-dependent) interaction Hamiltonian

$$H_{AB}(t) = e^{i(H_A+H_B)t/\hbar}H_{AB}e^{-i(H_A+H_B)t/\hbar}. \quad (2.11)$$

Unless entirely unambiguous (generally through explicit time dependence), we will label operators in the interaction picture with a superscript I .

2.3 The Born-Markov master equation

When the Kraus operators for a dynamical map are composable, in the sense that $K_j(t, t')K_j(t', t_0) = K_j(t, t_0)$ for $t > t'$, they form a semigroup — a set closed under multiplication, but without an inverse for every element. This property holds when one can neglect the build-up of correlations between system and environment and when the evolution of the system from a given point does not depend on its earlier state. The former of these approximations, a consequence of the (weak-coupling) Born approximation, is necessary for an intermediate dynamical map to be CP, whilst the latter Markovian approximation (along with an assumption about the relative timescales of Hamiltonian and environment-induced evolution known as the secular approximation) ensures the semigroup property.

In order to calculate the dynamical evolution of a reduced system (henceforth labelled S), we need to be able to write down an equation of motion for its state $\rho_S(t)$, similar to that in eq. (2.3). These are called quantum master equations and extend the concept of a classical master equation — which describes the evolution of a probability distribution under a stochastic process — to quantum statistical states. It was shown by Lindblad [35], as well as by Gorini, Kossakowski and Sudarshan [36], that the most general form for a quantum master equation which generates evolution under a dynamical semigroup, as described above, is

$$\frac{d}{dt}\rho_S(t) = -\frac{i}{\hbar}[H_S, \rho_S(t)] + \sum_k \gamma_k \left(L_k \rho_S(t) L_k^\dagger - \frac{1}{2} L_k^\dagger L_k \rho_S(t) - \frac{1}{2} \rho_S(t) L_k^\dagger L_k \right), \quad (2.12)$$

where H_S is the local Hamiltonian and the Lindblad operators $\{L_k\}$ span the operator space of S . That is, for an N -dimensional system S , there can be up to N^2 independent Lindblad operators (including the identity).

When the microscopic details of a system's environment are unknown or irrelevant, eq. (2.12) can be used with L_k 's which represent phenomenological environmental interaction processes, and whose corresponding rates γ_k parameterise the environment's influence. However, in this thesis we will usually be concerned with the dynamics which arise from a particular microscopic Hamiltonian describing interaction with the environment. For the remainder of this section we will derive the standard Born-Markov master equation which comes about from a joint system-environment Hamiltonian $H = H_S + H_E + H_{SE}$, before showing how, with one extra approximation, it can be brought into the form of eq. (2.12).

The starting point for the reduced-system master equation is the von Neumann equation (eq. (2.3)) for the full density operator $\rho_{SE}(t)$ written in the interaction picture with respect to the local part of the Hamiltonian ($H_S + H_E$),

$$\frac{d}{dt}\rho_{SE}^I(t) = -\frac{i}{\hbar}[H_{SE}(t), \rho_{SE}^I(t)]. \quad (2.13)$$

This has the formal solution (for separable initial state $\rho_{SE}(0) = \rho_S(0) \otimes \rho_E(0)$ and initial time $t_0 = 0$)

$$\rho_{SE}^I(t) = \rho_S(0) \otimes \rho_E(0) - \frac{i}{\hbar} \int_0^t ds [H_{SE}(s), \rho_{SE}^I(s)], \quad (2.14)$$

which can be substituted back into eq. (2.13) to obtain a equation of motion for $\rho_{SE}(t)$ up to second order in $H_{SE}(t)$:

$$\frac{d}{dt}\rho_{SE}^I(t) = -\frac{i}{\hbar}[H_{SE}(t), \rho_S(0) \otimes \rho_E(0)] - \frac{1}{\hbar^2} \int_0^t ds [H_{SE}(t), [H_{SE}(s), \rho_{SE}^I(s)]]. \quad (2.15)$$

By tracing out the environment, we arrive at a master equation for the reduced density operator $\rho_S^I(t)$,

$$\frac{d}{dt}\rho_S^I(t) = -\frac{1}{\hbar^2} \int_0^t ds \operatorname{tr}_E \{ [H_{SE}(t), [H_{SE}(s), \rho_{SE}^I(s)]] \}, \quad (2.16)$$

where we have assumed that $\operatorname{tr}\{H_{SE}(t)(\mathbb{1} \otimes \rho_E(0))\} = 0$ (it is always possible to reparation H such that this is the case when $\rho_E(0)$ is a stationary state). We now make the Born approximation, which assumes a weak coupling between system and environment, such that we can neglect any influence the system has on the environment's state. This allows us to write $\rho_{SE}^I(t) \simeq \rho_S^I(t) \otimes \rho_E(0)$, so that

$$\frac{d}{dt}\rho_S^I(t) \simeq -\frac{1}{\hbar^2} \int_0^t ds \operatorname{tr}_E \{ [H_{SE}(t), [H_{SE}(s), \rho_S^I(s) \otimes \rho_E(0)]] \}. \quad (2.17)$$

If we decompose the interaction Hamiltonian as $H_{SE} = \sum_j A_j \otimes B_j$, with A_j and B_j Hermitian, then the master equation can be written

$$\begin{aligned}
\frac{d}{dt}\rho_S^I(t) &\simeq -\frac{1}{\hbar^2} \int_0^t ds \operatorname{tr}_E \left\{ \left[\sum_j A_j(t) \otimes B_j(t), \left[\sum_k A_k(s) \otimes B_k(s), \rho_S^I(s) \otimes \rho_E(0) \right] \right] \right\} \\
&= -\frac{1}{\hbar^2} \sum_{jk} \int_0^t ds \left([A_j(t), A_k(s) \rho_S^I(s)] \operatorname{tr}_E \{ B_j(t) B_k(s) \rho_E(0) \} \right. \\
&\quad \left. - [A_j(t), \rho_S^I(s) A_k(s)] \operatorname{tr}_E \{ B_k(s) B_j(t) \rho_E(0) \} \right) \\
&= -\frac{1}{\hbar^2} \sum_{jk} \int_0^t d\tau \left([A_j(t), A_k(t-\tau) \rho_S^I(t-\tau)] \operatorname{tr}_E \{ B_j(t) B_k(t-\tau) \rho_E(0) \} \right. \\
&\quad \left. - [A_j(t), \rho_S^I(t-\tau) A_k(t-\tau)] \operatorname{tr}_E \{ B_k(t-\tau) B_j(t) \rho_E(0) \} \right) \quad (2.18)
\end{aligned}$$

where $A_j(t)$ and $B_j(t)$ are the interaction picture counterparts of A_j and B_j , and in the last line we have made the substitution $s = t - \tau$. Taking the initial state of the environment to be stationary ($[\rho_E(0), H_E] = 0$), we can write the environment correlation functions as $\operatorname{tr}_E \{ B_j(t) B_k(t-\tau) \rho_E(0) \} = \operatorname{tr}_E \{ B_j(\tau) B_k(0) \rho_E(0) \}$ (where we have used $B_j(t) = \exp(iH_E t/\hbar) B_j \exp(-iH_E t/\hbar)$). These correlation functions, which we label $\Lambda_{jk}(\tau)$, encode the memory of the environment — the faster they decay, the less important past states of the system are to its evolution. If they decay sufficiently quickly compared to the typical timescales over which the system's reduced state changes, we can make the Markovian approximation — we neglect any influence of past states of the system whatsoever. Mathematically this entails replacing $\rho_S^I(t-\tau)$ with $\rho_S^I(t)$ and taking the upper limit of the integral to infinity, casting the master equation in a time-local form:

$$\begin{aligned}
\frac{d}{dt}\rho_S^I(t) &\simeq -\frac{1}{\hbar^2} \sum_{jk} \int_0^\infty d\tau \left([A_j(t), A_k(t-\tau) \rho_S^I(t)] \Lambda_{jk}(\tau) \right. \\
&\quad \left. - [A_j(t), \rho_S^I(t) A_k(t-\tau)] \Lambda_{jk}^*(\tau) \right) \\
&= -\frac{1}{\hbar^2} \sum_{jk} \int_0^\infty d\tau \left([A_j(t), A_k(t-\tau) \rho_S^I(t)] \Lambda_{jk}(\tau) + \text{h.c.} \right). \quad (2.19)
\end{aligned}$$

Finally, we transform the density operator back into the Schrödinger picture, resulting in

$$\begin{aligned}
\frac{d}{dt}\rho_S(t) &= -\frac{i}{\hbar} [H_S, \rho_S(t)] \\
&\quad - \frac{1}{\hbar^2} \sum_{jk} \int_0^\infty d\tau \left([A_j, A_k(-\tau) \rho_S(t)] \Lambda_{jk}(\tau) + \text{h.c.} \right). \quad (2.20)
\end{aligned}$$

This is the standard Born-Markov master equation used in chapter 5 of this thesis. However, it is still not quite equivalent to eq. (2.12); for completeness, we will outline how to bring it into so-called Lindblad form. First we decompose the operators $A_j(t)$ into the eigenbasis $|E_n\rangle$ of the system Hamiltonian:

$$\begin{aligned} A_j(t) &= e^{iH_S t/\hbar} A_j e^{-iH_S t/\hbar} = \sum_{nm} e^{i(E_n - E_m)t/\hbar} |E_n\rangle \langle E_n| A_j |E_m\rangle \langle E_m| \\ &= \sum_{\omega} e^{i\omega t} A_j(\omega), \\ &= \sum_{\omega} e^{-i\omega t} A_j^\dagger(\omega). \end{aligned} \quad (2.21)$$

where

$$A_j(\omega) = \sum_{E_n - E_m = \hbar\omega} |E_n\rangle \langle E_n| A_j |E_m\rangle \langle E_m|. \quad (2.22)$$

We can then rewrite the interaction picture master equation as

$$\begin{aligned} \frac{d}{dt} \rho_S^I(t) &= -\frac{1}{\hbar^2} \sum_{jk\omega\omega'} \int_0^\infty d\tau \left(e^{i(\omega' - \omega)t} e^{i\omega\tau} [A_j(\omega'), A_k^\dagger(\omega) \rho_S^I(t)] \tilde{\Lambda}_{jk}(\tau) + \text{h.c.} \right) \\ &= -\frac{1}{\hbar^2} \sum_{jk\omega\omega'} \left(e^{i(\omega' - \omega)t} [A_j(\omega'), A_k^\dagger(\omega) \rho_S^I(t)] \tilde{\Lambda}_{jk}(\omega) + \text{h.c.} \right), \end{aligned} \quad (2.23)$$

where $\tilde{\Lambda}_{jk}(\omega)$ is the fourier transform of $\Lambda_{jk}(\tau)$. If we now assume that the change in the system due to the environment is slow compared to the typical coherent evolution timescales defined by $|\omega' - \omega|$, then we can make what is known as the secular approximation and drop the rapidly oscillating terms in eq. (2.23) for which $\omega' \neq \omega$. We then end up with the master equation

$$\frac{d}{dt} \rho_S^I(t) = -\frac{1}{\hbar^2} \sum_{jk\omega} \left([A_j(\omega), A_k^\dagger(\omega) \rho_S^I(t)] \tilde{\Lambda}_{jk}(\omega) + \text{h.c.} \right). \quad (2.24)$$

After transforming back into the Schrödinger picture again, we find that this Hamiltonian can be rewritten in the form of eq. (2.12) with a Lamb-shifted Hamiltonian $\tilde{H}_S = H_S + \sum_{jk\omega} \Im[\tilde{\Lambda}_{jk}(\omega)] A_j(\omega) A_k^\dagger(\omega)$. The Lindblad operators and corresponding rates can be found by diagonalising the matrix with elements $\Re[\tilde{\Lambda}_{jk}(\omega)]$ (for more details see chapter 3 of ref. [7]).

2.4 The time-convolutionless projection operator master equation

In this section, we sketch out the derivation of the time-convolutionless projection operator master equation used in chapter 3 of this thesis. This is more powerful than

the master equation derived in the previous section, since it allows for treatment of non-Markovian memory effects in the environment whilst still remaining time local (previous instances of the density operator do not appear on the right hand side of the equation).

The starting point is a projection super-operator (a linear map which takes operators to other operators) $\mathcal{P}$ which selects the part of the density operator which we are interested in

$$\mathcal{P}\rho_{SE}(t) = \text{tr}_E\{\rho_{SE}(t)\} \otimes \rho_R = \rho_S(t) \otimes \rho_R, \quad (2.25)$$

where ρ_R is some constant state of the environment. The counterpart of this super-operator, $\mathcal{Q} = 1 - \mathcal{P}$, similarly selects the irrelevant part of the density operator. We want to find an equation of motion for $\mathcal{P}\rho_{SE}(t)$ independent of $\mathcal{Q}\rho_{SE}(t)$, which we do by first writing eq. (2.13) as

$$\frac{d}{dt}\rho_{SE}^I(t) = \alpha\mathcal{L}(t)\rho_{SE}^I(t), \quad (2.26)$$

where the super-operator $\mathcal{L}(t)$ acts as

$$\mathcal{L}(t)\rho = -\frac{i}{\hbar}[H_{SE}(t), \rho], \quad (2.27)$$

and we have taken the (small) expansion parameter α outside the interaction Hamiltonian ($H_{SE}(t) \rightarrow \alpha H_{SE}(t)$). Noting that

$$\frac{d}{dt}\mathcal{P}\rho_{SE}^I(t) = \mathcal{P}\frac{d}{dt}\rho_{SE}^I(t) \quad \text{and} \quad \frac{d}{dt}\mathcal{Q}\rho_{SE}^I(t) = \mathcal{Q}\frac{d}{dt}\rho_{SE}^I(t),$$

we act with each of the projectors $\mathcal{P}$ and $\mathcal{Q}$ on eq. (2.26) and, using the identity $\rho_{SE}^I(t) = \mathcal{P}\rho_{SE}^I(t) + \mathcal{Q}\rho_{SE}^I(t)$, we obtain the coupled equations

$$\frac{d}{dt}\mathcal{P}\rho_{SE}^I(t) = \alpha\mathcal{P}\mathcal{L}(t)\mathcal{P}\rho_{SE}^I(t) + \alpha\mathcal{P}\mathcal{L}(t)\mathcal{Q}\rho_{SE}^I(t) \quad (2.28)$$

$$\frac{d}{dt}\mathcal{Q}\rho_{SE}^I(t) = \alpha\mathcal{Q}\mathcal{L}(t)\mathcal{P}\rho_{SE}^I(t) + \alpha\mathcal{Q}\mathcal{L}(t)\mathcal{Q}\rho_{SE}^I(t). \quad (2.29)$$

The latter can be solved formally using the time-ordered propagator

$$\mathcal{G}(t, s) = T_{\leftarrow} \exp \left[\alpha \int_s^t d\tau \mathcal{Q}\mathcal{L}(\tau) \right], \quad (2.30)$$

where $T_{\leftarrow(\rightarrow)}$ is the operator which orders expressions with time increasing to the left (right). $\mathcal{Q}\rho_{SE}^I(t)$ can then be written

$$\mathcal{Q}\rho_{SE}^I(t) = \mathcal{G}(t, 0)\mathcal{Q}\rho_{SE}^I(0) + \alpha \int_0^t ds \mathcal{G}(t, s)\mathcal{Q}\mathcal{L}(s)\mathcal{P}\rho_{SE}^I(s). \quad (2.31)$$

Substituting this expression back into eq. (2.28) would lead to a closed master equation for $\rho_S^I(t) = \text{tr}_E\{\mathcal{P}\rho_{SE}^I(t)\}$, known as the Nakajima-Zwanzig equation [37, 38]. This has the disadvantage of involving the time convolution in eq. (2.31), which, because it requires knowledge of the state for all previous times, is generally difficult to calculate. In order to bring the equation back into a time-local form, we introduce the reverse propagator

$$\mathcal{F}(t, s) = T_{\rightarrow} \exp \left[-\alpha \int_t^s d\tau \mathcal{L}(\tau) \right], \quad (2.32)$$

which evolves the density operator backwards in time: $\rho_{SE}^I(s) = \mathcal{F}(t, s)\rho_{SE}^I(t)$. Eq. (2.31) can be written without the time-convolution as

$$\begin{aligned} \mathcal{Q}\rho_{SE}^I(t) &= \mathcal{G}(t, 0)\mathcal{Q}\rho_{SE}^I(0) + \Sigma(t)(\mathcal{P} + \mathcal{Q})\rho_{SE}^I(t), \\ \Sigma(t) &= \alpha \int_0^t ds \mathcal{G}(t, s)\mathcal{Q}\mathcal{L}(s)\mathcal{P}\mathcal{F}(t, s), \end{aligned} \quad (2.33)$$

where we have used $1 = \mathcal{P} + \mathcal{Q}$. Rearranging and substituting into eq. (2.28), leads to a master equation of the form

$$\frac{d}{dt}\mathcal{P}\rho_{SE}^I(t) = \mathcal{K}(t)\mathcal{P}\rho_{SE}^I(t) + \mathcal{I}(t)\mathcal{Q}\rho_{SE}^I(0), \quad (2.34)$$

where

$$\mathcal{K}(t) = \alpha\mathcal{P}\mathcal{L}(t)\mathcal{P} + \alpha\mathcal{P}\mathcal{L}(t)[1 - \Sigma(t)]^{-1}\Sigma(t)\mathcal{P} \quad (2.35)$$

and

$$\mathcal{I}(t) = \alpha\mathcal{P}\mathcal{L}(t)[1 - \Sigma(t)]^{-1}\mathcal{G}(t, 0)\mathcal{Q}. \quad (2.36)$$

The super-operators $\mathcal{K}(t)$ and $\mathcal{I}(t)$ can be expanded in powers of α , as long as the super-operator $[1 - \Sigma(t)]^{-1}$ can be expanded in powers of $\Sigma(t)$ — and hence expanded in powers of α itself. $[1 - \Sigma(t)]^{-1}$ has a power expansion only if the system-environment coupling strength α and the evolution time t are suitably small; for larger couplings or longer times the subsequent form of the master equation can lead to unphysical results [7]. Writing

$$\mathcal{K}(t) = \sum_n \alpha^n \mathcal{K}_n(t), \quad (2.37)$$

we consider terms up to second order in α and find

$$\begin{aligned} \mathcal{K}_1(t) &= \mathcal{P}\mathcal{L}(t)\mathcal{P} \\ \mathcal{K}_2(t) &= \int_0^t ds (\mathcal{P}\mathcal{L}(t)\mathcal{L}(s)\mathcal{P} - \mathcal{P}\mathcal{L}(t)\mathcal{P}\mathcal{L}(s)\mathcal{P}). \end{aligned} \quad (2.38)$$

Expansion of the inhomogeneous term involving $\mathcal{I}(t)$ is somewhat more involved, as one would ideally like to rewrite it in terms of the relevant (system) part of the initial state, $\mathcal{P}\rho_{SE}^I(0)$. However, when the initial state is separable: $\rho_S(0) \otimes \rho_E(0)$, the inhomogeneous term can be eliminated for the choice $\rho_R = \rho_E(0)$. Henceforth, we make these choices of initial state and ρ_R ; for details of the general case, see chapter 9 of ref. [7]. When we trace out the environment in eq. (2.34) and substitute in for the second order expansion in eq. (2.37), we end up with a master equation for $\rho_S^I(t)$:

$$\frac{d}{dt}\rho_S^I(t) = \text{tr}_E \{ (\alpha\mathcal{K}_1(t) + \alpha^2\mathcal{K}_2(t))\mathcal{P}\rho_{SE}^I(t) \}. \quad (2.39)$$

Furthermore, when the interaction Hamiltonian has zero expectation value for the environment initial state $\rho_E(0)$,

$$\text{tr}_E \{ \mathcal{P}\mathcal{L}(t)\mathcal{P}\rho_{SE}^I(t) \} \propto \text{tr} \{ H_{SE}(t)\rho_E(0) \} = 0, \quad (2.40)$$

and $\mathcal{K}_1(t)$ and the second term in the integrand of $\mathcal{K}_2(t)$ vanish. The only remaining term in the master equation can be expanded out explicitly in terms of $H_{SE}(t)$ as

$$\begin{aligned} \frac{d}{dt}\rho_S^I(t) &= \int_0^t ds \text{tr}_E \{ \mathcal{P}\mathcal{L}(t)\mathcal{L}(s)\mathcal{P}\rho_{SE}(t) \} \\ &= -\frac{1}{\hbar^2} \int_0^t ds \text{tr}_E \{ [H_{SE}(t), [H_{SE}(s), \rho_S^I(t) \otimes \rho_E(0)]] \}. \end{aligned} \quad (2.41)$$

This is very similar in form to one of the intermediate stages (eq. (2.17)) in the derivation of the Born-Markov master equation in the previous section. However, it has been put into a time-local form without resorting to any Markov approximation, therefore it will correctly keep track of memory effects in the environment. If we again write $H_{SE}(t) = \sum_j A_j(t) \otimes B_j(t)$ and make the substitution $s = t - \tau$, we can expand out the commutators in a manner similar to the previous section:

$$\frac{d}{dt}\rho_S^I(t) = -\frac{1}{\hbar^2} \sum_{jk} \int_0^t d\tau ([A_j(t), A_k(t-\tau)\rho_S^I(t)]\Lambda_{jk}(\tau) + \text{h.c.}), \quad (2.42)$$

where the bath correlation functions are again defined as $\Lambda_{jk}(\tau) = \text{tr}_E \{ B_j(\tau)B_k(0)\rho_E(0) \}$. Finally, we move back into the Schrödinger picture to arrive at

$$\begin{aligned} \frac{d}{dt}\rho_S(t) &= -\frac{i}{\hbar}[H_S, \rho_S(t)] \\ &\quad -\frac{1}{\hbar^2} \sum_{jk} \int_0^t d\tau ([A_j, A_k(-\tau)\rho_S(t)]\Lambda_{jk}(\tau) + \text{h.c.}). \end{aligned} \quad (2.43)$$

We will use this master equation extensively in chapter 3 to investigate the validity of different choices of expansion Hamiltonian αH_{SE} .

2.5 A model for energy transport

In the later chapters of this thesis, we will be interested in modelling how open systems dynamically transition from one excited energy state to another. Since the excitations in these states are generally spatially separated, we call these processes energy transport — the energy in the initial and final states is localised in different places.

When constructing an energy transport model, it is important to isolate the degrees of freedom which are relevant to the problem at hand. The fully reductionist description of a system, in terms of the motion of, and interactions between, individual atoms and electrons — which for typical systems will number in the thousands — contains far more information than is necessary to explain the essential behaviour of excitation transfer. Atomistic simulations, such as those employing density functional theory [39], can be very useful for calculating the various states and energies of the often complicated physical systems involved in energy transfer; however, these problems can be exceedingly computationally complex [40] and rely on precise information about the spatial configurations of constituent atoms. For problems of energy transport, the molecules involved are often simply too large and too poorly characterised for these more complete simulations to be feasible. By focussing on the common features that underly energy transport in a broad range of systems, the more abstracted, coarse-grained model described here can be employed to satisfactorily extract useful results regarding these problems.

The system of interest is taken to have a finite number of relevant excited states — those that are dynamically accessible within the energy and time constraints of the problem at hand. In chapter 4, we investigate a system in which multiple (fermionic) excited states in each spatial region are important for the dynamics. More often than not though, each localised ‘site’ has only a single significant excited state associated with it, and the system as a whole can be considered as a collection of two-level subsystems with ground and excited states, $|g_n\rangle$ and $|e_n\rangle$, and local Hamiltonians

$$H_n = \frac{\varepsilon_n}{2}(|e_n\rangle\langle e_n| - |g_n\rangle\langle g_n|). \quad (2.44)$$

The individual sites are then coupled through the exchange Hamiltonians

$$H_{nm} = V_{nm}|e_n\rangle\langle g_m| + V_{nm}^*|g_n\rangle\langle e_m|, \quad (2.45)$$

which arise due to spatial overlap of the associated wavefunctions of the local excited states [41] and allow coherent transfer of excitations between sites. For N distinct

sites, the total system Hamiltonian

$$H_S = \sum_{n=1}^N H_n + \sum_{\text{pairs } \{n,m\}} H_{nm}, \quad (2.46)$$

is 2^N dimensional, but can be split into $N + 1$ disconnected subspaces containing a definite number of excitations. If the interactions with the environment, which we will discuss shortly, also preserve the total excitation number, then we can greatly reduce the effective dimension of the system by working within just one of these subspaces. In chapters 3 & 5, we will consider the simplest non-trivial case, in which we need only treat the N -dimensional subspace of states containing a single excitation. After redefining the zero of energy, the system Hamiltonian is

$$H_S = \sum_n \varepsilon_n |n\rangle\langle n| + \sum_{\text{pairs } \{n,m\}} V_{nm} |n\rangle\langle m| + V_{nm}^* |m\rangle\langle n|, \quad (2.47)$$

where $|n\rangle = \bigotimes_{m \neq n} |g_m\rangle \otimes |e_n\rangle$ and we will generally choose V_{nm} to be real.

The simplest way to model the environment for these systems is to use the phenomenological Lindblad operators from eq. (2.12). These operators can be generally split into three distinct classes based on their effect: dissipative hopping operators that incoherently transfer excitations between sites; dephasing operators that destroy quantum coherence between sites and localise excitations, and ‘sink’ operators that remove excitations from the system altogether. The latter are included to model the effect of irreversible loss of excitations from the system, and can be seen as dissipative hopping operators which take excitations to a site which is otherwise fully disconnected from the rest.

Based on the fundamental increase in speed of quantum random walks relative to their classical counterparts [42], one would expect a purely quantum evolution to be optimal for transporting excitations efficiently. However, studies using the phenomenological environments mentioned above have suggested that introducing decoherence can improve the speed and efficiency of transport between excitation sites in small disordered networks [43, 44], even for the case of pure dephasing [45]. Whilst capturing certain essential features of environment-assisted transport, these phenomenological interactions do not generally correspond precisely to those derived from more realistic models — in particular, they do not correctly take into account the energy scales of the environment to which the system dynamics is sensitive. Therefore, in order to more accurately investigate environmental influence on energy transport, we must describe the microscopic form of the system-environment interaction.

When the environment is not composed of identical fermions (as in chapter 4), and none of its individual degrees of freedom are too strongly coupled to the open system, we can treat it as a bath of harmonic oscillators representing its normal modes [23], whose Hamiltonian we can write

$$H_E = \sum_{\mathbf{k}} \omega_{\mathbf{k}} b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}}, \quad (2.48)$$

where $b_{\mathbf{k}}^{\dagger}$ is the creation operator for the mode with frequency $\omega_{\mathbf{k}}$. In general, the equilibrium positions of the modes depend on the excitation state of each site, such that, relative to their positions when the system is in the ground state, the oscillator modes are displaced as the excitation moves around the system. This manifests itself as the interaction Hamiltonian

$$H_{SE} = \sum_{\mathbf{k}} g_{n,\mathbf{k}} |n\rangle \langle n| (g_{n,\mathbf{k}} b_{\mathbf{k}}^{\dagger} + g_{n,\mathbf{k}}^* b_{\mathbf{k}}), \quad (2.49)$$

where $g_{n,\mathbf{k}}$ represents the degree to which the excitation on site n displaces the equilibrium of mode $\mathbf{k}$.

The combination $H = H_S + H_E + H_{SE}$ is known as the spin-boson Hamiltonian (see ref. [46] for a comprehensive review of the two-site case) and is the basic electron transport model which we will consider in chapters 3 & 5. Variations of this model have found use in a wide variety of systems, with applications ranging from simulating the dynamics of coupled quantum dots [47–50] in solid state physics, to those of impurities in lattice Bose-Einstein condensates [51]. However, it is in modelling excitation dynamics of microscopic biological systems that it has arguably had the most success in recent years. Examples include: Molecular complexes involved in photosynthesis, such as the *Fenna-Matthews-Olsen* complex in green sulphur bacteria [27, 52–61] and the light harvesting photosystems in green plants [62]; the electron transport chain in *Respiratory Complex I* [63]; certain models of magnetoreception in birds [64, 65] and the model of olfaction we study in chapter 5. In chapter 3 we further discuss this model in the context of excitonic excitations in discrete molecular networks, and describe how the properties of the environment enter into it. We then show how, using polaron transformations, the interaction Hamiltonian can be brought into a form more amenable to a perturbative master equation treatment.

This concludes our brief review of open systems theory. We have discussed several aspects of the field and have reproduced some of the results necessary for calculations in later chapters. Whilst the topics discussed and derivations presented here are by no means comprehensive, they emphasise the aspects of the theory most relevant for the remainder of this thesis.

Chapter 3

Variational polaron transformations for multi-site exciton transport models

3.1 Introduction

As discussed in chapter 2, master equation techniques provide an equation of motion for the reduced density matrix of an open system without having to track the full evolution of the environment. These are approximate methods for solving the system and normally involve some kind of perturbative expansion in a small parameter, such as the system-environment coupling strength. An advantage of the master equation approach is that it can offer insights into the mechanisms underlying the dynamics of a system by relating rates and energy shifts directly to microscopic parameters. However, the obvious drawback of many master equations is that they rely on certain Hamiltonian parameters being small. If this condition is not fulfilled, then the truncation of the perturbative expansion often leads to (potentially unphysical) results which can diverge wildly from the true dynamics [66].

In certain parameter regimes, performing unitary transformations, such as the polaron transformation [41, 48, 67–75] (also used in chapter 5), on the combined system-environment Hamiltonian can result in a smaller interaction energy in the transformed frame. The transformed system is then amenable to being modelled using a perturbative master equation. For example, the polaron transformation can work well over a broad range of parameters when the relevant timescales in the environment are short compared to those in the system — in fact, the polaron transformation diagonalises the Hamiltonian we use below when no electronic couplings are present between the sites. It is thus often used when the coupling between system and environment is

strong or when internal system couplings are small. Between the weak-coupling and polaron regimes, however, lies a region of parameter space for which neither model is appropriate. In addition, the polaron transformation runs into problems when applied to a system with an Ohmic or sub-Ohmic environment (one for which the environment spectral density scales linearly or sub-linearly, respectively, at low frequencies). In this case, infrared divergences arise which prevent certain master equations (such as the time-local form used in this chapter) from correctly predicting the dynamics in the transformed frame.

The variational polaron transformation [76–82] extends the standard polaron transformation and can allow one to derive a perturbative series which is as valid as possible (given the restricted form of the transformation) in all parameter regimes. This is achieved by performing an optimised, partial displacement on each of the environmental phonon modes. The displacement depends on their particular mode frequency, thereby interpolating between the weak-coupling and polaron representations for separate modes. Here we build on previous work on the variational transformation for two-site systems [78, 79, 81] which is in turn based on an idea originating with Silbey & Harris [76, 77]. In this chapter, we generalise of the formalism to any number of sites, allowing for the simulation of large networks across a range of environmental coupling parameters and temperatures. For comparison to other techniques, we have included examples of dynamics for systems in several different regimes. Throughout this chapter, we work with a system of units in which $\hbar = 1$. Unlike later chapters we primarily use cm^{-1} as a unit of energy; the conversion factor between cm^{-1} and meV — the unit used in later chapters — is $1 \text{ cm}^{-1} = 0.124 \text{ meV}$ ($1 \text{ meV} = 8.07 \text{ cm}^{-1}$).

3.2 Local and global environments in the transport model

As described in the previous chapter, the system (S) considered here is that of N , spatially-localised, coupled two-level systems, which we refer to as sites. Between them, they carry just one excitation — for molecular networks these are electronic excitations which, when they do not carry a net charge, are called excitons. The latter restriction to a single excitation allows for an exponential reduction in the size of the system Hilbert space, and is sufficient to describe the behaviour of many physically and biologically relevant systems [48, 49, 83]. For example, it is thought to be a valid approximation to the *in vivo* dynamics of the Fenna-Matthews-Olsen (FMO) complex studied in section 3.5 [55]. Each of the N sites is linearly-coupled

to the phonon environment (E). The Hamiltonian for the combined system and environment is given by

$$\begin{aligned} H &= H_S + H_E + H_I, & H_S &= \sum_n \varepsilon_n |n\rangle\langle n| + \sum_{n \neq m} V_{nm} |n\rangle\langle m|, \\ H_E &= \sum_{\mathbf{k}} \omega_{\mathbf{k}} b_{\mathbf{k}}^\dagger b_{\mathbf{k}}, & H_{SE} &= \sum_{n, \mathbf{k}} |n\rangle\langle n| (g_{n, \mathbf{k}} b_{\mathbf{k}}^\dagger + g_{n, \mathbf{k}}^* b_{\mathbf{k}}), \end{aligned} \quad (3.1)$$

where $b_{\mathbf{k}}$ is the annihilation operator for phonon mode $\mathbf{k}$, and $|n\rangle$ is the state of S in which only site n is excited. H_S describes the electronic degrees of freedom of the molecular network — each site n has a single excited level with associated self-energy ε_n relative to some overall ground state (which we do not include). The excited states at each site are coupled to one another, with coupling energies V_{nm} . In the context of molecular exciton transfer networks such as the FMO complex discussed in sec. 3.5.2, the energy ε_n is that required to produce a transition from the ground state to the electronic excited state of the molecule at site n without changing the configuration of nuclear coordinates (in other words without changing the phonon state of the environment). ε_n therefore involves two contributions: the electrostatic energy difference between the ground and excited states in equilibrium, and the reorganisation energy of the environment in the excited state [28]. The latter is the energy difference between the equilibrium configuration of the environment with the molecule in its excited state and the configuration after excitation from an equilibrated ground state (see eq. 3.4 below).

Whilst, in general, there will be a coupling between each phonon mode and each site of the system, we initially choose to make the approximation of purely local environments. That is, we assign each of the molecular sites its own bath of phonons with which it interacts exclusively. By making this approximation, we are assuming that the long-range, phonon-mediated coupling between sites is not important for the dynamics. Molecular dynamics simulations have suggested this to be the case for the FMO complex [58, 84]. However, for some energy transport models it has been shown that spatial correlations (between environments consisting of delocalised phonon modes) can affect dynamics considerably [48, 85–88]. At the end of the next section, we will discuss how the variational transformation can be extended to systems with more general, ‘global’ environments. However, for the majority of this chapter we deal with purely local phonon environments.

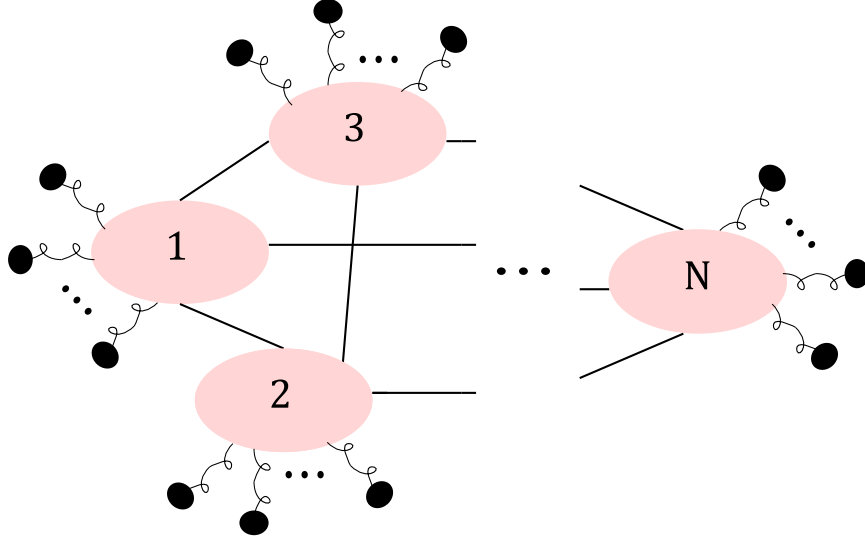


Figure 3.1: A schematic representation of the exciton transport network. The numbered ellipses represent the sites of the system, each of which is coupled to its own environment of phonon modes (masses on springs) and, in general, to every other site — via the black lines.

When restricted to local environments, the environment and interaction Hamiltonians become

$$H_E = \sum_{n,\mathbf{k}} \omega_{n,\mathbf{k}} b_{n,\mathbf{k}}^\dagger b_{n,\mathbf{k}}, \quad H_{SE} = \sum_{n,\mathbf{k}} |n\rangle\langle n| (g_{n,\mathbf{k}} b_{n,\mathbf{k}}^\dagger + g_{n,\mathbf{k}}^* b_{n,\mathbf{k}}), \quad (3.2)$$

where $b_{n,\mathbf{k}}$ is the annihilation operator for phonon mode $\mathbf{k}$ local to site n (see figure 3.1 for a cartoon visualisation of the above Hamiltonian). Since the environments at each site are independent, one can take the couplings $g_{n,\mathbf{k}}$ to be real for this model without loss of generality. In the more general case, however, the phase differences between the couplings to pairs of sites can encode the correlations between their environments.

The spectrum of the environment is usually taken to be a continuum, such that the couplings $g_{n,\mathbf{k}}$ can be described in terms of a spectral density $J_n(\omega)$. The spectral density is defined by

$$J_n(\omega) = \sum_{\mathbf{k}} |g_{n,\mathbf{k}}|^2 \delta(\omega - \omega_{\mathbf{k}}); \quad (3.3)$$

which encodes all the microscopic details (density of states, dispersion relation *etc.*) of the interaction with the environment. In the continuum case, a good measure of the strength of the system-environment coupling at each site is the reorganisation energy [28]:

$$\lambda_n = \int_0^\infty d\omega \frac{J_n(\omega)}{\omega}. \quad (3.4)$$

We assume that the environment is initially in a thermal (Gibbs) state at temperature $T = 1/(k_B\beta)$: $\rho_E(0) = e^{-\beta H_E} / \text{tr}(e^{-\beta H_E})$. In addition, the combined system-environment state is assumed to be initially separable, such that there are no system-environment correlations: $\rho(0) = \rho_S(0) \otimes \rho_E(0)$.

3.3 The variational polaron transformation

3.3.1 The variational transformation for systems with local environments

The Hamiltonian in eq. (3.1) is constructed in a way which is intuitive and transparent, in that H_S and H_E are the Hamiltonians for the system and environment in isolation and the interaction term H_{SE} is comparatively simple. However, one of the symmetries of quantum mechanics is that the physics of a system — even a composite one — is invariant under unitary transformations. As a consequence, we are not restricted to a single way of distinguishing two subsystems.

In the model outlined above, much of the energy associated with the interaction between system and environment is due to the excitation deforming the surrounding molecular structure, and hence affecting the state of the phonon environment. Applying the polaron transformation allows us to move into a reference frame where this back-action from system to environment is accounted for at the Hamiltonian level. The system is ‘dressed’ by the environment, and the environmental phonon modes are displaced in phase space conditional on the state of the system. The polaron transformation involves displacing the phonon modes of the environment, conditional on the state of the system; the explicit form of the transformation is

$$\tilde{H} = e^G H e^{-G}, \quad \text{where} \quad G = \sum_{n,\mathbf{k}} |n\rangle\langle n| \omega_{n,\mathbf{k}}^{-1} (f_{n,\mathbf{k}} b_{n,\mathbf{k}}^\dagger - f_{n,\mathbf{k}}^* b_{n,\mathbf{k}}), \quad (3.5)$$

leading to a transformed Hamiltonian:

$$\begin{aligned} \tilde{H} &= \tilde{H}_0 + \tilde{H}_{SE}, \\ \tilde{H}_0 &= \tilde{H}_S + \tilde{H}_E, \quad \tilde{H}_{SE} = \tilde{H}_L + \tilde{H}_D, \\ \tilde{H}_S &= \sum_n (\varepsilon_n + R_n) |n\rangle\langle n| + \sum_{n \neq m} \mathcal{B}_n \mathcal{B}_m V_{nm} |n\rangle\langle m|, \\ \tilde{H}_L &= \sum_{n,\mathbf{k}} |n\rangle\langle n| \left[(g_{n,\mathbf{k}} - f_{n,\mathbf{k}}) b_{n,\mathbf{k}}^\dagger + (g_{n,\mathbf{k}} - f_{n,\mathbf{k}})^* b_{n,\mathbf{k}} \right], \\ \tilde{H}_D &= \sum_{n \neq m} V_{nm} |n\rangle\langle m| B_{nm}, \quad \tilde{H}_E = H_E. \end{aligned} \quad (3.6)$$

The interaction Hamiltonian $\tilde{H}_{SE}$ now contains two terms. One, $\tilde{H}_L$, is of the same linear form as the interaction in the untransformed Hamiltonian, albeit with modified coupling strength. The other term, $\tilde{H}_D$, contains a new kind of interaction between off-diagonal system operators and products of environmental displacement operators $\mathcal{D}_{n,\mathbf{k}}(\alpha) = \exp[\alpha b_{n,\mathbf{k}}^\dagger - \alpha^* b_{n,\mathbf{k}}]$, these can be written

$$\begin{aligned} B_{nm} &= B_{mn}^\dagger = \prod_{\mathbf{k}} \mathcal{D}_{n,\mathbf{k}}(f_{n,\mathbf{k}}/\omega_{n,\mathbf{k}}) \mathcal{D}_{m,\mathbf{k}}(-f_{m,\mathbf{k}}/\omega_{m,\mathbf{k}}) - \mathcal{B}_n \mathcal{B}_m \\ &= \exp \left[\sum_{\mathbf{k}} \omega_{n,\mathbf{k}}^{-1} (f_{n,\mathbf{k}} b_{n,\mathbf{k}}^\dagger - f_{n,\mathbf{k}}^* b_{n,\mathbf{k}}) - \sum_{\mathbf{k}} \omega_{m,\mathbf{k}}^{-1} (f_{m,\mathbf{k}} b_{m,\mathbf{k}}^\dagger - f_{m,\mathbf{k}}^* b_{m,\mathbf{k}}) \right] \\ &\quad - \mathcal{B}_n \mathcal{B}_m. \end{aligned} \quad (3.7)$$

Here, the expectation values $(\mathcal{B}_n \mathcal{B}_m)$ of the displacement operators in the above expression have been taken into the system Hamiltonian, and are thus treated as renormalised couplings between the sites. The $\mathcal{B}_n$'s are given by

$$\begin{aligned} \mathcal{B}_n &= \text{tr} \left\{ \exp \left[\sum_{\mathbf{k}} \omega_{n,\mathbf{k}}^{-1} (f_{n,\mathbf{k}} b_{n,\mathbf{k}}^\dagger - f_{n,\mathbf{k}}^* b_{n,\mathbf{k}}) \right] \rho_E \right\} \\ &= \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} \frac{|f_{n,\mathbf{k}}|^2}{\omega_{n,\mathbf{k}}^2} \coth(\beta \omega_{n,\mathbf{k}}/2) \right], \end{aligned} \quad (3.8)$$

for a thermal equilibrium environmental state ρ_E , where the expression for the trace has been obtained using a coherent state representation for the environment [89]. The site energies after transformation are also shifted in comparison to the original frame by a factor R_n , defined as

$$R_n = \sum_{\mathbf{k}} \omega_{n,\mathbf{k}}^{-1} [|f_{n,\mathbf{k}}|^2 - 2\Re(f_{n,\mathbf{k}} g_{n,\mathbf{k}}^*)]. \quad (3.9)$$

Usually when the polaron transformation is discussed in the literature (*e.g.* in refs. [74, 75]), what is meant is the *fully-displaced* version of eq. (3.5), in which $f_{n,\mathbf{k}} = g_{n,\mathbf{k}}$, for all n and $\mathbf{k}$, and $\tilde{H}_L = 0$. This leaves only the new displacement interaction term in the Hamiltonian: $\tilde{H}_{SE} = \tilde{H}_D$. In the variational case, however, the $f_{n,\mathbf{k}}$ are left as free parameters, and minimisation over an upper bound on the free energy, as described below, determines their values. The idea underlying the work in this chapter, is that the optimisation inherent to the variational approach allows us to minimise the effect of the interaction Hamiltonian $\tilde{H}_{SE}$, given the form of the transformation. This is done here in order to validate the use of perturbation series in the derivation of a master equation for the system, which must in practice

be truncated at some finite order. In general, the ‘smaller’ $\tilde{H}_{SE}$ is, the more accurate the low-order dynamics are likely to be.

Since, most of the time, there is no single parameter in $\tilde{H}_{SE}$ which determines exactly how small its effect is, we choose instead to optimise the variational transformation by minimising the contribution of $\tilde{H}_{SE}$ to the free energy (the average energy of a thermal state of the system). This choice is consistent with earlier variational treatments [76, 77] and ensures that the steady state of the resulting dynamics is as accurate as possible — in equilibrium the free energy should be at a minimum. As it is generally impossible to find an exact analytical expression for the free energy, it is the Feynman-Bogoliubov upper bound [90] that we will minimise. The bound is given by

$$A_B = -\frac{1}{\beta} \ln \left[\text{tr}(e^{-\beta \tilde{H}_0}) \right] + \langle \tilde{H}_{SE} \rangle_{\tilde{H}_0} + \mathcal{O} \left(\langle \tilde{H}_{SE}^2 \rangle_{\tilde{H}_0} \right), \quad (3.10)$$

where $\langle X \rangle_{\tilde{H}_0} = \text{tr} \left(X e^{-\beta \tilde{H}_0} \right)$. The true free energy A is related to this bound by the inequality $A \leq A_B$. Given that we want to end up with $\tilde{H}_{SE}$ small, it is reasonable to neglect the higher order terms in 3.10 as a first approximation. This also vastly simplifies the minimisation procedure. Furthermore, the interaction Hamiltonian in the transformed frame has been constructed to be traceless, such that the second term goes to zero, $\langle \tilde{H}_{SE} \rangle_{\tilde{H}_0} = 0$. Therefore, minimisation amounts to maximising the value of $\text{tr}(e^{-\beta \tilde{H}_0})$. Although, perhaps counter-intuitively, $\tilde{H}_{SE}$ now appears to be absent from A_B , its influence is in fact still present implicitly in $\tilde{H}_0$; both of these operators depend on the variational parameters $f_{n,\mathbf{k}}$, which are fixed by the minimisation.

The transformed system Hamiltonian can be written as a function of the renormalisation parameters $\{R_n, \mathcal{B}_n\}$, therefore the minimisation condition can be written:

$$\frac{\partial A_B}{\partial f_{n,\mathbf{k}}} = \frac{\partial A_B}{\partial R_n} \frac{\partial R_n}{\partial f_{n,\mathbf{k}}} + \frac{\partial A_B}{\partial \mathcal{B}_n} \frac{\partial \mathcal{B}_n}{\partial f_{n,\mathbf{k}}} = 0 \quad \forall n, \mathbf{k}, \quad (3.11)$$

which, after using the expressions for the renormalisation parameters in eq. (3.9) allows us to write $f_{n,\mathbf{k}} = F_n(\omega_{n,\mathbf{k}})g_{n,\mathbf{k}}$, with

$$F_n(\omega_{n,\mathbf{k}}, \{R_n, \mathcal{B}_n\}) = \frac{2\omega_{n,\mathbf{k}} \frac{\partial A_B}{\partial R_n}}{2\omega_{n,\mathbf{k}} \frac{\partial A_B}{\partial R_n} - \mathcal{B}_n \frac{\partial A_B}{\partial \mathcal{B}_n} \coth(\beta\omega_{n,\mathbf{k}}/2)}. \quad (3.12)$$

In the continuum limit for the environment, the minimisation procedure for an N -site system amounts to solving the $2N$ coupled integral equations given by the definitions of the renormalisation parameters:

$$\mathcal{B}_n = \exp \left[-\frac{1}{2} \int_0^\infty d\omega \frac{F_n(\omega, \{R_n, \mathcal{B}_n\})^2 J_n(\omega)}{\omega^2} \coth(\beta\omega/2) \right], \quad (3.13)$$

$$R_n = \int_0^\infty d\omega \frac{J_n(\omega)}{\omega} F_n(\omega, \{R_n, \mathcal{B}_n\}) [F_n(\omega, \{R_n, \mathcal{B}_n\}) - 2]. \quad (3.14)$$

The derivatives present in the functions F_n , and hence in these simultaneous equations, can be calculated numerically using the definition of the Feynman-Bogoliubov bound in eq. (3.10).

3.3.2 Extending the transformation to spatially-correlated environments

We now proceed to derive a closed form for the variational parameters, in the case that the environment is not partitioned between the different sites of the system. In this case, each phonon mode $\mathbf{k}$ can have arbitrary couplings $g_{n,\mathbf{k}}$ to excitations on any site n . These couplings and their corresponding variational parameters $f_{n,\mathbf{k}}$ are now allowed to be complex, and we will often write them explicitly in terms of their modulus and argument: $g_{n,\mathbf{k}} = |g_{n,\mathbf{k}}| \exp(i\theta_{n,\mathbf{k}})$ and $f_{n,\mathbf{k}} = |f_{n,\mathbf{k}}| \exp(i\phi_{n,\mathbf{k}})$.

Performing a polaron transformation on the Hamiltonian in eq. (3.1), leads to an expression analogous to that in eq. (3.6), with

$$\begin{aligned}\tilde{H}_S &= \sum_n (\varepsilon_n + R_n) |n\rangle\langle n| + \sum_{n \neq m} \mathcal{B}_{nm} V_{nm} |n\rangle\langle m|, \\ \tilde{H}_L &= \sum_{n,\mathbf{k}} |n\rangle\langle n| \left[(g_{n,\mathbf{k}} - f_{n,\mathbf{k}}) b_{\mathbf{k}}^\dagger + (g_{n,\mathbf{k}} - f_{n,\mathbf{k}})^* b_{\mathbf{k}} \right], \\ \tilde{H}_D &= \sum_{n \neq m} V_{nm} |n\rangle\langle m| B_{nm}, \quad \tilde{H}_E = H_E,\end{aligned}\tag{3.15}$$

where the bath displacement operators, in this case, are

$$B_{nm} = \exp \left[\sum_{\mathbf{k}} \omega_{\mathbf{k}}^{-1} \left((f_{n,\mathbf{k}} - f_{m,\mathbf{k}}) b_{\mathbf{k}}^\dagger - (f_{n,\mathbf{k}} - f_{m,\mathbf{k}})^* b_{\mathbf{k}} \right) \right] - \mathcal{B}_{nm}.$$

The renormalisation parameters R_n and $\mathcal{B}_{nm}$, the latter of which cannot be split into a product of two functions dependent on single-site parameters, now take the slightly more complicated forms

$$\begin{aligned}\mathcal{B}_{nm} &= \exp \left[-\frac{1}{2} \sum_{\mathbf{k}} \frac{|f_{n,\mathbf{k}} - f_{m,\mathbf{k}}|^2}{\omega_{\mathbf{k}}^2} \coth(\beta\omega_{\mathbf{k}}/2) \right], \\ R_n &= \sum_{\mathbf{k}} \omega_{\mathbf{k}}^{-1} \left[|f_{n,\mathbf{k}}|^2 - 2|f_{n,\mathbf{k}}||g_{n,\mathbf{k}}| \cos(\phi_{n,\mathbf{k}} - \theta_{n,\mathbf{k}}) \right],\end{aligned}\tag{3.16}$$

where we can expand out

$$|f_{n,\mathbf{k}} - f_{m,\mathbf{k}}|^2 = |f_{n,\mathbf{k}}|^2 + |f_{m,\mathbf{k}}|^2 - 2|f_{n,\mathbf{k}}||f_{m,\mathbf{k}}| \cos(\phi_{n,\mathbf{k}} - \phi_{m,\mathbf{k}}).$$

There are now several ways to proceed with the minimisation of the free energy bound A_B , depending on whether we allow the magnitudes of the $f_{n,\mathbf{k}}$, their phases $\phi_{n,\mathbf{k}}$, or both to vary. Variation of the magnitudes in this case makes sense for the same reason the variation makes sense in the local environment case — the ‘size’ of the interaction Hamiltonian depends on their value (through the reorganisation energy defined in eq. (3.4)). Variation of the phases doesn’t have such an intuitive interpretation; since the phase differences encode the spatial correlations between phonon modes at each site [48], modification of these phase differences would indicate some kind of redistribution of the correlations. In the end, however, this point is moot, as it turns out in the following derivation that one can only find a closed form for the varied phases in the case where the phase differences between sites are left unchanged.

Taking the derivative of the free energy with respect to the global variational parameters we find

$$\begin{aligned} \frac{\partial A_B}{\partial |f_{n,\mathbf{k}}|} &= \frac{2}{\omega_{\mathbf{k}}} [|f_{n,\mathbf{k}}| - |g_{n,\mathbf{k}}| \cos(\phi_{n,\mathbf{k}} - \theta_{n,\mathbf{k}})] \frac{\partial A_B}{\partial R_n} \\ &- \frac{\coth(\beta\omega_{\mathbf{k}}/2)}{\omega_{\mathbf{k}}^2} \sum_{m \neq n} [|f_{n,\mathbf{k}}| - |f_{m,\mathbf{k}}| \cos(\phi_{n,\mathbf{k}} - \phi_{m,\mathbf{k}})] \mathcal{B}_{nm} \frac{\partial A_B}{\partial \mathcal{B}_{nm}}, \end{aligned} \quad (3.17)$$

for the magnitudes, and

$$\begin{aligned} \frac{\partial A_B}{\partial \phi_{n,\mathbf{k}}} &= 2 \frac{|g_{n,\mathbf{k}}| |f_{n,\mathbf{k}}|}{\omega_{\mathbf{k}}} \frac{\partial A_B}{\partial R_n} \sin(\phi_{n,\mathbf{k}} - \theta_{n,\mathbf{k}}) \\ &+ \sum_{m \neq n} \coth(\beta\omega_{\mathbf{k}}/2) \frac{|f_{n,\mathbf{k}}| |f_{m,\mathbf{k}}|}{\omega_{\mathbf{k}}^2} \mathcal{B}_{nm} \frac{\partial A_B}{\partial \mathcal{B}_{nm}} \sin(\phi_{n,\mathbf{k}} - \phi_{m,\mathbf{k}}), \end{aligned} \quad (3.18)$$

for the phases. We then set these derivatives to zero in order to find the set of $f_{n,\mathbf{k}}$ which minimise the free energy. Whilst the former of these expressions is linear in $|f_{n,\mathbf{k}}|$, both together describe a set of non-linear coupled equations, which cannot in general be separated out and solved analytically. There is one case, however, in which we can find a closed form solution for both the magnitudes and the varied phases, that in which $\phi_{n,\mathbf{k}} = \theta_{n,\mathbf{k}} + \psi_{\mathbf{k}}$ for all n . Substituting this into eq. (3.18) and rearranging gives

$$\tan \psi_{\mathbf{k}} = \frac{\sum_{n,m} h_{n,\mathbf{k}} h_{m,\mathbf{k}} \sin(\theta_{n,\mathbf{k}} - \theta_{m,\mathbf{k}}) \coth(\beta\omega_{\mathbf{k}}/2) \mathcal{B}_{nm} \frac{\partial A_B}{\partial \mathcal{B}_{nm}}}{\sum_n 2 |g_{n,\mathbf{k}}| h_{n,\mathbf{k}} \omega_{\mathbf{k}} \frac{\partial A_B}{\partial R_n}}, \quad (3.19)$$

with $h_{n,\mathbf{k}} = |f_{n,\mathbf{k}}| / \cos \psi_{\mathbf{k}}$. Using eq. (3.17), we can then find an expression for the $h_{n,\mathbf{k}}$ independent of the variational phases $\psi_{\mathbf{k}}$:

$$h_{n,\mathbf{k}} = 2 \sum_{m \neq n} (\mathbf{M}^{-1})_{nm} |g_{m,\mathbf{k}}| \frac{\partial A_B}{\partial R_m}, \quad (3.20)$$

where $\mathbf{M}$ is the $N \times N$ symmetric matrix:

$$\begin{aligned} \mathbf{M} &= \begin{pmatrix} \Gamma_{1,\mathbf{k}} & \Lambda_{12,\mathbf{k}} c_{12,\mathbf{k}} & \cdots & \Lambda_{1N,\mathbf{k}} c_{1N,\mathbf{k}} \\ \Lambda_{12,\mathbf{k}} c_{12,\mathbf{k}} & \Gamma_{2,\mathbf{k}} & & \\ \vdots & & \ddots & \\ \Lambda_{1N,\mathbf{k}} c_{1N,\mathbf{k}} & & & \Gamma_{N,\mathbf{k}} \end{pmatrix}, \\ \Lambda_{nm,\mathbf{k}} &= \coth(\beta\omega_{\mathbf{k}}/2) \frac{\mathcal{B}_{nm}}{\omega_{\mathbf{k}}} \frac{\partial A_B}{\partial \mathcal{B}_{nm}}, \quad c_{nm,\mathbf{k}} = \cos(\theta_{n,\mathbf{k}} - \theta_{m,\mathbf{k}}), \\ \Gamma_{n,\mathbf{k}} &= 2 \frac{\partial A_B}{\partial R_n} - \sum_{m \neq n} \Lambda_{nm,\mathbf{k}}. \end{aligned} \quad (3.21)$$

Like in the local bath case, the minimising values of the $f_{n,\mathbf{k}}$ are found by self consistently solving for the renormalisation parameters R_n and $\mathcal{B}_{nm}$ in eq. (3.16). For global baths, however, there are $N(N+1)/2$ simultaneous integral equations to solve (as opposed to $2N$ in the local bath case), and they are considerably more complicated in form. This means that the minimisation procedure quickly becomes unwieldy as the number of sites is increased, and one of the benefits of using a master equation approach over more exact methods — the relatively efficient scaling of computability with system size — is negated. For the remainder of this chapter, we therefore restrict ourselves to systems with local environments only.

3.4 The time-local projection operator Master Equation in the variational frame

As outlined in the previous section, a truncated perturbative expansion in the new interaction Hamiltonian $\tilde{H}_{SE}$ should, following the optimisation procedure, be as accurate as possible, given the form of the transformation and the minimisation condition used. The next step, therefore, is to derive a master equation in the variational frame using standard techniques, which we truncate at second order in $\tilde{H}_{SE}$. Here, we choose to derive a time-local projection-operator master equation, due to the relative ease with which it can be solved numerically. We follow the formal procedure outlined in chapter 2, utilising a projection operator $\mathcal{P}$, which acts as $\mathcal{P}\tilde{\rho} = \text{tr}_E(\tilde{\rho}) \otimes \rho_R$, and end up with the following expression for the evolution of $\tilde{\rho}$:

$$\frac{\partial}{\partial t} \text{tr}_E \{ \mathcal{P}\tilde{\rho}(t) \} = \text{tr}_E \{ \mathcal{K}_2(t) \mathcal{P}\tilde{\rho}(t) \} + \text{tr}_E \{ [\mathcal{I}_1(t) + \mathcal{I}_2(t)] (1 - \mathcal{P})\tilde{\rho}(0) \}, \quad (3.22)$$

where $\mathcal{K}_2$, $\mathcal{I}_1$ and $\mathcal{I}_2$ are super-operators acting on $\mathcal{P}\tilde{\rho}$ and $(1 - \mathcal{P})\tilde{\rho}$ respectively, which have been curtailed to second order in $\tilde{H}_{SE}$.

In the equivalent expression in the untransformed frame, the separable initial state means that the second, inhomogeneous term in eq. (3.22) disappears for the choice $\rho_R = \rho_E(0)$. In the variational frame this is no longer the case — the initial state is no longer separable, $\tilde{\rho}(0) \neq \tilde{\rho}_S(0) \otimes \tilde{\rho}_E(0)$ — and the inhomogeneous term must be taken into account. For simplicity we neglect the inhomogeneous term, which amounts to assuming that the environment relaxes into its displaced state instantaneously. One would expect this to be a good approximation at finite temperatures for smooth spectral densities and when the typical environment timescales are much shorter than the transition timescales in the system [72–75, 79]. The examples we present in sec. 3.5 satisfy each of these conditions.

After following the remainder of the derivation in chapter 2, and writing $\tilde{H}_{SE} = \sum_{i=1}^{N^2} S_i \otimes B_i$ (with interaction picture counterpart $\tilde{H}_{SE}(t) = \sum_{i=1}^{N^2} S_i(t) \otimes B_i(t)$), we end up with the Schrödinger picture master equation

$$\begin{aligned} \frac{\partial \tilde{\rho}_S(t)}{\partial t} = & -i[\tilde{H}_S, \tilde{\rho}_S(t)] \\ & - \sum_{i,j} \int_0^t ds \left(\Lambda_{ij}(s) \{S_i S_j(-s) \tilde{\rho}_S(t) - S_j(-s) \tilde{\rho}_S(t) S_i\} + \text{h.c.} \right). \end{aligned} \quad (3.23)$$

The interaction Hamiltonian system operators S_i can be split into three distinct groups in the following way:

$$S_i = \begin{cases} |n\rangle\langle n| = S_n^z & 1 \leq i \leq N, \\ |n\rangle\langle m| + |m\rangle\langle n| = S_{nm}^x & N < i \leq \frac{1}{2}N(N+1), \\ i|n\rangle\langle m| - i|m\rangle\langle n| = S_{nm}^y & \frac{1}{2}N(N+1) < i \leq N^2, \end{cases} \quad (3.24)$$

which leads in turn to three varieties of non-zero bath correlation function, $\Lambda_{ij}(s) = \text{tr}_E \{B_i(s)B_j(0)\rho_R\}$. The first type are due to the linear interaction term, $\tilde{H}_L$, and are therefore of the same form as those that appear in the standard weak coupling master equation:

$$\begin{aligned} \Lambda_n^{zz}(t) &= \phi_n^{zz}(t) \\ &= \int_0^\infty d\omega J_n(\omega) [1 - F_n(\omega)]^2 [\cos(\omega t) \coth(\beta\omega/2) - i \sin(\omega t)], \end{aligned} \quad (3.25)$$

where $F_n(\omega)$ is the continuum version of the optimised function in eq. (3.12). The second type come from the displacement-operator interaction, $\tilde{H}_D$, and are the only

type to appear in the fully displaced polaron master equation:

$$\begin{aligned}
\Lambda_{nmpq}^{xx}(t) &= \frac{1}{2} V_{nm} V_{pq} \mathcal{B}_n \mathcal{B}_m \mathcal{B}_p \mathcal{B}_q \left\{ \exp [\delta_{np} \phi_n^{xy}(t) + \delta_{mq} \phi_m^{xy}(t)] \right. \\
&\quad \left. + \exp [-\delta_{np} \phi_n^{xy}(t) - \delta_{mq} \phi_m^{xy}(t)] - 2 \right\}, \\
\Lambda_{nmpq}^{yy}(t) &= \frac{1}{2} V_{nm} V_{pq} \mathcal{B}_n \mathcal{B}_m \mathcal{B}_p \mathcal{B}_q \left\{ \exp [\delta_{np} \phi_n^{xy}(t) + (\delta_{mq} - \delta_{mp}) \phi_m^{xy}(t)] \right. \\
&\quad \left. - \exp [-\delta_{np} \phi_n^{xy}(t) - (\delta_{mq} - \delta_{mp}) \phi_m^{xy}(t)] \right\}, \quad (3.26)
\end{aligned}$$

where

$$\phi_n^{xy}(t) = \int_0^\infty d\omega \frac{J_n(\omega)}{\omega^2} F_n(\omega)^2 [\cos(\omega t) \coth(\beta\omega/2) - i \sin(\omega t)], \quad (3.27)$$

and the δ_{nm} are Kronecker deltas. Finally, the third type appear in the more general variational master equation due to an overlap between the two types of interaction:

$$\Lambda_{nmp}^{yz}(t) = \delta_{np} V_{nm} \mathcal{B}_n \mathcal{B}_m \phi_n^{yz}(t), \quad (3.28)$$

with

$$\phi_n^{yz}(t) = \int_0^\infty d\omega \frac{J_n(\omega)}{\omega} F_n(\omega) [1 - F_n(\omega)] [\sin(\omega t) \coth(\beta\omega/2) + i \cos(\omega t)]. \quad (3.29)$$

Many of these correlation functions are identically zero, and they require the calculation of only the $3N$ functions $\phi_n^{zz}(t)$, $\phi_n^{xy}(t)$ and $\phi_n^{yz}(t)$. This means that the (local bath) variational master equation is not significantly more difficult to solve than its weak coupling counterpart.

For a global bath, many more of the correlation functions Λ_{ij} are non-zero, and require the calculation of $\mathcal{O}(N^4)$ independent functions of time. As with the minimisation procedure, this poor scaling of the complexity of the problem with N could limit the usefulness of the variational transformation for systems in which spatial correlations in the environment play a significant role.

Eq. (3.23) can be used to calculate the dynamics of the density matrix in the variationally transformed frame. In order to consider quantities in the original frame, we must perform the inverse of the transformation in eq. (3.5). The site populations (diagonal elements of the density matrix) do not change, since the operators $|n\rangle\langle n|$ commute with the transformation. However, in general, the inverse transformation's effect on the coherences (off-diagonal elements of the density matrix) is much more

difficult to calculate and depends on the initial state of the system $\rho_S(0)$. In the case that the inhomogeneous term in eq. (3.23) is ignored, we can make the approximation [75] $(\rho_S(t))_{nm} = \mathcal{B}_n \mathcal{B}_m (\tilde{\rho}_S(t))_{nm}$ for $n \neq m$, where $\tilde{\rho}_S(t)$ is the system density matrix in the variational frame and $\rho_S(t)$ is that in the untransformed frame. This is equivalent to making a Born approximation in the transformed frame. Under such an approximation, the transformed frame state is $\tilde{\rho}(t) \simeq \tilde{\rho}_S(t) \otimes \rho_R$ for all times. States of this form transform in the same way under the inverse variational transformation as the system Hamiltonian in eq. (3.1) does under the forward transformation. This leads to the factors of $\mathcal{B}_n \mathcal{B}_m$ for the off-diagonal elements, as mentioned above.

3.5 Example dynamics

3.5.1 A three-site comparison

We would like to compare dynamics calculated in the variational frame, using eq. (3.23), with other techniques. After two sites, the next simplest system with a Hamiltonian of the form of that in eq. (3.1) has three sites and only nearest neighbour couplings. Fig. 3.2 shows the dynamics for such a system in several parameter regimes, calculated in the variational frame. For comparison, we have also plotted the dynamics calculated in the fully-displaced polaron frame $f_{n,\mathbf{k}} = g_{n,\mathbf{k}}$ as well as that calculated using the untransformed Hamiltonian $f_{n,\mathbf{k}} = 0$ (equivalent to the weak-coupling, or Redfield, approximation). The system is characterised by its on-site energies $\{E_n\}$, inter-site couplings V_{12} and V_{23} , and spectral densities, which we choose to be of the form

$$J_n(\omega) = \frac{\lambda_n}{2} \frac{\omega^3}{\omega_c^3} e^{-\omega/\omega_c}. \quad (3.30)$$

Column (a) in fig. 3.2 represents a regime where the system frequencies ($\sim 20\text{cm}^{-1}$) are much smaller than the environment cutoff frequency $\omega_c = 200\text{cm}^{-1}$. In this case, the fully-displaced polaron transformation is expected to do well [80], and we would like the variational transformation to match it, which it indeed does. The untransformed dynamics fails to reach the correct steady state, due to a reasonably large reorganisation energy for the environment. We also found that the weak coupling approximation can lead to unphysical results for parameters differing from those in column (a) only by their intersite coupling. This was not the case for the dynamics in the variational or full polaron frames.

The second column, (b), shows dynamics in a regime for which neither the weak-coupling nor full-polaron transformation are ideally suited. System frequencies are

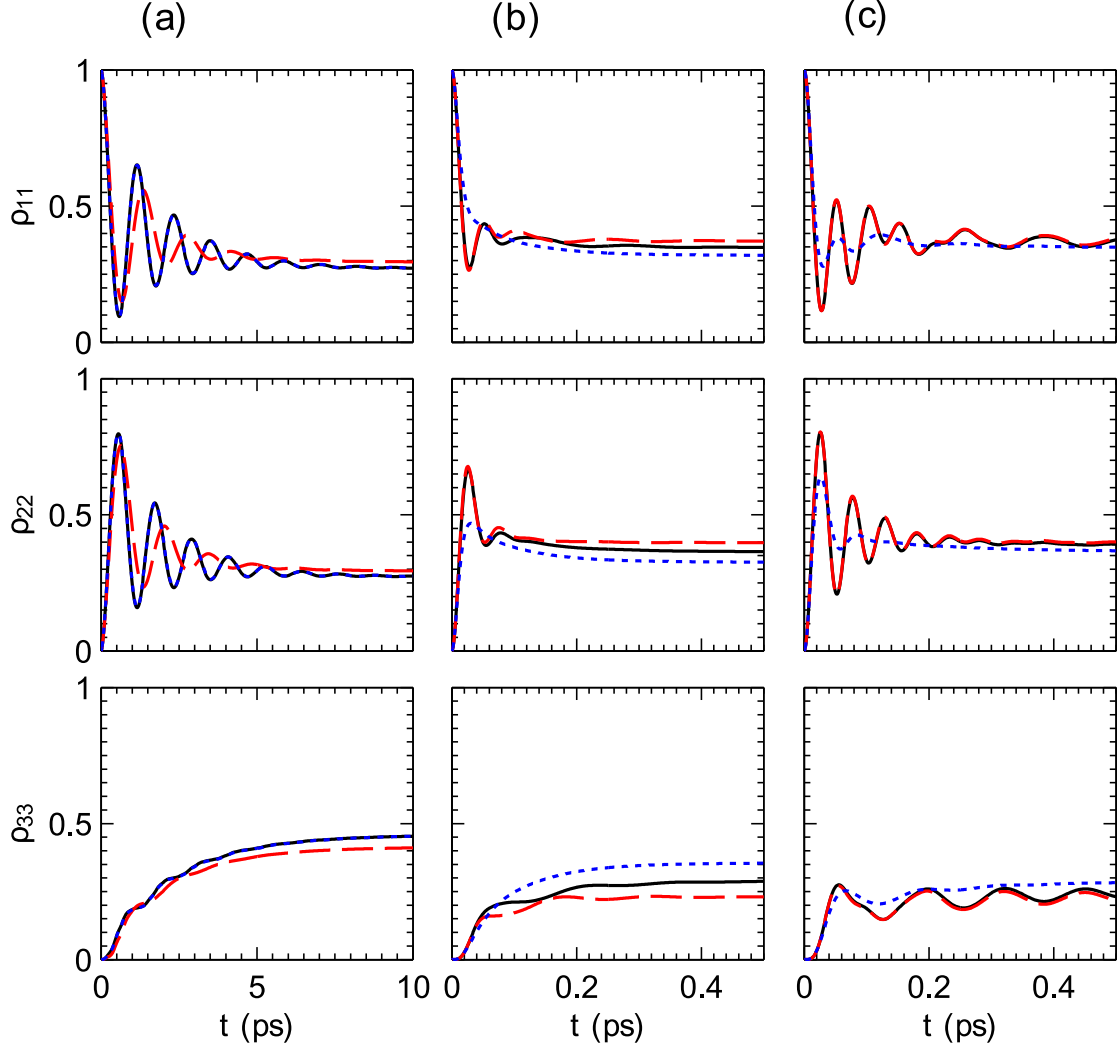


Figure 3.2: Population dynamics of a three-site system calculated using the variational (solid black), full-polaron (blue dotted) and weak-coupling (red dashed) master equations plotted as a function of time (in ps). The system parameters and spectral densities are as described in the text and in eq. (3.30), with $\omega_c = 200\text{cm}^{-1}$, $E_1 = E_2 = 50\text{cm}^{-1}$, $E_3 = 0\text{cm}^{-1}$ and $T = 300\text{K}$ in all cases. The remaining parameters for the individual subplots are: (a) $\lambda_1 = \lambda_2 = 60\text{cm}^{-1}$, $\lambda_3 = 120\text{cm}^{-1}$, $V_{12} = V_{23} = 20\text{cm}^{-1}$; (b) $\lambda_1 = \lambda_2 = \lambda_3 = 180\text{cm}^{-1}$, $V_{12} = 300\text{cm}^{-1}$, $V_{23} = 100\text{cm}^{-1}$; (c) $\lambda_1 = \lambda_2 = \lambda_3 = 60\text{cm}^{-1}$, $V_{12} = 300\text{cm}^{-1}$, $V_{23} = 100\text{cm}^{-1}$.

comparable to environment frequencies, and the coupling to the environment (parameterised by the reorganisation energy λ) is not small. The variational dynamics appear to interpolate between the two other results. It is clear that it agrees with the weak-coupling dynamics at short times, before settling on a different set of steady state populations. The comparatively large coupling energies in the system prevent the polaron transformation from dealing correctly with the lower frequency parts of the environment, leading to the dynamics in the full-polaron frame overestimating the damping of coherent oscillations. The variational transformation preserves coherence here, precisely due to the fact that it optimises the frequency dependence of the polaron transformation, as opposed to indiscriminately displacing every phonon mode by the full amount.

Finally, in column (c), the reorganisation energy is much lower than in column (b), but the system frequencies are still large. A weak coupling approximation is therefore valid in this case, and one would expect the dynamics in the untransformed frame to be more accurate than that in the full polaron frame. The curves representing weak-coupling and variational frame dynamics in this panel almost sit on top of each other, showing that the latter agree with the weak coupling results, and corroborating the fact that the variational transformation allows us to capture the dynamics across a broad range of coupling strengths. It is interesting to note that both the weak-coupling and polaron approaches can overestimate the damping of coherence in comparison to the variational method, dependent on the parameter regime (cf. panels (a) and (c)).

3.5.2 The Fenna-Matthews-Olsen complex

We now analyse the predictions of the variational master equation for a larger system, namely the FMO complex. This is usually assumed to be a seven-site system (although more recent results suggest there is in fact an additional eighth site [58]) and thus has a much larger parameter space than the three site system in fig. 3.2. Despite this, one can see from fig. 3.3, which compares FMO dynamics across a range of reorganisation energies and temperatures, that the variational transformation performs the same kind of interpolation between weak-coupling and full-polaron dynamics as in the three-site case. The FMO system Hamiltonian used in this section — taken

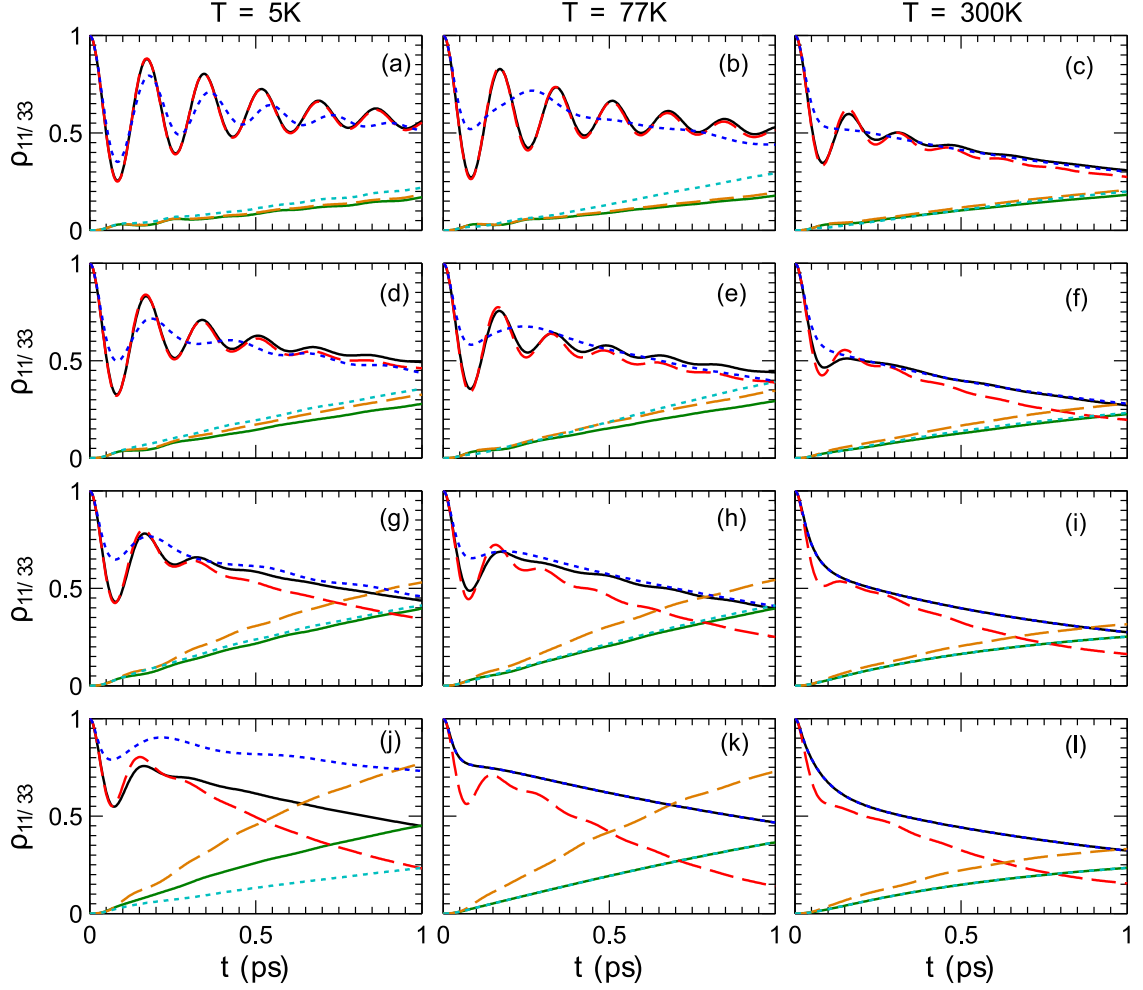


Figure 3.3: Variational (solid), weak-coupling (dashed) and full-polaron (dotted) dynamics for the populations of site 1 (black, red, blue) and site 3 (olive, orange, cyan) of the FMO complex. Although all seven sites were modelled, only the input (1) and output (3) site populations are shown for clarity. The system Hamiltonian used is the same as that in ref. [91] and the spectral density is given in eq. (3.32). Panels (a-c) have $\eta = \frac{1}{2}$, (d-f) have $\eta = 1$, (g-i) have $\eta = 2$, and (j-l) have $\eta = 4$. The dynamics in the first column of plots were calculated at 5 K, the second at 77 K, and the third at 300 K.

from ref. [91] — is:

$$H_{FMO} = \begin{pmatrix} 240 & -87.7 & 5.5 & -5.9 & 6.7 & -13.7 & -9.9 \\ -87.7 & 315 & 30.8 & 8.2 & 0.7 & 11.8 & 4.3 \\ 5.5 & 30.8 & 0 & -53.5 & -2.2 & -9.6 & 6.0 \\ -5.9 & 8.2 & -53.5 & 130 & -70.7 & -17.0 & -63.3 \\ 6.7 & 0.7 & -2.2 & -70.7 & 285 & 81.1 & -1.3 \\ -13.7 & 11.8 & -9.6 & -17.0 & 81.1 & 435 & 39.7 \\ -9.9 & 4.3 & 6.0 & -63.3 & -1.3 & 39.7 & 245 \end{pmatrix} \text{cm}^{-1}, \quad (3.31)$$

and the spectral density — the smooth part of that from [91] — is of the form:

$$J_n(\omega) = 3.053 \times 10^{-5} \times \eta \frac{\omega^5}{\omega_1^4} e^{-\sqrt{\omega/\omega_1}} + 1.908 \times 10^{-5} \times \eta \frac{\omega^5}{\omega_2^4} e^{-\sqrt{\omega/\omega_2}}, \quad (3.32)$$

with $\omega_1 = 0.575 \text{cm}^{-1}$ and $\omega_2 = 2 \text{cm}^{-1}$.

Fig. 3.3 provides an example of the importance of the interplay between coherent and incoherent dynamics in excitonic energy transport. The biological purpose of the FMO complex is to transport excitations from site 1 (or sometimes site 6) to site 3, from which the excitation is then removed [54] (although we do not model the removal process here). It is therefore beneficial to have the population on site 3 build up as fast as possible. One can see from the figure (most clearly in the second column), that the optimum rate of transfer (panels (j), (h) and (i)) occurs in the variational theory when coupling to the environment is neither too strong nor too weak. That is, incoherent, phonon-assisted transport is enhanced by the presence of some degree of coherence in the system. These optimal cases appear to lie in the intermediate region of parameter space, outside the remit of weak-coupling or polaron master equations, for which something like the variational approach is required.

The full, seven-site dynamics for the cases where $\eta = 1$, at $T = 77 \text{K}$ and $T = 300 \text{K}$, are shown in fig. 3.4. These plots correspond to the parameter regimes of the FMO dynamics in fig. 2 of ref. [91]. However, the exact calculations presented in that paper include a significant peak in the spectral density which, in any master equation approach, would ideally be treated separately from the rest of the environment in order to capture its effect on the dynamics non-perturbatively — in a similar manner to the treatment of the odorant mode in chapter 5. Moreover, a variational polaron treatment of such a peak would likely cause there to be significant system-environment correlations in the transformed frame, which would not be taken into account without the inclusion of inhomogeneous terms in the master equation. That being said, the qualitative agreement of the variational dynamics shown in the figure with the results in ref. [91] is surprisingly good. A comparison with the smooth Ohmic spectral density

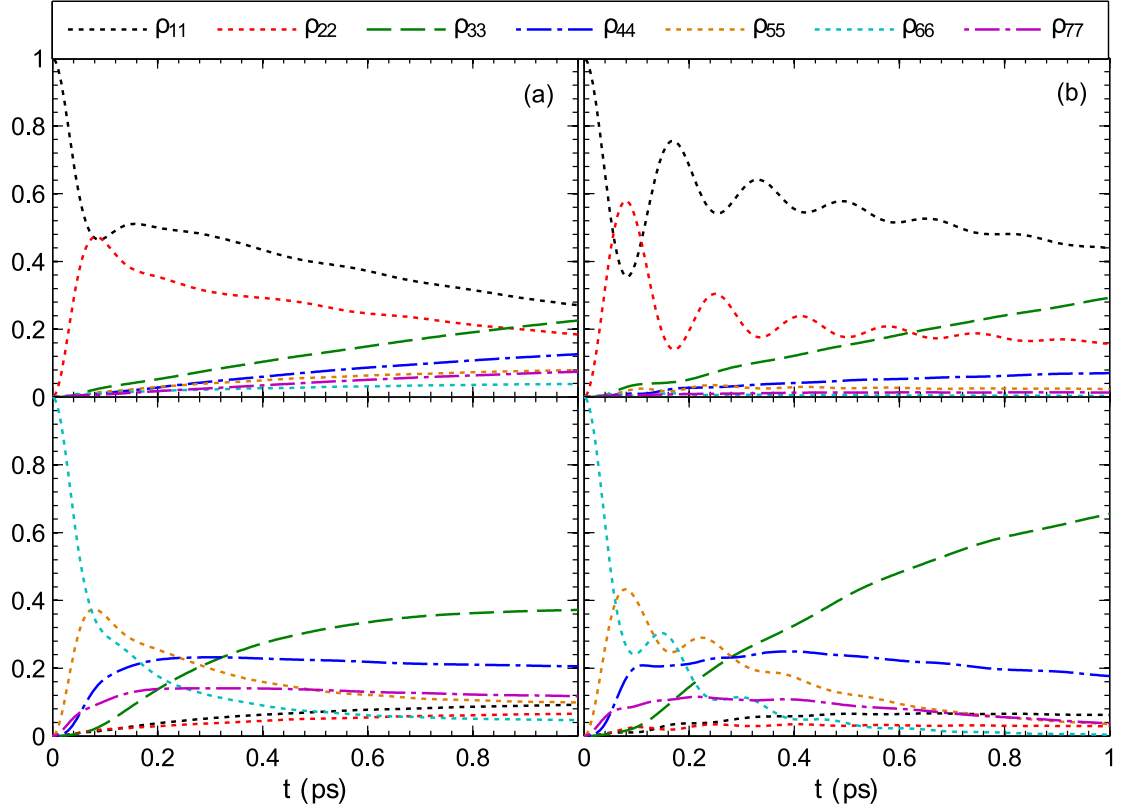


Figure 3.4: Variational frame population dynamics for the FMO complex with the same parameters as fig. 2 of ref. [91], with the exception that only the smooth, non-peaked part of the spectral density was used. The dynamics in panel (a) were calculated at 300 K whilst those in (b) were calculated at 77 K. Two different initial states: $\rho_S(0) = |1\rangle\langle 1|$ and $\rho_S(0) = |6\rangle\langle 6|$ were used for the upper and lower plots, respectively.

presented in this reference is prevented due to the infrared divergences discussed in the conclusion of this chapter.

3.6 Conclusions

There are several advantages to using master equations over other approaches to open quantum systems dynamics. Primarily, these are the efficiency with which one can solve them, and the potential insights into underlying physics which they can give. We can see from the various terms in eq. (3.23) exactly how the parameters in the Hamiltonian enter into the system dynamics, and the relative magnitude of these terms can give us an idea of the parameter regime of a given system — in the sense of which quantities contribute most to the dynamics.

Moving into the variational frame prior to solving the master equation gives us the ability to calculate sensible dynamics — in the sense that they do not diverge — over a larger range of parameters compared to the more standard weak-coupling or full-polaron approaches. As can be seen from sec. 3.5, the variational master equation can capture the dynamics in both the weak and strong coupling regimes, agreeing with both the weak-coupling and polaron master equations, respectively, when they are expected to do well. It is also able to bridge the gap between the two in intermediate regimes.

The variational master equation can in principle handle arbitrary system Hamiltonians and spectral densities. However, like the full polaron transformation, it should work best in the scaling limit [80], in which important environmental frequencies (ω_c) are large compared to relevant system frequencies (V_{nm}). The corresponding downside is that moving into the variational frame is expected to provide less of an advantage in terms of improving the accuracy of the dynamics when the typical environmental timescales are significantly longer than those of the system, and the coupling between the two is strong. The intuition for this is that the low frequency phonon modes are too ‘sluggish’ to keep up with the motion of the exciton as it moves through the system and do not, therefore, dress the system in the same way as higher frequency modes. They may still, however, have a profound impact on the system dynamics, which a transformation of displacement form is unable to capture. Methods using Ehrenfest dynamics [92, 93] and system reaction coordinates [94] have had some success at treating lower frequency modes in spin-boson energy transfer models, and it may be that they could be adapted into the variational framework presented here.

Whilst the variational master equation appears to interpolate between the dynamics of the weak-coupling and polaron master equations, its accuracy can only be definitively determined by a comparison with numerically exact methods. One such comparison was presented in ref. [95] for three-site systems using hierarchical equations of motion. The results suggest that the accuracy of the variational method is not much better than that of the other master equations in the intermediate parameter regimes, and furthermore that the accuracy is highly parameter dependent. However, the spectral density used in this comparison is Ohmic and can suffer from the problems of infrared divergence discussed below, therefore the variational transformation is not necessarily expected to do well in this case.

One aspect of our method which might benefit from modification is the specific minimisation condition used. Whilst we expect the first term of eq. (3.10) to be a good metric for the size of the interaction, it does not directly correspond to the quantity

which we expand perturbatively in the master equation derivation. In fact, the next highest order term, ($\mathcal{O}(H_{SE}^2)$), is mathematically more similar [96], albeit much more complicated. One issue with the current condition is that, as one smoothly varies the Hamiltonian parameters, the optimum transformation can jump, as different local minima become global minima. This effect has been studied for the case of two sites [82], and it was found that the variational predictions are less accurate around the discontinuity. For multiple sites, the free energy landscape becomes yet more complex and more local minima emerge in parameter space, hence there is greater scope for this kind of jumping. Whilst not optimal, the transformations corresponding to such local minima are still likely to lead to more accurate dynamics than those calculated in the untransformed frame.

There is also the question of whether to consider the full polaron displacement as a better choice of transformation than any partial displacement when its corresponding free energy is lower. It is often the case in strong coupling regimes that, although it doesn't satisfy eq. (3.12), the full displacement is the minimum energy transformation. One would expect that a partial transformation always does better, since, as previously mentioned, the full-displacement never treats the low frequency modes correctly. In which case, the lower free energy in the full-polaron case is merely an artifact of the minimisation condition used. For Ohmic baths the situation is a little less clear, since even partial transformations satisfying the minimisation condition can include full displacements of one or more sites; in this case there is an infrared divergence in the calculation of the renormalised couplings, setting them to zero and destroying any coherent oscillations of the population of that site. Such solutions are unfavourable as they lose information about the system and would hence reduce the accuracy of the dynamics.

In summary, we have outlined a variational method for solving open quantum systems dynamics in molecular networks with local environments and have discussed a possible extension to those with global environments. The method appears to be valid over a wide range of parameters and is efficient to compute. By moving into a reference frame in which the system and environment are less strongly interacting, one is able to use a perturbative master equation to potentially more accurately calculate dynamics. For our Hamiltonian in eq. (3.2), the approach surpasses both weak-coupling and full-polaron master equations in terms of breadth of applicability. Once its accuracy has been verified, it can be used to model interesting biological systems which sit in difficult intermediate coupling regimes, such as the FMO complex, and allows for the systematic study of the effects of certain parameters on the dynamics.

There is still ample room for improvement, and the general concept of redrawing the boundary between system and environment has far greater reach than the implementation presented in this paper. For instance, one could augment the form of the transformation, perhaps by including squeezing in addition to displacement. The technique we have developed utilises one of the most fundamental properties of quantum mechanics, namely the invariance of dynamical laws under unitary transformations, and gives insight into the important physical mechanisms underlying the evolution of open quantum systems. Whilst future master equation approaches may go beyond the polaron transformation, they are likely to benefit from a kind of variational minimisation in the spirit of that which we have outlined here.

Chapter 4

Excitation and relaxation in a superconducting double quantum dot

4.1 Introduction

In this chapter, we theoretically model a device composed of a pair of superconducting quantum dots, which has potential use as a ‘click-detector’ for single microwave photons [2]. We simulate the system and investigate the various ways in which it can be excited, as well as the pathways for subsequent excitations to exit the device. We use our results to interpret experimental data from ref. [2] and discuss whether the observed behaviour indicates detection of EM radiation.

Circuits involving nanoscale superconducting devices are one of the most promising candidates for realising a quantum computer in the near future [97, 98]. In such circuits, superconducting qubits are coupled to microwave frequency resonant modes [12–14, 99] and in this way are externally controlled and measured. Due to its binary signal, the device we describe in this chapter could have potential use as a click detector for measuring photons in these modes. Such non-Gaussian measurement (in the photon number basis) is necessary to perform quantum computing tasks which are not classically simulable [100].

Single superconducting islands form the basis of several superconducting qubit architectures [12, 101] as well as other devices such as single cooper pair transistors [102]. In the limit of nano-scale islands (quantum dots), the behaviour of individual quasiparticle excitations is of great importance for the functioning of these devices and their dynamics has been the subject of much recent study [103–108].

The superconducting double quantum dot (SDD) device which we consider here consists of a pair of nano-scale superconducting islands separated by an insulating barrier of low resistance, which are each also coupled to normally conducting leads via

higher resistance barriers. The electrical potential on each of the islands is controlled by capacitively coupled electrostatic gates, causing different charge states on the islands to have well defined energies. The whole system is embedded in a microwave-frequency, LC resonating circuit. By measuring the complex reflection coefficient of a weak driving signal, the latter is used to determine the effective capacitance of the device, which in turn depends on the quantum state of the SDD (as detailed in sec. 4.4 below). Fig. 4.1 shows a schematic representation of the device as well as a scanning electron micrograph of the real SDD described in ref. [2].

By tuning the gate voltages, we are able to form an energetic ground state for the device in which an excess Cooper-pair is superposed between the two superconducting islands. This state contributes significantly to the quantum capacitance of the SDD, whereas higher lying excited states do not. The excitation, or ‘breaking’, of this ground state can occur by a number of means, including by the absorption of a photon, but is experimentally measured in each case as an identical jump in capacitance. In this chapter, therefore, we will be primarily concerned with characterising the different excitation and relaxation processes affecting the device and whether the experimentally observed breaking of the Cooper-pair ground state is due to the absorption of microwave light from the environment.

Unless otherwise specified, all the device parameters used in this chapter come from the experiment performed in ref. [2] and are listed in the appendix.

4.2 BCS model and tunnelling across a barrier

Type I superconductors can be described by the theory of Bardeen, Cooper and Schrieffer (BCS) [109] and are distinguished by the pairing up of electrons with opposite momenta into so-called Cooper pairs with an associated binding energy Δ . At zero temperature and in the absence of an external magnetic field, this energy is characteristic of the material in which superconductivity is being observed. As temperature or magnetic field strength are increased, the Cooper pairs become less and less tightly bound (Δ decreases) until, at some critical value, a phase transition occurs and the normal conduction state becomes energetically preferable. The pairing effect arises from a phonon-mediated interaction between electrons, which is encoded in the many-body BCS Hamiltonian [110]

$$\begin{aligned}
 H = & \sum_{\mathbf{k}} \xi_{\mathbf{k}} \left(c_{\mathbf{k}}^{\dagger} c_{\mathbf{k}} + c_{-\mathbf{k}}^{\dagger} c_{-\mathbf{k}} \right) \\
 & + \sum_{\mathbf{k}\mathbf{k}'} V_{\mathbf{k}\mathbf{k}'} c_{\mathbf{k}}^{\dagger} c_{-\mathbf{k}}^{\dagger} c_{\mathbf{k}'} c_{-\mathbf{k}'},
 \end{aligned} \tag{4.1}$$

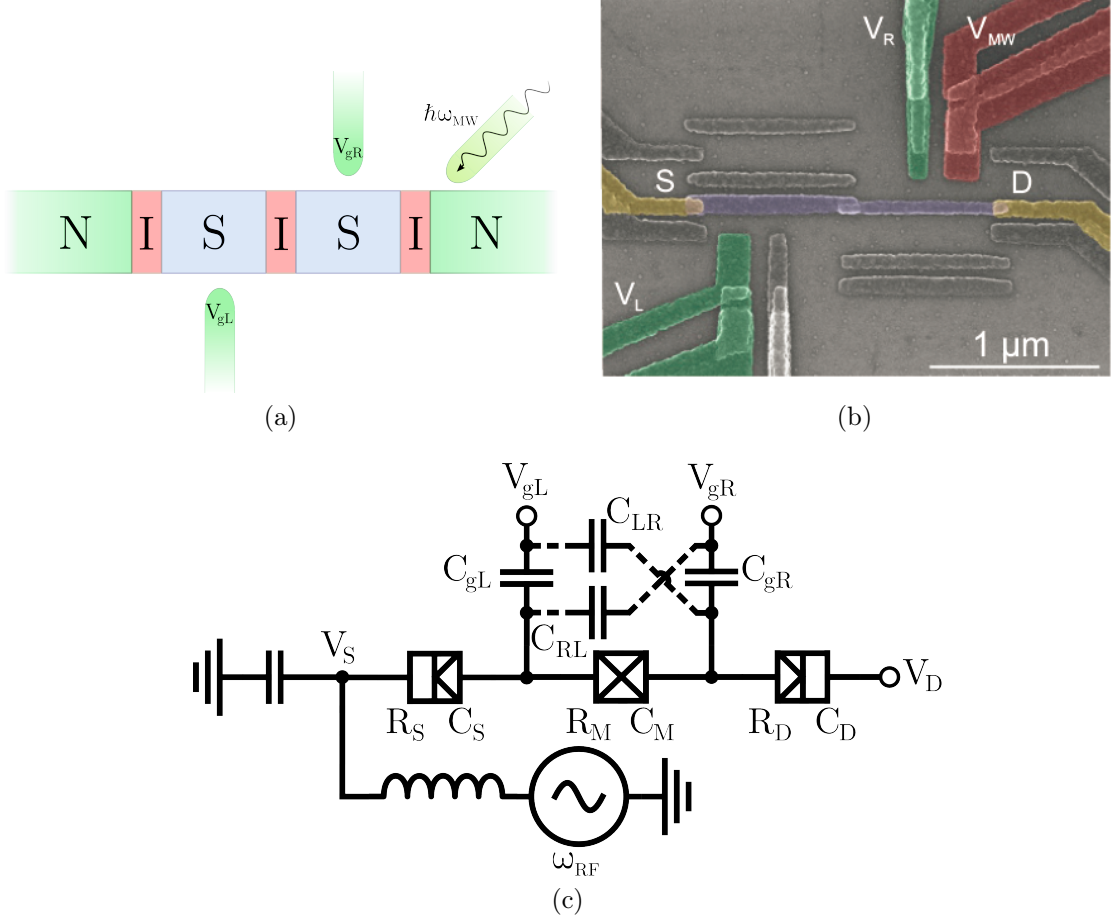


Figure 4.1: (a) A schematic representation of the superconducting double dot. S indicates a superconducting region, N indicates a normally conducting region and I indicates an insulating barrier. The gate electrodes and microwave photons in the environment are also represented. (b) A false colour scanning electron micrograph of a real SDD, taken from ref. [2]. The dc gates are in green, the source and drain contacts are in yellow, the superconducting islands are coloured purple and the red region contains a microwave source which we do not consider in this chapter. Uncoloured metal regions are artefacts of the fabrication process. (c) An equivalent circuit for the superconducting double dot. The boxes with full and half crosses represent SIS and NIS junctions respectively; these each behave electronically as a resistor and capacitor coupled in parallel.

where $\{c_{\mathbf{k}}^\dagger, c_{-\mathbf{k}}^\dagger\}$ are the electron creation operators for momentum modes $\{\mathbf{k}, -\mathbf{k}\}$ (where modes with opposite signs are implicitly assumed to have opposite spin) and $\xi_{\mathbf{k}}$ is the associated kinetic energy of mode $\mathbf{k}$ relative to the Fermi energy (in the absence of the interaction term, the model is that of free electrons [111]). $V_{\mathbf{k}\mathbf{k}'}$ is the energy associated with the phonon-mediated interaction. This Hamiltonian can be simplified using mean-field theory, by assuming that the operator $c_{\mathbf{k}}c_{-\mathbf{k}}$ has only small fluctuations about its mean value $\langle c_{\mathbf{k}}c_{-\mathbf{k}} \rangle$. We also make the approximation $V_{\mathbf{k}\mathbf{k}'} = V$. The Hamiltonian then reads

$$H \simeq \sum_{\mathbf{k}} \xi_{\mathbf{k}} \left(c_{\mathbf{k}}^\dagger c_{\mathbf{k}} + c_{-\mathbf{k}}^\dagger c_{-\mathbf{k}} \right) + \sum_{\mathbf{k}} \left(\Delta e^{-i\phi} c_{\mathbf{k}} c_{-\mathbf{k}} + \Delta e^{-i\phi} c_{\mathbf{k}}^\dagger c_{-\mathbf{k}}^\dagger \right) + C, \quad (4.2)$$

where $\Delta e^{i\phi} = \sum_{\mathbf{k}} V \langle c_{\mathbf{k}} c_{-\mathbf{k}} \rangle$ and C is a constant (dependent on Δ , ϕ and V).

Before specifically discussing the SDD, we must first remind ourselves of some of the results of BCS theory — for a more detailed account and derivation from first principles of the results in this section, see for example refs. [110,112]. In BCS theory, (unpaired) excitations above the Cooper pair ground state, known as quasiparticles, consist of a superposition of electron and hole states with opposite momenta. For each pair of momentum modes $\{\mathbf{k}, -\mathbf{k}\}$ there are two quasiparticle modes with creation operators

$$\gamma_{\mathbf{k}\uparrow}^\dagger = u_{\mathbf{k}} c_{-\mathbf{k}}^\dagger + v_{\mathbf{k}} e^{-i\phi} c_{\mathbf{k}}, \quad (4.3)$$

$$\gamma_{\mathbf{k}\downarrow}^\dagger = u_{\mathbf{k}} c_{\mathbf{k}}^\dagger - v_{\mathbf{k}} e^{-i\phi} c_{-\mathbf{k}}, \quad (4.4)$$

where ϕ is the coherent phase associated with the superconducting ground state. The quasiparticle operators satisfy the usual fermionic anticommutation relations

$$\begin{aligned} \{\gamma_{\mathbf{k}\sigma}, \gamma_{\mathbf{k}'\sigma'}^\dagger\} &= \delta_{\mathbf{k}\mathbf{k}'} \delta_{\sigma\sigma'}, \\ \{\gamma_{\mathbf{k}\sigma}^\dagger, \gamma_{\mathbf{k}'\sigma'}^\dagger\} &= 0, \\ \{\gamma_{\mathbf{k}\sigma}, \gamma_{\mathbf{k}'\sigma'}\} &= 0. \end{aligned} \quad (4.5)$$

The $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ coefficients are given in terms of the kinetic energy $\xi_{\mathbf{k}}$ of the electronic state associated with $\mathbf{k}$, and its associated quasiparticle energy $E_{\mathbf{k}} = \sqrt{\xi_{\mathbf{k}}^2 + \Delta^2}$:

$$u_{\mathbf{k}} = \sqrt{\frac{1}{2} \left(1 + \frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}} \right)}, \quad (4.6)$$

$$v_{\mathbf{k}} = \sqrt{\frac{1}{2} \left(1 - \frac{\xi_{\mathbf{k}}}{E_{\mathbf{k}}} \right)}. \quad (4.7)$$

These are the coefficients of the Bogoliubov transformation — satisfying $u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2 = 1$ — that takes the mean-field, electronic BCS Hamiltonian in eq. 4.2 into its diagonal form

$$H^{BCS} = \sum_{\mathbf{k}} E_{\mathbf{k}} \left(\gamma_{\mathbf{k}\uparrow}^\dagger \gamma_{\mathbf{k}\uparrow} + \gamma_{\mathbf{k}\downarrow}^\dagger \gamma_{\mathbf{k}\downarrow} \right) + E_0^{BCS}, \quad (4.8)$$

where E_0 is the energy of the ground state, which when written in terms of the electronic creation and annihilation operators is

$$|E_0^{BCS}\rangle = \prod_{\mathbf{k}} \left(u_{\mathbf{k}} + v_{\mathbf{k}} e^{i\phi} c_{\mathbf{k}}^\dagger c_{-\mathbf{k}}^\dagger \right) |0\rangle, \quad (4.9)$$

where $|0\rangle$ is the full Fermi sea.

Ignoring, for the moment, the various bosonic fields with which our device can interact, the Hamiltonian for our device can be partitioned in the following way:

$$H_{SSD} = H_L^{BCS} + H_R^{BCS} + H_L^{Lead} + H_R^{Lead} + H_{Mid}^I + H_L^I + H_R^I. \quad (4.10)$$

$H_{L(R)}^{BCS}$ is the BCS Hamiltonian in eq. (4.8) for the left (right) superconducting island, $H_{L(R)}^{Lead}$ is the Hamiltonian for the left (right) lead — normally conducting metal held at a fixed potential — and H_L^I , H_R^I and H_{Mid}^I are the Hamiltonians for electron transfer across the left, right and middle insulating barriers respectively. The latter tunnelling Hamiltonians are all of the form

$$H^I = \sum_{\mathbf{k}\mathbf{k}'} \left(t_{\mathbf{k}\mathbf{k}'} c_{\mathbf{k}} c_{\mathbf{k}'}'^\dagger + t_{-\mathbf{k}-\mathbf{k}'} c_{-\mathbf{k}} c_{-\mathbf{k}'}'^\dagger + \text{h.c.} \right), \quad (4.11)$$

where the unprimed operators act on one side of the barrier and the primed operators on the other. If one side of the barrier is superconducting, then the Hamiltonian can be rewritten in terms of the quasiparticle operators. For an NIS junction separating one of the islands from the leads

$$\begin{aligned} H_{NIS}^I = \sum_{\mathbf{k}\mathbf{k}'} & \left(\left(t_{-\mathbf{k}-\mathbf{k}'} u_{\mathbf{k}'} c_{-\mathbf{k}} + t_{\mathbf{k}\mathbf{k}'}^* e^{i\phi'} v_{\mathbf{k}'} c_{\mathbf{k}}^\dagger \right) \gamma_{\mathbf{k}'}'^\dagger \right. \\ & \left. + \left(t_{\mathbf{k}\mathbf{k}'} u_{\mathbf{k}'} c_{\mathbf{k}} - t_{-\mathbf{k}-\mathbf{k}'}^* e^{i\phi'} v_{\mathbf{k}'} c_{-\mathbf{k}}^\dagger \right) \gamma_{\mathbf{k}'}'^\dagger + \text{h.c.} \right), \end{aligned} \quad (4.12)$$

whilst the central SIS junction Hamiltonian can be written entirely in terms of quasi-

particle operators:

$$\begin{aligned}
H_{SIS}^I = & \sum_{\mathbf{k}\mathbf{k}'} t_{\mathbf{k}\mathbf{k}'} \left(u_{\mathbf{k}} u_{\mathbf{k}'} \gamma_{\mathbf{k}\downarrow} \gamma_{\mathbf{k}'\downarrow}'^\dagger + e^{i\phi} v_{\mathbf{k}} u_{\mathbf{k}'} \gamma_{\mathbf{k}\uparrow} \gamma_{\mathbf{k}'\downarrow}'^\dagger \right. \\
& \left. + e^{-i\phi'} u_{\mathbf{k}} v_{\mathbf{k}'} \gamma_{\mathbf{k}\downarrow} \gamma_{\mathbf{k}'\uparrow}' + e^{-i(\phi'-\phi)} v_{\mathbf{k}} v_{\mathbf{k}'} \gamma_{\mathbf{k}\uparrow} \gamma_{\mathbf{k}'\uparrow}'^\dagger \right) \\
& + t_{-\mathbf{k}-\mathbf{k}'} \left(u_{\mathbf{k}} u_{\mathbf{k}'} \gamma_{\mathbf{k}\uparrow} \gamma_{\mathbf{k}'\uparrow}'^\dagger - e^{i\phi} v_{\mathbf{k}} u_{\mathbf{k}'} \gamma_{\mathbf{k}\downarrow} \gamma_{\mathbf{k}'\uparrow}'^\dagger \right. \\
& \left. - e^{-i\phi'} u_{\mathbf{k}} v_{\mathbf{k}'} \gamma_{\mathbf{k}\uparrow} \gamma_{\mathbf{k}'\downarrow}' + e^{-i(\phi'-\phi)} v_{\mathbf{k}} v_{\mathbf{k}'} \gamma_{\mathbf{k}\downarrow} \gamma_{\mathbf{k}'\downarrow}'^\dagger \right) \\
& + \text{h.c.}
\end{aligned} \tag{4.13}$$

4.2.1 Tunnelling across a barrier in the normal state

In order to calculate the tunnelling rates in sec. 4.5, we treat the barrier Hamiltonians perturbatively. For some of the calculations, we will make the approximation $|t_{\mathbf{k}\mathbf{k}'}|^2 = |t_{-\mathbf{k}-\mathbf{k}'}|^2 = |t|^2$, that is we assume that the coupling between modes either side of the barrier can be replaced by some average value. We can do this because, although the coupling will in general depend on the angle of incidence and energy of the initial electron modes [113], there is no other angular dependence in the single electron tunnelling rates (for the higher order processes in sec. 4.5.2 we must take angular dependence into account); the momentum distribution in the metal is taken to be isotropic, therefore the angular dependence of the couplings $t_{\mathbf{k}\mathbf{k}'}$ can be averaged over. Furthermore, the energy associated with the operating temperature ($k_B T = 10.8 \mu\text{eV}$ for $T = 125 \text{ mK}$) and energy differences between different states of the device ($\sim 0.5 \text{ meV}$) are both much smaller than the Fermi energy of the metal forming the SDD ($\sim 10 \text{ eV}$). The energies involved in transitions will therefore be strongly peaked around the Fermi energy and can be assumed to be constant for the purposes of calculating the coupling constants $t_{\mathbf{k}\mathbf{k}'}$ [114]. The value of $|t|^2$ can be calculated by considering the tunnelling current in the normally conducting phase as follows. Using Fermi's golden rule, we can write down a rate for the elastic electron tunnelling process in terms of (first order) matrix elements of H^I

$$\Gamma_{\rightarrow} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}\mathbf{k}'}^{\xi_{\mathbf{k}}=\xi_{\mathbf{k}'}} |\langle 0_{\mathbf{k}} | \langle 1'_{\mathbf{k}'} | H^I | 1_{\mathbf{k}} \rangle | 0'_{\mathbf{k}'} \rangle|^2 \langle c_{\mathbf{k}}^\dagger c_{\mathbf{k}} \rangle \langle c_{\mathbf{k}'}' c_{\mathbf{k}'}'^\dagger \rangle, \tag{4.14}$$

where we are using the same convention as in eq. (4.11) by labelling quantities on one side of the barrier with primes and the other side without. For example, $|1_{\mathbf{k}}\rangle$ is the state on the left with an electron in mode $\mathbf{k}$, whilst $|1'_{\mathbf{k}'}\rangle$ is that on the right in mode

$\mathbf{k}'$ (other modes are assumed to remain unchanged). The arrow indicates that we are only considering tunnelling in one direction. Taking the initial state to be thermal, the occupation probabilities are given by $\langle c_{\mathbf{k}}^\dagger c_{\mathbf{k}} \rangle = f(\xi_{\mathbf{k}})$ and $\langle c_{\mathbf{k}'}' c_{\mathbf{k}'}'^\dagger \rangle = 1 - f(\xi_{\mathbf{k}'} - e\delta V)$, where

$$f(E) = \frac{1}{1 + e^{\frac{E}{k_B T}}} \quad (4.15)$$

is the Fermi-Dirac distribution at temperature T , and δV is the difference in electrical potential between the two sides of the barrier. Substituting in for H^I and noting that the sum over momenta in eq. (4.14) includes those which are written as explicitly negative in eq. (4.11), we find

$$\Gamma_{\rightarrow} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}\mathbf{k}'}^{\xi_{\mathbf{k}}=\xi_{\mathbf{k}'}-e\delta V} (|t_{\mathbf{k}\mathbf{k}'}|^2 + |t_{-\mathbf{k}-\mathbf{k}'}|^2) f(\xi_{\mathbf{k}}) (1 - f(\xi_{\mathbf{k}'} - e\delta V)), \quad (4.16)$$

where the sum now includes the negative momenta explicitly (as in eq. (4.11)) and we have used the fact that $\xi_{\mathbf{k}} = \xi_{-\mathbf{k}}$. We now make the aforementioned assumption of homogeneous tunnelling coefficients and convert the sum into an integral:

$$\Gamma_{\rightarrow} = \frac{4\pi|t|^2}{\hbar} \rho(0)\rho'(0) \int_{-\infty}^{\infty} d\xi f(\xi) (1 - f(\xi - e\delta V)). \quad (4.17)$$

The rate now includes factors $\rho(0)$ and $\rho'(0)$, which are the density of states at the Fermi energy on either side of the barrier. These are constants which depend on the material from which the conductors are made — in our case aluminium for the superconducting islands and copper for the leads. Since none of the tunnelling processes we discuss in this chapter are spin dependent, we implicitly include the sum over different spin states in the density of states. An analogous rate $\Gamma_{\leftarrow}$ can be found for transfer in the opposite direction; the difference of the two (multiplied by the electron charge) gives the net current across the barrier:

$$\begin{aligned} I_{net} &= -e (\Gamma_{\rightarrow} + \Gamma_{\leftarrow}) \\ &= -4\pi|t|^2 \frac{e}{\hbar} \rho(0)\rho'(0) \int_{-\infty}^{\infty} d\xi (f(\xi) (1 - f(\xi - e\delta V)) - f(\xi - e\delta V) (1 - f(\xi))) \\ &= -4\pi|t|^2 \frac{e}{\hbar} \rho(0)\rho'(0) \int_{-\infty}^{\infty} d\xi (f(\xi) - f(\xi - e\delta V)) \\ &= 4\pi|t|^2 \frac{e^2}{\hbar} \rho(0)\rho'(0)\delta V. \end{aligned} \quad (4.18)$$

Using Ohm's law ($V = IR$), one can write the tunnelling coefficient t in terms of the normal state resistance of the barrier R ,

$$|t|^2 = \frac{\hbar}{4\pi e^2 \rho(0)\rho'(0)R}. \quad (4.19)$$

4.2.2 The Josephson effect

For two superconductors separated by an insulating barrier, the tunnelling Hamiltonian H^I , when taken to second order, allows for the transfer of Cooper pairs via virtual quasiparticle states. This is the well known Josephson effect [115]. In our device we rely on this coupling to create an avoided crossing in the energy level structure, which we can detect experimentally. The associated energy E_J is known as the Josephson energy and can be found from second order perturbation theory as follows [116].

The second order contribution to the energy coupling unperturbed eigenstates $|i\rangle$ and $|f\rangle$ for a perturbation Hamiltonian H^I is given by

$$E_{if}^{(2)} = \sum_j \frac{\langle f|H^I|j\rangle\langle j|H^I|i\rangle}{E_i - E_j}, \quad (4.20)$$

where the sum is over unperturbed eigenstates. When $|i\rangle$ and $|f\rangle$ are superconducting ground states (with no quasiparticles on either side of the barrier) and H^I is the SIS junction tunnelling Hamiltonian in eq. (4.13), there is no first order coupling, and the second order energy is the largest contribution. The intermediate states in this case are those with a single quasiparticle on each of the islands: $\gamma_{\mathbf{k}\sigma}^\dagger \gamma_{\mathbf{k}'\sigma'}^\dagger |i\rangle$. Eq. (4.20) becomes, after discarding terms which don't contribute,

$$E_{if}^{(2)} = \sum_{\mathbf{k}\mathbf{k}'} \frac{t_{\mathbf{k}\mathbf{k}'} t_{-\mathbf{k}-\mathbf{k}'} e^{i(\phi' - \phi)} u_{\mathbf{k}} v_{\mathbf{k}'} u_{\mathbf{k}'} v_{\mathbf{k}} + \text{h.c.}}{E_{\mathbf{k}} + E_{\mathbf{k}'}} \times \langle f| \left(\gamma_{\mathbf{k}\downarrow} \gamma_{\mathbf{k}'\uparrow} \gamma_{\mathbf{k}\downarrow}^\dagger \gamma_{\mathbf{k}'\uparrow}^\dagger + \gamma_{\mathbf{k}\uparrow} \gamma_{\mathbf{k}'\downarrow} \gamma_{\mathbf{k}\uparrow}^\dagger \gamma_{\mathbf{k}'\downarrow}^\dagger \right) |i\rangle, \quad (4.21)$$

where $E_{\mathbf{k}} = \sqrt{\xi_{\mathbf{k}}^2 + \Delta^2}$ is the energy of the quasiparticle in momentum mode $\mathbf{k}$. Taking the initial state as $|i\rangle = |\tilde{N}\rangle |\tilde{N} + 2\rangle$ — where $|\tilde{N}\rangle$ is the superconducting ground state on either the left or right of the barrier with $\tilde{N}/2$ Cooper pairs — and the final state as $|f\rangle = |\tilde{N} + 2\rangle |\tilde{N}\rangle$, we find

$$\begin{aligned} \langle f| \gamma_{\mathbf{k}\uparrow} \gamma_{\mathbf{k}'\downarrow} \gamma_{\mathbf{k}\uparrow}^\dagger \gamma_{\mathbf{k}'\downarrow}^\dagger |i\rangle &= \langle f| \gamma_{\mathbf{k}\downarrow} \gamma_{\mathbf{k}'\uparrow} \gamma_{\mathbf{k}\downarrow}^\dagger \gamma_{\mathbf{k}'\uparrow}^\dagger |i\rangle \\ &= v_{\mathbf{k}}^2 v_{\mathbf{k}'}^2, \end{aligned} \quad (4.22)$$

in which we have used $|\tilde{N} + 2\rangle = \sum_{\mathbf{q}} e^{i\phi} (v_{\mathbf{q}}/u_{\mathbf{q}}) c_{\mathbf{q}}^\dagger c_{-\mathbf{q}}^\dagger |\tilde{N}\rangle$ (from eq. (4.9)). After making the approximation $t_{\mathbf{k}\mathbf{k}'} t_{-\mathbf{k}-\mathbf{k}'} = |t|^2$, the coupling energy (which we now equate to half the Josephson energy) is

$$\begin{aligned} \frac{E_J}{2} &= 8|t|^2 \rho(0)^2 \cos(\phi' - \phi) \int_{-\infty}^{\infty} d\xi_{\mathbf{k}} \int_{-\infty}^{\infty} d\xi_{\mathbf{k}'} \frac{(u_{\mathbf{k}} v_{\mathbf{k}}^3)(u_{\mathbf{k}'} v_{\mathbf{k}'}^3)}{E_{\mathbf{k}} + E_{\mathbf{k}'}} \\ &= 8|t|^2 \rho(0)^2 \cos(\phi' - \phi) \int_0^{\infty} d\xi_{\mathbf{k}} \int_0^{\infty} d\xi_{\mathbf{k}'} \frac{\Delta}{2E_{\mathbf{k}}} \frac{\Delta}{2E_{\mathbf{k}'}} \frac{1}{E_{\mathbf{k}} + E_{\mathbf{k}'}} \end{aligned} \quad (4.23)$$

where in the second equality we have used the symmetries of $u_{\mathbf{k}}$ and $v_{\mathbf{k}}$ and the fact that $u_{\mathbf{k}}v_{\mathbf{k}} = \Delta/2E_{\mathbf{k}}$. By making the substitutions $\xi_{\mathbf{k}(\prime)}/\Delta = \sinh \theta^{(\prime)}$, the integral can be performed, giving

$$\begin{aligned} \frac{E_J}{2} &= 2|t|^2 \rho(0)^2 \Delta \cos(\phi' - \phi) \frac{\pi^2}{4} \\ &= \frac{\hbar \Delta \pi}{8e^2 R_M} \cos(\phi' - \phi) = \frac{1}{16} \frac{R_K}{R_M} \Delta \cos(\phi' - \phi), \end{aligned} \quad (4.24)$$

where $R_K = h/e^2 \simeq 26 \text{ k}\Omega$ is the von Klitzing constant. In order to substitute in for $|t|^2$ in terms of the central junction resistance R_M , we have used an expression analogous to eq. (4.19). From here onwards, we assume that the superconducting phase is equal on both islands of the SDD, such that $\cos(\phi' - \phi) = 1$.

4.2.3 Lifetime broadening and the Dynes density of states

Many of the transition rates between different energy levels of the SDD involve integrating over the quasiparticle density of states $\nu_{BCS}(E) = E/\sqrt{E^2 - \Delta^2}$, which arises when converting integrals over electronic energies ξ to integrals over quasiparticle energies $E = \sqrt{\xi^2 + \Delta^2}$

$$\int_0^\infty d\xi = \int_\Delta^\infty \nu_{BCS}(E) dE. \quad (4.25)$$

However, when the final quasiparticle states have a finite lifetime τ , their energy distribution is broadened by a factor $\hbar/\tau$ (by convolving the integrand with a Lorentzian of this width), leading to the possibility of quasiparticles tunnelling below the gap energy Δ . Tunnelling to a lifetime broadened energy distribution has been shown to be closely equivalent to using the so-called Dynes density of states $\nu_D(E) = \Re[(E - i\hbar/\tau)/\sqrt{(E - i\hbar/\tau)^2 - \Delta^2}]$ [117, 118] (although another form has been suggested in ref. [119]). The integrals in eq. (4.25) can then be written

$$\int_0^\infty d\xi = \int_0^\infty \nu_D(E) dE. \quad (4.26)$$

This is valid as long as $\hbar/\tau \ll k_B T$, otherwise the Fermi-Dirac distribution appearing in the rate expressions would also have to be modified. For the parameters we consider, the lifetimes are always much greater than $\hbar/k_B T \simeq 60 \text{ ps}$, so the Dynes density of states works well.

4.3 The energy eigenstates of the superconducting double dot

As mentioned earlier in this chapter, the electrostatic gates effectively cause states of definite charge on the islands to have definite energy. The BCS ground state in eq. (4.9) consists of a superposition of different numbers of electrons (bound in Cooper pairs), however this degeneracy is broken by the electrostatic potential on the islands, and states with differing numbers of Cooper pairs have different energies. In addition to the electrostatic contribution to the energy, which we calculate here using standard results for double quantum dots [120], there are two main contributions to the SDD's energy level structure: The Cooper pair binding energy Δ — which acts as a band gap for states with quasiparticle excitations — and the Josephson energy, which couples states with different numbers of Cooper pairs on either side of the junction. In this section we calculate the energies of the different levels, reproducing the results of ref. [3].

We label the states (N_L, N_R) according to the number of charges on each island relative to an arbitrary even parity state $(0, 0)$ (containing only Cooper pairs), where N_L and N_R are the number of excess charges on the left and right superconducting islands respectively. Odd parity states (those with an odd number of charges on an island) must contain quasiparticles, since there is no way for the lone electrons to form Cooper pairs. Adding an extra unpaired electron to an island already containing a quasiparticle would incur an energetic cost of $\Delta = 250 \mu\text{eV}$ (double quasiparticle states would lie above the purple line in fig. 4.2a). Since $k_B T \ll \Delta$ at the operating temperatures of the device ($k_B T = 10.8 \mu\text{eV}$ for $T = 125 \text{ mK}$), we only expect states with at most a single quasiparticle on either island to be present on a measurable timescale. Therefore, odd parity states contain quasiparticles whereas even parity states do not — the quasiparticle number on the left (right) island is given by $Q_{L(R)} = N_{L(R)} \bmod 2$.

The relevant states of the SDD in the parameter regime we are interested in are: The states in the $(2, 0)/(0, 2)$ subspace; the state with a quasiparticle on each island $(1, 1)$; the single-quasiparticle states $(1, 0)$, $(0, 1)$, $(1, 2)$ and $(2, 1)$ and the even charge Cooper-pair states $(0, 0)$ and $(2, 2)$.

Following ref. [120], the electrical potentials on the two islands (V_L and V_R), and hence the electrostatic energy, of the two dots can be calculated by solving the matrix

equation

$$\begin{pmatrix} eN_L \\ eN_R \end{pmatrix} = \begin{pmatrix} C_L & -C_M \\ -C_M & C_R \end{pmatrix} \begin{pmatrix} V_L \\ V_R \end{pmatrix} + \begin{pmatrix} -C_S & -C_{gL} & -C_{RL} & 0 \\ 0 & -C_{LR} & -C_{gR} & -C_D \end{pmatrix} (V_S, V_{gL}, V_{gR}, V_D)^T \quad (4.27)$$

for a given charge state (N_L, N_R) , where $C_L = C_S + C_{gL} + C_{RL} + C_M$ and $C_R = C_D + C_{gR} + C_{LR} + C_M$, and the other capacitances are those depicted in fig. 4.1c. The electrostatic energy is then given by

$$U(N_L, N_R) = \frac{1}{2} (V_L, V_R) \begin{pmatrix} C_L & -C_M \\ -C_M & C_R \end{pmatrix} \begin{pmatrix} V_L \\ V_R \end{pmatrix}. \quad (4.28)$$

In addition to this electrostatic contribution, quasiparticle states with momentum $\mathbf{k}$ have an associated energy $E_{\mathbf{k}} = \sqrt{\xi_{\mathbf{k}}^2 + \Delta^2}$ relative to the Cooper-pair state we are using as a reference, where $\xi_{\mathbf{k}}$ is the associated electron kinetic energy. At the low temperatures at which the device operates, the quasiparticles are overwhelmingly likely to be found at close to the minimum energy of Δ . So the effective energy of a given charge configuration is

$$E_{(N_L, N_R)} = U(N_L, N_R) + \Delta (N_L \bmod 2 + N_R \bmod 2). \quad (4.29)$$

Finally, excess Cooper pairs can tunnel across the junction between the two islands (as described in the previous section), so the levels are coupled to each other and have an associated tunnelling matrix element. For certain values of the gate voltages on the islands, V_{gL} and V_{gR} , the $(2, 0)$ and $(0, 2)$ levels are degenerate. This leads to an avoided crossing and a splitting into a lower-energy, symmetric (S) and higher-energy, antisymmetric (A) state. The energies, E_S and E_A , of these two states are given by the eigenvalues of the $(2, 0)/(0, 2)$ subspace Hamiltonian

$$H_{(2,0)/(0,2)} = \begin{pmatrix} U(2, 0) & E_J/2 \\ E_J/2 & U(0, 2) \end{pmatrix}, \quad (4.30)$$

where $E_J = \Delta R_K / 8 R_M$ is the Josephson energy of the central junction connecting the two superconducting islands.

Pairs of quasiparticle states in $(2, 1)/(1, 2)$ and $(0, 1)/(1, 0)$ will also be coupled by the central barrier Hamiltonian, in this case by single-quasiparticle tunnelling at first order in H^I . However, in this case the coupling energy is small ($\sim |t| = \sqrt{R_K / 8 \pi^2 R_M \rho(0)^2}$) compared to the electrostatic energies of the states. This means we can effectively treat the single-quasiparticle states as eigenstates and assume that

the avoided crossing between these levels does not contribute significantly to the measured quantum capacitance of the system.

Figure 4.2 plots the energies of the different states of the device along two different directions in gate voltage space. The two directions are defined first by the avoided crossing — where $U(2, 0) = U(0, 2)$ — parameterised by ε , and second by the (perpendicular) direction of maximum increase in $|U(2, 0) - U(0, 2)|$, which we parameterise by δ .

4.4 Quantum capacitance and measurement

As mentioned above, the SDD is coupled to an LC-circuit (through the source voltage V_S depicted in fig. 4.1c), with which we can determine the state of the system by measuring its response to a weak probe signal. Depending on its charge state, the presence of the device can cause a phase shift in the reflected signal. In addition to the shift produced by the standard geometric capacitance, there is a contribution arising from curvature in the **energy level** structure of the device. This is known as the ‘quantum capacitance’ of the device [121, 122].

If the external driving frequency ω_{RF} , is sufficiently detuned from the energy gaps in the SDD, then a small amplitude oscillation is unlikely to cause transitions between energy levels in the device. In this limit, from the perspective of the external circuit, we can simply treat the SDD as a network of capacitors coupled through V_S . We then associate the energy of the device with a charging energy $E = \frac{1}{2}CV_S^2$ which we use to define the total capacitance

$$C = \frac{\partial^2 E}{\partial V_S^2}. \quad (4.31)$$

Using eq. (4.28) we can calculate this capacitance for the definite charge states of the SDD. The quadratic dependence on V_S is independent of the particular charge configuration and of the gate voltages. It is therefore solely due to the normal geometric capacitance of the device, which we find to be

$$C_{Geom} = \frac{1}{2} \frac{C_S^2 C_L}{C_L C_R - C_M^2}. \quad (4.32)$$

However, the eigenstates in the $(2, 0)/(0, 2)$ subspace have an extra dependence on V_S due to the avoided crossing, which is constant along the ε direction in gate voltage space — as defined in the previous section. The quantum capacitance is the

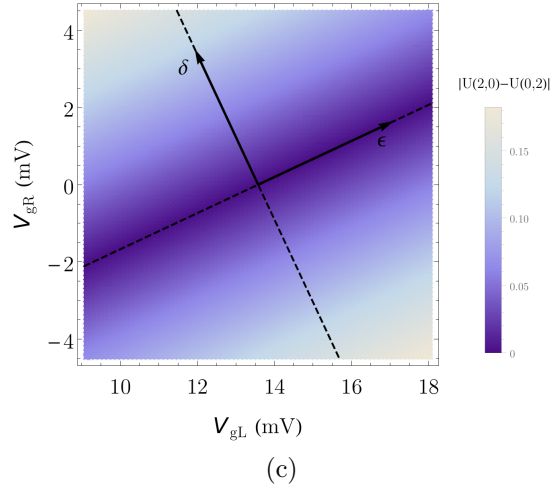
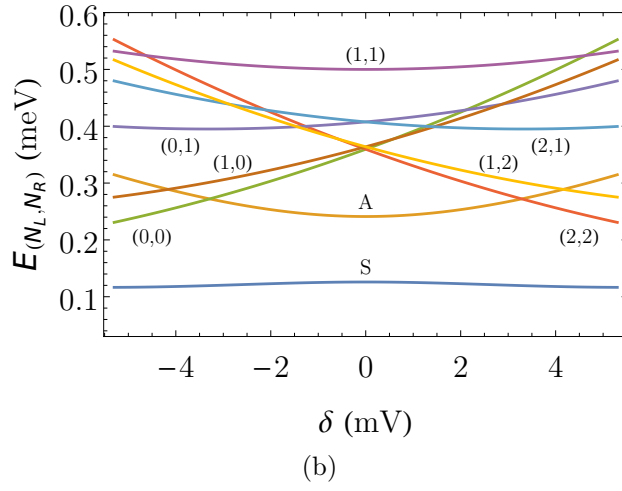
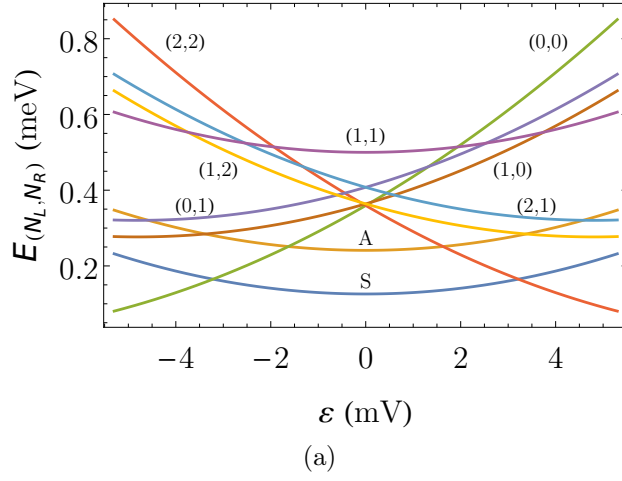


Figure 4.2: (a) Effective energy levels in the SDD as a function of detuning parameter ε . Other than the symmetric (S) and antisymmetric (A) superposition states, levels are labelled by their charge configuration. (b) Effective energy levels in the SDD as a function of detuning parameter δ . (c) Detuning directions ε and δ in gate voltage space. The shading indicates the value of $|U(2,0) - U(0,2)|$.

difference between the total capacitance of these states and the geometric capacitance of the device

$$\delta C = \frac{\partial^2 E}{\partial V_S^2} - C_{Geom}. \quad (4.33)$$

Further from the avoided crossing, the magnitude of the quantum capacitance for the S and A states decreases. The symmetric state has a negative quantum capacitance, whilst the antisymmetric excited state has a positive value.

Quantum capacitance is measured through the phase-shift of reflected waves in the LC-circuit — the argument of the reflection coefficient of an electrical load (such as our device) depends on its capacitance [14]. Reflected waves interfere with the incident waves dependent on their relative phase, and it is this interference which can be directly observed (see fig. 4.5c for an example of the experimental output as a function of time).

4.5 Dynamical processes in the double dot

We are interested in modelling the dynamics of the SDD and predicting the observed quantum capacitance signal; in order to do so, we require an understanding of the different processes which can cause transitions between energy levels in the device. Once we have identified all the relevant processes, we can go about describing the device's behaviour. We choose to constrain the gate voltages, V_{gL} and V_{gR} , to lie on the avoided crossing between the $(2, 0)$ and $(0, 2)$ levels (parameterised by ε), such that the quantum capacitance signal is maximised. This has the advantage of leaving constant some of the most important energy gaps, allowing certain rates to be fitted experimentally. It is important to note that the initial to final state energy differences used in the calculations in this section do not include the extra gap energy ascribed to quasiparticle states in sec. 4.3, *e.g.* we use $U(1, 0)$ rather than $E_{(1,0)}$. This is because the exact energy is allowed to vary depending on the state the quasiparticle occupies, and the calculations take into account the fact that the minimum quasiparticle energy is Δ above the electrostatic energy.

The SDD can be thought of as an open system with several environments which can cause transitions between the lowest energy levels of the device. In addition to the electron reservoirs in the normally conducting leads — separated from the SDD by imperfect insulating barriers — the device will be coupled to a plethora of photonic and phononic modes. In order to simplify the subsequent calculations, we assume that the device is strongly coupled enough to the phononic environment that the phonons can thermalise the quasiparticles on a timescale much shorter than other

transitions in the system. This allows us to use equilibrium distributions, such as the Fermi-Dirac distribution for the calculation of transition rates. Additionally, we assume that the $(2, 0)/(0, 2)$ subspace is quickly decohered to the symmetric state S (its ground state at operational temperatures). Experimental evidence suggests that this is the case for the parameters considered here [2], as the quantum capacitance measured never corresponds to the antisymmetric excited state. However, we do not expect the phonon environment to aid significantly in the various tunnelling processes, since the energy required to overcome the energy gap Δ and create quasiparticles is much higher than $k_B T$ (for the temperature of the islands).

Unless otherwise indicated, we label the transition rates between specific energy levels i and f , $\Gamma_{i \rightarrow f}$, where $i, f \in \{S, A, (N_L, N_R)\}$.

4.5.1 Single-quasiparticle tunnelling

Tunnelling of single electrons to and from the leads creates and destroys quasiparticles on the two islands of the SDD. There are four classes of single particle process which can occur, involving different combinations of the charge increasing or decreasing by one unit on an island and the number of quasiparticles increasing or decreasing. We now proceed to calculate Fermi golden rule rates for each of these processes using the NIS tunnelling Hamiltonian in eq. (4.12). For the moment, we will label these rates $\Gamma_{\delta N, \delta Q}(\delta E_{if})$, where δN , δQ and δE_{if} are the changes (between the final and initial states) in: number of charges on the island, quasiparticle number and energy respectively. Later we will revert to labelling rates by the states they connect, where it should be clear that *e.g.* $\Gamma_{(1,1) \rightarrow (0,1)} = \Gamma_{-1,-1}(U(0,1) - U(1,1))$.

Following the same prescription as in sec. 4.2.1, we can write down expressions for the rates analogous to that in to eq. (4.14). For example, the rate $\Gamma_{+1+1}(\delta E_{if})$ is

$$\Gamma_{+1+1}(\delta E_{if}) = \frac{2\pi}{\hbar} \sum_{\mathbf{k}\mathbf{k}', \sigma \in \{\uparrow, \downarrow\}}^{\xi_{\mathbf{k}} = E_{\mathbf{k}'} + \delta E_{if}} |\langle 0_{\mathbf{k}} | \langle \tilde{1}'_{\mathbf{k}'\sigma} | H^I | 1_{\mathbf{k}} \rangle | \tilde{0}'_{\mathbf{k}'\sigma} \rangle|^2 \langle c_{\mathbf{k}}^\dagger c_{\mathbf{k}} \rangle \langle \gamma'_{\mathbf{k}'\sigma} \gamma_{\mathbf{k}'\sigma}^\dagger \rangle, \quad (4.34)$$

where $|\tilde{1}'_{\mathbf{k}'\sigma}\rangle$ and $|\tilde{0}'_{\mathbf{k}'\sigma}\rangle$ signify states with occupied and unoccupied quasiparticle modes respectively. Analogous expressions exist for $\Gamma_{-1+1}(\delta E_{if})$, $\Gamma_{+1-1}(\delta E_{if})$ and $\Gamma_{-1-1}(\delta E_{if})$. There are two main differences between these tunnelling rates and those across a normally conducting barrier. The first is that the matrix element picks up an extra factor with modulus $u_{\mathbf{k}'}$ or $v_{\mathbf{k}'}$ depending on whether the quasiparticle being created or destroyed is an electron or a hole respectively. This follows from the form of the Hamiltonian in eq. (4.12). The second difference is that the quasiparticle

distribution is not necessarily the Fermi-Dirac distribution (due to the gap in allowed states) and depends on the exact number of quasiparticles present in the initial state. For simplicity's sake we follow [108] and use a Fermi-Dirac distribution with a rescaled temperature such that the total number of particles calculated using the quasiparticle density of states agrees with the number Q_i initially on the island. That is, we solve

$$Q_i = 2\rho(0)V \int_{\Delta}^{\infty} dE \frac{\nu_{BCS}(E)}{1 + e^{\frac{E}{k_B T_S}}} \quad (4.35)$$

for T_S . Where $\rho(0)$ is the density of states at the Fermi energy in the normal state on the island and V is the volume. Henceforth, the Fermi-Dirac distribution at temperature $T_S(Q_i)$ we label $f_S(E, T_S(Q_i))$, whereas the distribution at the actual temperature of the device is simply $f(E)$. Only those levels for which $Q_i = 0$ or 1 are important for the dynamics of the device in our case, for which we find $T_S(1) \simeq 300$ mK and, trivially, $T_S(0) = 0$ mK. Taking all this into account, the rate in eq. (4.34) becomes

$$\Gamma_{+1+1}(\delta E_{if}) = \frac{1}{e^2 R} \sum_{\mathbf{k}\mathbf{k}', \sigma \in \{\uparrow, \downarrow\}}^{\xi_{\mathbf{k}} = E_{\mathbf{k}'} + \delta E_{if}} u_{\mathbf{k}'}^2 f(\xi_{\mathbf{k}}) [1 - f_S(E_{\mathbf{k}'}, T_S(Q_i))], \quad (4.36)$$

where we have used eq. (4.19) to simplify the constant prefactor. When converted into an integral, the rate is

$$\begin{aligned} \Gamma_{+1+1}(\delta E_{if}) &= \frac{1}{e^2 R} \int_{-\infty}^{\infty} d\xi \int_{-\infty}^{\infty} d\xi' u(\xi')^2 f(\xi) \\ &\quad \times [1 - f_S(E(\xi'), T_S(Q_i))] \delta(\xi - E(\xi') - \delta E_{if}), \end{aligned} \quad (4.37)$$

with $E(\xi) = \sum_{\mathbf{k}} E_{\mathbf{k}} \delta(\xi_{\mathbf{k}} - \xi)$ and $u(\xi) = \sum_{\mathbf{k}} u_{\mathbf{k}} \delta(\xi_{\mathbf{k}} - \xi)$ (similarly $v(\xi) = \sum_{\mathbf{k}} v_{\mathbf{k}} \delta(\xi_{\mathbf{k}} - \xi)$). Using the fact that $E(-\xi') = E(\xi')$ and that $u(-\xi') = v(\xi')$, we can rewrite the integral as

$$\begin{aligned} \Gamma_{+1+1}(\delta E_{if}) &= \frac{1}{e^2 R} \int_{-\infty}^{\infty} d\xi \int_0^{\infty} d\xi' (u(\xi')^2 + v(\xi')^2) f(\xi) \\ &\quad \times [1 - f_S(E(\xi'), T_S(Q_i))] \delta(\xi - E(\xi') - \delta E_{if}) \\ &= \frac{1}{e^2 R} \int_{-\infty}^{\infty} d\xi \int_0^{\infty} d\xi' f(\xi) [1 - f_S(E(\xi'), T_S(Q_i))] \\ &\quad \times \delta(\xi - E(\xi') - \delta E_{if}). \end{aligned} \quad (4.38)$$

After making a change of variables from ξ' to $E(\xi')$ and integrating over the electron energy ξ , we arrive at the following form for the rate:

$$\Gamma_{+1+1}(\delta E_{if}) = \frac{1}{e^2 R} \int_0^{\infty} dE \nu_D(E) f(E + \delta E_{if}) [1 - f_S(E, T_S(Q_i))]. \quad (4.39)$$

Similarly, with the subtle distinction that the integral is now over initial rather than final energies, the reverse process has the rate

$$\Gamma_{-1-1}(\delta E_{if}) = \frac{1}{e^2 R} \int_0^\infty dE \nu_D(E) [1 - f(E - \delta E_{if})] f_S(E, T_S(Q_i)). \quad (4.40)$$

The hole tunnelling rates differ in that the electron states involved in tunnelling lie below the Fermi level in the leads. This leads to the rates

$$\begin{aligned} \Gamma_{-1+1}(\delta E_{if}) &= \frac{1}{e^2 R} \int_0^\infty dE \nu_D(E) f(-E - \delta E_{if}) [1 - f_S(-E, T_S(Q_i))] \\ &= -\frac{1}{e^2 R} \int_{-\infty}^0 dE \nu_D(E) f(E - \delta E_{if}) [1 - f_S(E, T_S(Q_i))] \end{aligned} \quad (4.41)$$

and

$$\begin{aligned} \Gamma_{+1-1}(\delta E_{if}) &= \frac{1}{e^2 R} \int_0^\infty dE \nu_D(E) f_S(-E, T_S(Q_i)) [1 - f(-E + \delta E_{if})] \\ &= -\frac{1}{e^2 R} \int_{-\infty}^0 dE \nu_D(E) f_S(E, T_S(Q_i)) \\ &\quad \times [1 - f(E + \delta E_{if})]. \end{aligned} \quad (4.42)$$

The quasiparticle tunnelling rates to and from the states S and A are reduced by a further factor of $\frac{1}{2}$, for example $\Gamma_{S \rightarrow (2,1)} = \frac{1}{2} \Gamma_{-1,+1}(U(2,1) - E_S)$. This is due to the fact that the matrix element for a given process picks out only one of the charge states $(2,0)$ or $(0,2)$. S and A are equal magnitude superpositions of these states.

4.5.2 Andreev reflection

It is possible to transfer a pair of electrons (holes) simultaneously across an NIS tunnel barrier to create (or remove) a single Cooper pair from the superconducting side. This process is known as Andreev reflection [123], and in our device leads to direct transitions between the $(2,0)/(0,2)$ subspace and the states $(0,0)$ and $(2,2)$. In addition, it couples the $(1,0)/(0,1)$ states to the $(1,2)/(2,1)$ states.

Andreev reflection is a second order process, whereby an electron or hole tunnels to create a virtual quasiparticle state on the island, before a second particle tunnels to form a Cooper pair with the first. Here, we closely follow the approach in ref. [113] to derive approximate rates for the process. From second order perturbation theory, the amplitude for a pair of electrons of momentum $\mathbf{k}$ and $\mathbf{k}'$ to tunnel from the leads to form a Cooper pair depends on the energy of the intermediate quasiparticle state

(including the change in electrostatic energy $\delta E_{N \rightarrow N+1}$) and is given by

$$A_{\mathbf{k}\mathbf{k}'} = \sum_{\mathbf{p}} \frac{\langle 0_{\mathbf{k}} 0_{\mathbf{k}'} | \langle \tilde{N} + 2 | H^I | 0_{\mathbf{k}} 1_{\mathbf{k}'} \rangle | \tilde{1}_{\mathbf{p}\sigma} \rangle \langle 0_{\mathbf{k}} 1_{\mathbf{k}'} | \langle \tilde{1}_{\mathbf{p}\sigma} | H^I | 1_{\mathbf{k}} 1_{\mathbf{k}'} \rangle | \tilde{N} \rangle}{\xi_{\mathbf{k}} - E_{\mathbf{p}} - \delta E_{N \rightarrow N+1}} + \frac{\langle 0_{\mathbf{k}} 0_{\mathbf{k}'} | \langle \tilde{N} + 2 | H^I | 1_{\mathbf{k}} 0_{\mathbf{k}'} \rangle | \tilde{1}_{\mathbf{p}\sigma} \rangle \langle 1_{\mathbf{k}} 0_{\mathbf{k}'} | \langle \tilde{1}_{\mathbf{p}\sigma} | H^I | 1_{\mathbf{k}} 1_{\mathbf{k}'} \rangle | \tilde{N} \rangle}{\xi_{\mathbf{k}'} - E_{\mathbf{p}} - \delta E_{N \rightarrow N+1}}, \quad (4.43)$$

where $|\tilde{N}\rangle$ is the state with N electrons bound in Cooper pairs. We now substitute in for the NIS tunnelling Hamiltonian to arrive at

$$A_{\mathbf{k}\mathbf{k}'} = \sum_{\mathbf{p}} t_{\mathbf{k}\mathbf{p}} t_{\mathbf{k}'\mathbf{p}} u_{\mathbf{p}} v_{\mathbf{p}} \left(\frac{1}{\xi_{\mathbf{k}} - E_{\mathbf{p}} - \delta E_{N \rightarrow N+1}} + \frac{1}{\xi_{\mathbf{k}'} - E_{\mathbf{p}} - \delta E_{N \rightarrow N+1}} \right). \quad (4.44)$$

We can write the second order rate as

$$\Gamma_{\tilde{N} \rightarrow \tilde{N}+2} = \frac{2\pi}{\hbar} \sum_{\mathbf{k}\mathbf{k}'}^{\xi_{\mathbf{k}} + \xi_{\mathbf{k}'} = \delta E_{if}} |A_{\mathbf{k}\mathbf{k}'}|^2 f(\xi_{\mathbf{k}}) f(\xi_{\mathbf{k}'}). \quad (4.45)$$

The junctions in our device are thin layers of insulator sandwiched between thin layers of metal in the same plane as the bulk of the superconducting islands and leads (see ref. [2] for details of fabrication). This means that electrons are likely to scatter off one another and move diffusively in the region of the junction before tunnelling through. The coherence length of the electrons ($\xi_{cor}^L = \sqrt{\hbar D_{Cu}/k_B T} = 948 \text{ nm}$ in the copper leads and $\xi_{cor}^I = \sqrt{\hbar D_{Al}/\Delta} = 132 \text{ nm}$ on the aluminium islands, where D_i is the diffusion constant in material i [124]) is significantly larger than the size of the junction $\sqrt{S} = 30 \text{ nm}$ — where $S \simeq 900 \text{ nm}^2$ is the area of the junction. We therefore expect interference effects between electrons to play an important role in second order tunnelling. Hence, we cannot make the approximation $t_{\mathbf{k}\mathbf{p}} t_{\mathbf{k}'\mathbf{p}} \simeq t^2$, and we need to consider correlations between different intermediate virtual states. Using the results of refs. [113, 125], we can write the full rate as

$$\Gamma_{\tilde{N} \rightarrow \tilde{N}+2} = \frac{2\pi}{\hbar} \int d\xi d\xi' d\zeta d\zeta' F(\zeta; \xi, \xi') F(\zeta'; \xi, \xi') \Xi(\zeta, \zeta'; \xi, \xi') f(\xi) f(\xi') \times \delta(\xi + \xi' - \delta E_{if}),$$

$$F(\zeta; \xi, \xi') = \frac{\Delta}{2E(\zeta)} \left(\frac{1}{\xi - \delta E_{N \rightarrow N+1} - E(\zeta)} + \frac{1}{\xi' - \delta E_{N \rightarrow N+1} - E(\zeta)} \right). \quad (4.46)$$

The function $\Xi(\zeta, \zeta'; \xi, \xi')$ encodes the electron correlations and can be split into two significant parts, corresponding to contributions arising from interference in the leads ($\Xi_L(\zeta, \zeta'; \xi, \xi') = \Xi_L(\xi - \xi')$) and on the island ($\Xi_I(\zeta, \zeta'; \xi, \xi') = \Xi_I(\zeta - \zeta')$). For the

particular geometry of our junctions (long, thin leads coupled to thin superconducting islands), these are

$$\begin{aligned}\Xi_I(\zeta - \zeta') &= \frac{R_K^2}{16\pi^4 R^2 l_x l_y l_z \rho_I(0)} \delta(\zeta - \zeta'), \\ \Xi_L(\xi - \xi') &= \frac{R_K}{16e^2 \pi^5 R^2 D_{Cu} d_L \rho_L(0)} \ln \left(\frac{\hbar}{|\xi - \xi'| \tau} \right),\end{aligned}\quad (4.47)$$

where R is the resistance of the junction, l_x , l_y and l_z are the dimensions of the islands, d_L is the thickness of the lead at the junction and $\rho_I(0)$ and $\rho_L(0)$ are the density of states per unit volume at the Fermi energy on the island and in the leads respectively. $\tau = S/D_{Cu} = 62$ fs is a measure of the average time spent by an electron in the region of the junction in the leads. With these correlation functions, the two rates become

$$\begin{aligned}\Gamma_{\tilde{N} \rightarrow \tilde{N}+2}^I &= \frac{R_K^2 \Delta^2}{8\pi^3 \hbar R^2 l_x l_y l_z \rho_I(0)} \int_{-\infty}^{\infty} d\xi \int_{\Delta}^{\infty} dE f(\xi) f(\delta E_{if} - \xi) \\ &\times \left| \frac{(\xi - \delta E_{N \rightarrow N+1} - E)^{-1} + (\delta E_{if} - \xi - \delta E_{N \rightarrow N+1} - E)^{-1}}{\sqrt{E^2 - \Delta^2}} \right|^2, \\ \Gamma_{\tilde{N} \rightarrow \tilde{N}+2}^L &= \frac{R_K \Delta^2}{16e^2 \pi^5 R^2 D_{Cu} d_L \rho_L(0)} \int_{-\infty}^{\infty} d\xi \ln \left(\frac{\hbar}{|2\xi - \delta E_{if}| \tau} \right) \\ &\times f(\xi) f(\delta E_{if} - \xi) |G(\xi) + G(\delta E_{if} - \xi)|^2, \\ G(x) &= \int_{\Delta}^{\infty} dE \frac{1}{\sqrt{E^2 - \Delta^2}} \frac{1}{x - \delta E_{N \rightarrow N+1} - E} \\ &= \frac{\arccos[(x - \delta E_{N \rightarrow N+1})/\Delta] - \pi}{\sqrt{\Delta^2 - (x - \delta E_{N \rightarrow N+1})^2}}.\end{aligned}\quad (4.48)$$

We simplify the calculation of $\Gamma_{\tilde{N} \rightarrow \tilde{N}+2}^I$, by making the low temperature approximation

$$\begin{aligned}f(\xi) f(\delta E_{if} - \xi) &\simeq \begin{cases} \Theta(-\xi) \Theta(\xi - \delta E_{if}) & \delta E_{if} \leq 0, \\ e^{-\frac{\delta E_{if}}{k_B T}} \Theta(\xi) \Theta(\xi - \delta E_{if}) & \delta E_{if} > 0, \end{cases} \\ \Theta(x) &= \begin{cases} 0 & x \leq 0, \\ 1 & x > 0, \end{cases}\end{aligned}\quad (4.50)$$

which is valid as long as $\delta E_{if} \gg k_B T$. The breakdown of this approximation leads to ‘kinks’ in the calculated rates (seen in figs. 4.3 & 4.4) at points where the S and $(2, 2)/(0, 0)$ states are equal in energy ($\varepsilon = \pm 3.3$ mV). After substituting in for eq. (4.50), the integral over ξ can be calculated analytically (although we omit the full form here due to its unwieldiness). This leaves only integrals over single variables, which we calculate numerically.

The reverse process $\Gamma_{\tilde{N} \rightarrow \tilde{N}-2}$ of Andreev reflection of holes rather than electrons, whereby a Cooper pair is lost from the island to the leads, has exactly the same form for its rate as $\Gamma_{\tilde{N} \rightarrow \tilde{N}+2}$, except that the intermediate electrostatic energy difference $\delta E_{N \rightarrow N+1}$ is replaced by $\delta E_{N \rightarrow N-1}$.

For certain values of the energy differences δE_{if} and $\delta E_{N \rightarrow N+1}$, the intermediate states become resonant and the rate $\Gamma_{\tilde{N} \rightarrow \tilde{N}+2}^I$ diverges. This can be dealt with in one of two ways, either by including higher order terms in the perturbation expansion [126, 127], or by taking into account lifetime broadening of the virtual state energies [128, 129]. Since we are already including lifetime effects in other rates (through the Dynes density of states), we choose the latter approach and introduce a broadening parameter $\gamma_q = \hbar/\tau_q$ (where τ_q is the lifetime of the intermediate quasiparticle state) to the virtual quasiparticle energy by making the substitution $E \rightarrow E - i\gamma_q$ in eq. (4.48). In addition, we include the effect of the final state lifetime τ_f by adding an imaginary part of magnitude $\gamma_f = \hbar/\tau_f$ to the final state energy difference: $\delta E_{if} \rightarrow \delta E_{if} - i\gamma_f$. We then take the real part of the integral as a whole as the rate.

The discontinuities seen in the results of sec. 4.6 at $\varepsilon \simeq \pm 0.2$ mV are a consequence of the transition from two electron to single electron tunnelling. At these detuning values there is just enough energy to create one of the two intermediate, single-quasiparticle states: $E_{(2,2)} = E_{(1,2)}$ or $E_{(0,0)} = E_{(1,0)}$ (see fig. 4.2a), and the rates $\Gamma_{(2,2) \rightarrow S}$ and $\Gamma_{(0,0) \rightarrow S}$ respectively jump in value. One would expect a similar discontinuity around $\varepsilon \simeq \pm 1.4$ mV, where the energies of the other single-quasiparticle states equal those of the states (2, 2) or (0, 0). However, this is not visible in the results, since at these detuning values, the higher-energy Cooper-pair states have a very low probability of being occupied and therefore do not significantly contribute to the dynamics.

Analogously to the single-quasiparticle tunnelling case, rates for transitions to and from the superposition states S and A have an extra factor of $\frac{1}{2}$. Since the Cooper pair can tunnel off either island, transition rates from these states include contributions from both channels. For example, $\Gamma_{S \rightarrow (2,2)} = \frac{1}{2}(\Gamma_{\tilde{0} \rightarrow \tilde{2}}(U(2,2) - E_S, U(2,1) - E_S) + \Gamma_{\tilde{0} \rightarrow \tilde{2}}(U(2,2) - E_S, U(1,2) - E_S))$.

4.5.3 Cooper-pair splitting and photon absorption

Performing a simple Fermi's golden rule calculation for the rates $\Gamma_{S \leftrightarrow (1,1)}$, using the central-barrier tunnelling Hamiltonian, gives

$$\begin{aligned}
\Gamma_{S \rightarrow (1,1)} &= \frac{1}{e^2 R_M} \int_0^\infty d\xi \int_0^\infty d\xi' \delta(E(\xi) + E(\xi') + U(1,1) - E_S) \\
&= \frac{1}{e^2 R_M} \int_0^{E_S - U(1,1)} dE \nu_D(E) \nu_D(E_S - U(1,1) - E), \\
\Gamma_{(1,1) \rightarrow S} &= \int_0^{E_S - U(1,1)} dE \nu_D(E) \nu_D(E') \\
&\quad \times f_S(E, T_S(1)) f_S(E_S - U(1,1) - E, T_S(1)). \quad (4.51)
\end{aligned}$$

Using final state lifetimes consistent with other decay rates in the system, we find $\Gamma_{S \rightarrow (1,1)} = 0.04 \text{ Hz}$ and $\Gamma_{(1,1) \rightarrow S} = 2 \times 10^{-5} \text{ Hz}$. These are very small, since there is no way to conserve energy for $|E_S - U(1,1)| \leq 2\Delta$ (which is always the case along the avoided crossing parameterised by ε). The only way to easily split (or reform) the Cooper pairs in this way is to absorb (or emit) photons from the environment. In the presence of an environment, the delta function $\delta(E_f - E_i)$ in the integrals is replaced by the probability distribution $P(E_f - E_i)$ for absorbing energy $E_f - E_i$ [112,130,131].

For coupling to photons in an RLC-circuit with AC impedance $Z(\omega)$ at temperature T_{env} , the energy absorption distribution can be written [132,133]

$$\begin{aligned}
P(E_f - E_i) &= \frac{1}{2\pi\hbar} \int_{-\infty}^\infty dt \exp\left(F(t) + i\frac{E_f - E_i}{\hbar}t\right), \\
F(t) &= \frac{1}{\pi R_K} \int_0^\infty \frac{d\omega}{\omega} \Re\left(\frac{1}{i\omega C_{coup} + 1/Z(\omega)}\right) \\
&\quad \times \left(\coth\left(\frac{\hbar\omega}{2k_B T_{env}}\right) (\cos\omega t - 1) - i \sin\omega t\right), \quad (4.52)
\end{aligned}$$

where C_{coup} is the capacitance through which the external circuit is coupled. Since the wavelength of the photons required to overcome the energy gap Δ is much longer ($\sim 0.8 \text{ mm}$) than the size of the SDD ($\sim 2\mu\text{m}$), we expect the coupling to be insensitive to the internal structure of the device. Therefore $P(E_f - E_i)$ should be consistent across all transitions. Furthermore, if we make the assumption of a low-resistance, high-temperature environment (the temperature of the photons need not be the same as that of the device), we can assume a Lorentzian form [132] with width $\gamma_{env} = k_B T_{env} R/R_K$. This has the same effect as increasing the lifetime broadening of each of the states (see the discussion in sec. 4.2.3).

Since the photon environment's temperature is difficult to experimentally characterise, we choose to fit the broadening parameter γ_{env} to the experimental data in [2]

(shown in fig. 4.5). We do this by self-consistently calculating the rates for various processes (as detailed below in sec. 4.6) at $\varepsilon = 0$ with different values of γ_{env} until the total breaking rate agrees with the experimental value. This also determines the rates $\Gamma_{S \leftrightarrow (1,1)}$ for all values of ε , since they do not vary with detuning.

4.6 Results and comparison with experimental data

Since it is only possible to determine whether the system is in the $(2, 0)/(0, 2)$ subspace or not at any given time, we are interested in the timescales of ‘breaking’ processes which take the SDD out of this subspace and ‘recombination’ processes which return it. It will turn out that there are several different pathways through the energy levels which the SDD can take and its behaviour is, in general, complicated. However, for some values of the gate voltages, certain pathways dominate and an analysis can be made in terms of simple rates. In general, we must resort to a (classical) master equation to extract expected recombination times.

Throughout this section we continue to use the parameters given in the appendix, along with a temperature of $T = 125$ mK for the electrons in the leads and zero external magnetic field ($B = 0$ mT).

To calculate dynamical properties of the device, we write down a (classical) Markovian master equation which tells us how the vector $\mathbf{p}(t)$ evolves, where the elements of $\mathbf{p}(t)$ are the probabilities of finding the SDD in each of the states $\{S, A, (N_L, N_R)\}$:

$$\dot{\mathbf{p}}(t) = \mathcal{M} \mathbf{p}(t), \quad (4.53)$$

where the matrix $\mathcal{M}$ has the properties

$$\begin{aligned} \mathcal{M}_{nm} &= \Gamma_{m \rightarrow n} \quad m \neq n, \\ \sum_n \mathcal{M}_{nm} &= 0. \end{aligned} \quad (4.54)$$

Together these imply that the diagonal elements of $\mathcal{M}$ are $\mathcal{M}_{mm} = -\sum_n \Gamma_{m \rightarrow n}$.

As mentioned at the beginning the previous section, we assume that the lifetime of the state A is negligible and that it always decays to the state S — through decoherence of the $(2, 0)/(0, 2)$ subspace by the environment (and constant measurement of the quantum capacitance) on a very short timescale. Therefore we reduce the dimension of $\mathcal{M}$ and $\mathbf{p}(t)$ by one and treat transitions to A as direct transitions to S . That is we make the substitution $\Gamma_{i \rightarrow S} \rightarrow \Gamma_{i \rightarrow S} + \Gamma_{i \rightarrow A}$. By effectively treating the $(2, 0)/(0, 2)$ subspace as a single state, we neglect any quantum coherence which

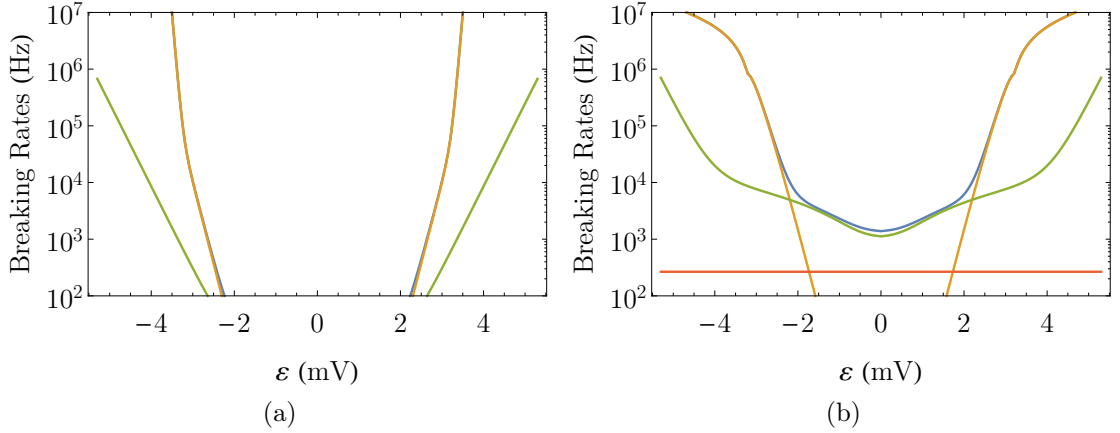


Figure 4.3: Theoretically calculated breaking rates. Total breaking rate Γ_B (blue) and breaking rates due to: single-quasiparticle tunnelling $\Gamma_{S \rightarrow (1,0)/(0,1)/(1,2)/(2,1)}$ (green), Andreev reflection $\Gamma_{S \rightarrow (0,0)/(2,2)}$ (yellow) and Cooper-pair splitting $\Gamma_{S \rightarrow (1,1)}$ (red) with (a) no photon environment and (b) an environment consistent with a breaking rate at $\varepsilon = 0$ of 1385 Hz.

builds up between the S and A states; this coherence arises from the fact that the interaction with the leads couples to the charge eigenstates $(2, 0)$ and $(0, 2)$ rather than S and A . If this were non-negligible, eq. (4.53) would have to be replaced by a quantum master equation describing the evolution of the density matrix of the system.

Lifetime broadening plays a significant role in determining the rate of many of the transitions encoded in $\mathcal{M}$. However, the lifetime of a given state i is equal to $-1/\mathcal{M}_{ii}$, which in turn depends on other transition rates. In order to ensure the master equation is consistent, we iteratively recalculate $\mathcal{M}$ with lifetimes based on its diagonal elements until the matrix as a whole is converged. For each iteration, we use the total transition rate away from a particular state — calculated in the previous iteration — to determine lifetime broadening for transitions to that state. Eventually, the transition rates settle on fixed values (up to some level of precision) consistent with the lifetimes of each of the states and no further iteration is performed. The extra broadening parameter due to environmental interaction is fixed such that the theoretically calculated value of $-\mathcal{M}_{SS}$ agrees with the experimental breaking rate at zero detuning ($\Gamma = 1385$ Hz). From the experimental data in ref. [2], we find $\gamma_{env} = 4.2 \times 10^{-5} \Delta = 11$ neV.

4.6.1 Breaking pathways

Once initialised in the symmetric state S , the device can transition to any of the states $(1, 0)/(0, 1)/(2, 1)/(1, 2)$ via single-quasiparticle tunnelling from the leads, to either of the states $(0, 0)/(2, 2)$ through Andreev reflection or to $(1, 1)$ by direct splitting of a Cooper pair. In fig. 4.3, the rates for each of these processes are plotted along with their sum, the total breaking rate $\Gamma_B = -\mathcal{M}_{SS}$, on a log scale. We not only plot rates for an environment fitted to experimental data, but also those we would expect in the absence of an environment.

The Cooper-pair splitting rate in the presence of the environment, $\Gamma_{S \rightarrow (1,1)} = 264\text{Hz}$, is many orders of magnitude greater than the value calculated in the previous section in its absence. However, it is a constant function of ε , since the only energy difference it depends on ($U(1, 1) - E_S$) does not vary along the avoided crossing. It therefore only contributes significantly to the total breaking rate close to $\varepsilon = 0$, where other rates are at a minimum, and even then it is not the most likely breaking process. For small detunings, single-quasiparticle tunnelling from the leads dominates. These processes are heavily suppressed in the absence of an electromagnetic environment, due to the minimum quasiparticle energies lying well above the ground state S .

As detuning increases, the $(2, 2)$ and $(0, 0)$ states decrease in energy until Andreev reflection from the leads becomes viable. This quickly becomes the fastest breaking rate for $\varepsilon \gtrsim 2\text{mV}$. At $\varepsilon = -3.3\text{mV}$ and $\varepsilon = 3.3\text{mV}$, the energy E_S equals that of the $(0, 0)$ and $(2, 2)$ states respectively; at greater detunings, these states supplant S as the ground state. As discussed in the previous section, the kink at the crossover points is an artefact of a low temperature approximation made in the calculation of the Andreev reflection rates.

For much larger detunings (outside the range of fig. 4.3), as the energies of the single-quasiparticle states decrease below E_S , single-quasiparticle tunnelling will once again take over as the leading breaking process.

4.6.2 Recombination pathways

Depending on the state of the SDD after a breaking process has occurred, there are several different pathways through the state space that the system can take to return to S . Experimentally, all that can be measured is a distribution of recombination times — the time it takes to return to S after a breaking event — from which an average value is extracted and used to define a recombination rate. In the language of stochastic processes, the expected time $\langle t_{if} \rangle$ to reach state f from a given initial state

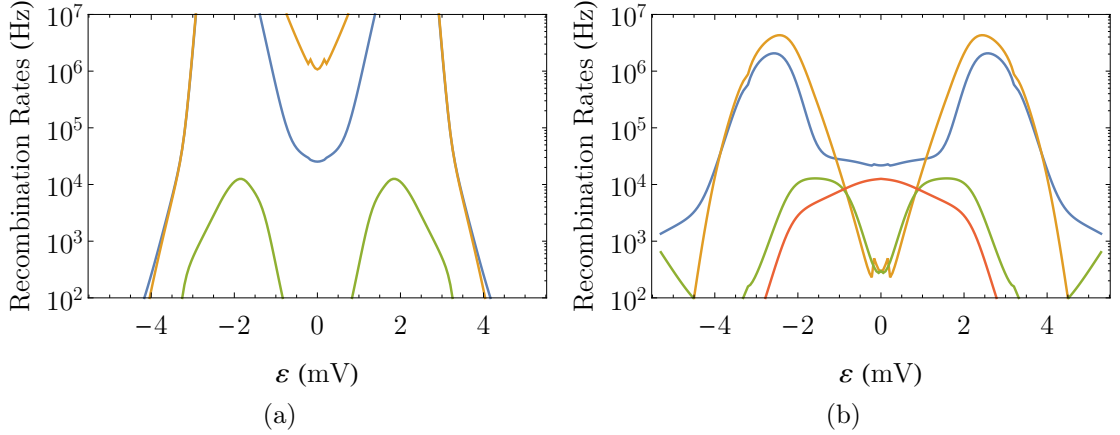


Figure 4.4: Theoretically calculated recombination rates with (a) no photon environment and (b) an environment consistent with experimental data. Total recombination rate Γ_R (blue), calculated from average hitting times of the rate matrix $\mathcal{M}$ is plotted, along with weighted direct recombination rates $\sum_i P(S \rightarrow i \rightarrow S) \Gamma_{i \rightarrow S}$ for: Cooper-pair states $i \in \{(0, 0), (2, 2)\}$ (yellow) and single-quasiparticle states $i \in \{(1, 0), (0, 1), (1, 2), (2, 1)\}$ (green), the latter also includes contributions from $(1, 0) \rightarrow (0, 0)$ and similar processes, which for small detunings precede an immediate return to S . The intermediate rate $(\Gamma_{S \rightarrow (1,1)} / \Gamma_B) \sum_i \Gamma_{(1,1) \rightarrow i}$ for $i \in \{(1, 0), (0, 1), (1, 2), (2, 1)\}$ (red) is also plotted.

i is known as the ‘hitting time’ and can be calculated for continuous time Markovian processes on a finite state space [134], such as that described in eq. (4.53). The hitting times to reach state f are given by the minimum positive solution of

$$\begin{aligned} \langle t_{ff} \rangle &= 0, \\ \sum_i \langle t_{if} \rangle \mathcal{M}_{ij} &= -1 \quad \text{for } j \neq f, \end{aligned} \quad (4.55)$$

which we solve numerically.

In order to compare with experiment, we find the hitting times to reach S for each of the possible states after a breaking event. We then sum them, weighted by the probability of breaking to that state. The recombination rate Γ_R is therefore given by the inverse of

$$\Gamma_R^{-1} = \sum_i \frac{\Gamma_{S \rightarrow i}}{\sum_j \Gamma_{S \rightarrow j}} \langle t_{iS} \rangle, \quad (4.56)$$

which we plot as a function of ε in fig. 4.4.

For large ε -detunings, the recombination rate is dictated almost entirely by the rate $\Gamma_{(0,0)/(2,2) \rightarrow S}$. This is due to the high likelihood of being in either $(0, 0)$ or $(2, 2)$ (depending on the sign of ε) after a given breaking process, along with the comparatively low rates for processes taking these Cooper-pair states anywhere other than

S . The direct recombination rate from $(0,0)$ or $(2,2)$, weighted by the probability of it occurring, $P(S \rightarrow (0,0)/(2,2) \rightarrow S)$, is plotted in fig. 4.4 for comparison with the total recombination rate, and one can see that it has roughly the same shape as the main curve. It is worth noting again that the discontinuous behaviour of these rates around $\varepsilon = \pm 0.2 \text{ mV}$ is due to the transition between single and double electron tunnelling at second order (see the discussion above in sec. 4.5.2). The probability $P(S \rightarrow i \rightarrow S)$, where i is some intermediate state, can be written in terms of conditional probabilities $P(S \rightarrow i \rightarrow S) = P(S \rightarrow i | S)P(i \rightarrow S | i)$. These are in turn calculated from the elements of $\mathcal{M}$: $P(i \rightarrow j | i) = -\mathcal{M}_{ji}/\mathcal{M}_{ii}$.

Around $\varepsilon = 0$ the dynamics is somewhat more complicated, since the dominant breaking rates are $\Gamma_{S \rightarrow (1,0)/(0,1)/(1,2)/(2,1)}$ and, to a lesser extent, $\Gamma_{S \rightarrow (1,1)}$. Direct recombination from these final states is not the most likely pathway to return to S , especially for the latter process, for which it is much more likely that first one of the quasiparticles and then the other will sequentially tunnel into the leads.

Once the system is in one of the single-quasiparticle states, there are two principal pathways for further decay to S : $(1,0) \rightarrow S$ and $(1,0) \rightarrow (0,0) \rightarrow S$ (and analogous processes via other single-quasiparticle states). For small $|\varepsilon|$, the processes $(0,0)/(2,2) \rightarrow S$ are almost instantaneous, so we can use $\Gamma_{(1,0) \rightarrow (0,0) \rightarrow S} \simeq \Gamma_{(1,0) \rightarrow (0,0)}$ *etc.* We plot the weighted sum of these recombination pathways (given that the original breaking process involved quasiparticle tunnelling from the leads) along with the total recombination rate. It can be seen that direct recombination from the single-quasiparticle states is not a likely event for low detuning. Instead, since the various single-quasiparticle states are close in energy, the system is much more likely to transition between them than directly back to S . The weighted intermediate rate $\sum_i P(S \rightarrow (1,1) \rightarrow i) \Gamma_{(1,1) \rightarrow i}$, for $i \in \{(1,0), (0,1), (1,2), (2,1)\}$, is also plotted in fig. 4.4 for completeness, since it is the limiting rate for recombination from $(1,1)$. However, it does not significantly affect the average behaviour of the device.

The much lower recombination rate at large detunings in the case of no environment can be explained by the lack of available energy to excite the ground states in this region — $(0,0)$ and $(2,2)$ — to the state S . The other main difference between the two cases — the difference in size of the peaks — is due the suppressing effect of the environment on the Andreev reflection rates $\Gamma_{(2,2)/(0,0) \rightarrow S}$.

Of course, the intermediate rates plotted in fig. 4.4 only represent the most direct transitions back to S . The total average recombination rate is always smaller than the sum of these, since it takes into account the more convoluted possible trajectories of the system.

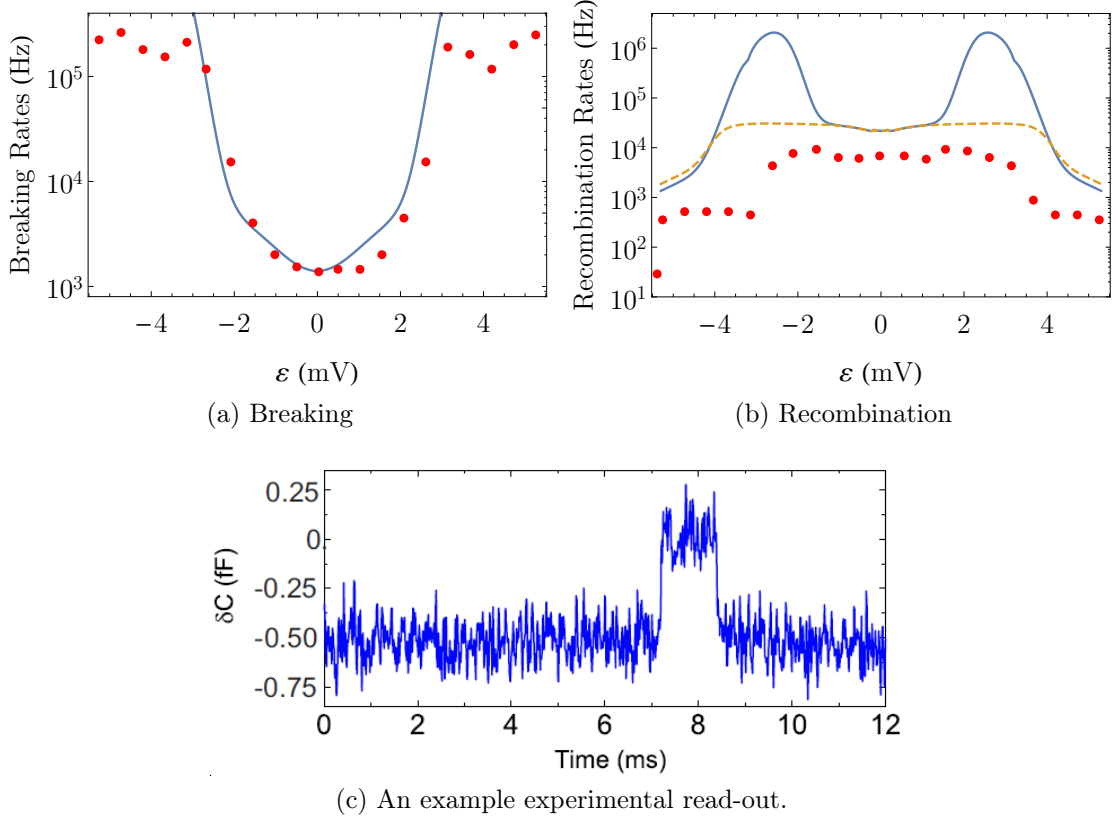


Figure 4.5: (Data from ref. [2]) (a) Experimentally measured breaking rates (red dots) as a function of detuning ε . The theoretically predicted rate is plotted (blue curve) on the same axes for comparison. (b) Experimentally measured recombination rates (red dots) as a function of detuning ε . As well as the total theoretically predicted recombination rate (solid blue), we also plot the recombination rate predicted if all Andreev reflection mediated breaking processes are ignored (dashed yellow). (c) An example of the time-domain signal read out in the experiment. Jumps in the measured quantum capacitance are interpreted as breaking and recombination events.

4.6.3 Comparison with experimental data

Fig. 4.5 (data taken from [2]) shows experimentally measured breaking and recombination rates for a SDD system with the parameters given in the appendix. As can be seen, the breaking rate behaviour is qualitatively similar to that predicted from theory. The exception being that there is a sharp cutoff in the experimentally measured rates at ~ 200 kHz. This can be simply explained by the finite time resolution of the experimental apparatus (the frequency bandwidth quoted in ref. [2] is 100 kHz); breaking events which occur on too short a timescale are not registered as such, and act to extend the measured recombination time.

On the other hand, the measured recombination rate does not appear to behave

much at all like that seen in fig. 4.4. The prominent peaks at $\varepsilon \sim \pm 3 \text{ mV}$ are absent from the experimental data and the overall rate is markedly lower, especially for the largest values of ε . This can again be partly explained by the the finite resolution of the experiment: Firstly, as mentioned above, the recombination rate at larger detunings will be measured to be much smaller than its real value. This is due to the large breaking rate, which will prevent the detection of recombination processes (and hence decrease the apparent rate) by removing the system from the state S faster than it can be detected. Secondly, for the same reason, measurement of the recombination rate will be biased towards that arising from breaking processes with lower rates. The large peaks in the theoretically calculated rates are due to direct recombination from $(0,0)$ and $(2,2)$; the relatively quick breaking rate to go to these states from S means that they are often not registered as separate events. The average recombination rate from all breaking processes except $S \rightarrow (0,0)/(2,2)$ is plotted in fig. 4.5, this gives a much closer fit to the shape of the experimental data, if not to the quantitative values.

The source of the discrepancy between theoretical and experimental recombination rates could come from any of the many assumptions that have gone into the calculations of sec. 4.5. Principal culprits are the assumption of instantaneous thermalisation and of a high temperature thermal distribution for the photon environment. Dropping the former, which allows us to ‘forget’ how a given quasiparticle state was formed for the purposes of calculating transition rates, would not affect the breaking rate, since the state S would still have a well defined energy (as opposed to the quasiparticle states which in reality have a spread of energies). However, it would decrease the recombination rate, bringing the theoretical predictions closer to experiment. This is due to the extra time it would take to dissipate quasiparticle energy to the point where modes with the correct energy to allow transitions would be significantly occupied. Lifting the assumption of a thermal environment could also reduce the recombination rate, by favouring transitions of a certain energy, for example, though it would also likely affect the breaking rate. The relaxation of either of these assumptions would significantly increase the complexity of the calculations required to model the system.

4.7 Conclusions

In this chapter, we have modelled the excitation dynamics of a superconducting double dot in the presence of several environments. By calculating transition rates between the various energy levels of the system and by considering a particular experimental

set-up, we have predicted the observed behaviour of the device and used the underlying model to explain real experimental data.

If our simulations are to be believed, the majority of breaking processes around $\varepsilon = 0$ are indeed assisted by the absorption of photons from the environment, since the predicted breaking rate in their absence is orders of magnitude lower than that measured. However, the principle breaking process is tunnelling from the leads, rather than direct splitting of the Cooper pair on the islands, as is assumed in ref. [2]. Whilst there is still a significant energy gap ($\sim \Delta$) to overcome in this case, lifetime broadening effects mean that there will always be a significant background tunnelling rate for quasiparticles to enter the island without absorbing a photon. The process $S \rightarrow (1, 1)$, on the other hand, has a larger gap ($\sim 2\Delta - E_S$) and will generally have a much lower background rate at low temperatures, partly due to the longer lifetime of the $(1, 1)$ state. In order to move into a lower noise regime, in which Cooper-pair splitting dominates, one could increase the resistance of the outer tunnel junctions, thereby suppressing tunnelling from the leads.

In a solid-state quantum computing setting, the states of the electromagnetic field which one would like to detect are likely to be far from thermally distributed — as is assumed in this chapter. A non-thermal environment would partially modify the environment influence function in eq. (4.52) and hence the form of the transition rates between energy states. Further calculations which treat the environment in a more realistic setting, for example taking a microscopic circuit QED Hamiltonian as a starting point [13, 135], are required to judge the device’s suitability as a useful detector outside the regime we study here.

Finally, a similar approach to that taken in this chapter could be used to calculate the energy structure and dynamics of larger networks of coupled islands. The extra degrees of freedom in the energy landscape of these networks could be used to further tune the energies of the excited states, in order to produce the desired dynamical behaviour. One could also create more exotic ground states in such networks, involving, for instance, even larger spatial superpositions of single Cooper pairs. In any case, the relevant environmentally induced transition rates would be given by expressions similar to those presented here.

Appendix

In this chapter we use the parameters of the device considered in ref. [2] for all of the numerical simulations. The fabricated SDD consists of aluminium superconducting

Capacitance	Value (aF)	Capacitance	Value (aF)
C_{gL}	11.8	C_L	330
C_{gR}	23.5	C_R	530
C_{LR}	11.8	C_M	220
C_{RL}	4.7		

Table 4.1: Measured capacitance for the SDD. Taken from ref. [2].

islands — of dimensions $l_x \simeq 1000$ nm, $l_y \simeq 100$ nm and $l_z \simeq 20$ nm — coupled through thin aluminium oxide barriers — of area $S \simeq 30$ nm $\times$ 30 nm = 900 nm² and resistance $R_D = R_S = 4$ M Ω — to copper leads of thickness $d_L \simeq 30$ nm. The two islands are similarly separated by a weaker barrier of resistance $R_M = 7$ k Ω . The measured values of the various capacitances of the device (see fig. 4.1c for reference) are given in table 4.1.

At zero external field, the superconducting gap constant is measured to be $\Delta = 250$ μ eV. For all calculations we assume an electron temperature of $T = 125$ mK. The electron diffusion coefficients in the aluminium islands and copper leads are taken to be $D_{Al} = 66.1$ cm²s⁻¹ and $D_{Cu} = 147$ cm²s⁻¹ respectively [124]. For the calculations in sec. 4.3, we use $V_S = V_D = 0$ mV.

Chapter 5

Olfaction as a vibrationally-activated molecular switch

5.1 Introduction

Resonant interactions between vibrational degrees of freedom of the environment and those inherent to an open system are thought to play an important role in numerous physical processes [136–147]. In this chapter, by focusing on a proposed model for olfaction as a vibrationally-activated molecular switch, we explore the detailed effects of the environment on the dynamics of electron transfer in an open quantum system, aiming to gain physical insight into vibrationally-assisted transport processes more generally.

Furthermore, obtaining a deep understanding of molecular recognition in olfaction, the mechanism for which is still being actively debated [148–157], is an important problem in its own right for both fundamental science and industry [158–162]. The prevailing theory, known as the lock-and-key model, explains how the size and shape of a molecule (labelled the odorant in this context) can provide discrimination in an olfactory receptor [163]. However, there is evidence that it may be possible for some organisms to distinguish between the smells of some very similar odorants, for example between those whose only difference is in whether or not they have been deuterated [153, 157, 164]. Since these molecules have effectively the same shape, the lock-and-key model would predict that they would bind in exactly the same way to receptors and would hence be indistinguishable. It has been suggested that an additional detection mechanism, based on sensing the vibrational spectra of odorants, could supplement the lock-and-key model [165–167] and allow for the distinction of molecules which otherwise have the same properties. The most promising proposal for this mechanism is that it occurs via electron transfer in the receptor [148, 149]. More

recent work — constructing and exploring model systems that capture the important physical processes [151, 154] — has shown that this is indeed a viable proposition. The suggested mechanism, which harnesses vibrationally-assisted electron transfer in a similar manner to inelastic electron tunnelling spectroscopy [168, 169], can be viewed as an example of a molecular switch, wherein specific vibrational modes of an external molecule actuate the receptor and lead to a pronounced increase in electron flow. The need for clear discrimination of the difference in electron transfer dynamics in the presence and absence of the odorant imposes certain design principles on the molecular switch, which may or may not lead to the employment of quantum phenomena to optimise its performance.

Previously, a receptor-odorant spin-boson model, not too dissimilar from the model described in chapters 2 & 3, was introduced to describe the vibrationally-assisted electron transfer process at the heart of the mechanism discussed above [151, 154]. Using an analysis based on the semi-classical Marcus-Jortner formula for the electron transfer rate [170–174], it was shown that for certain parameter values the electron transfer rates in the presence and absence of the odorant can differ drastically. This explains how the electron transfer process could help in molecular recognition via sensing of vibrational spectra; sensitivity of the switch to the presence or absence of a particular odorant can be understood as a significant difference in typical timescales, or more generally in the population dynamics of different electronic states, for processes with or without the odorant coupled to the receptor. Additionally, in refs. [154, 156] further evidence supporting a vibrationally-assisted mechanism was obtained from sophisticated quantum chemistry calculations.

Inspired by the possibility of vibrational sensing in olfaction, we focus here on the physical model of a molecular switch tuned for frequency detection. We go beyond the Marcus-Jortner approach presented in previous works to look at both the frequency selectivity and detailed dynamics of a molecular switch in a variety of regimes in which a semi-classical analysis can break down. Starting from a microscopic Hamiltonian describing a vibrational mode of the odorant (as an oscillator), the receptor (as a donor-acceptor two-level system), and their environment (as a collection of independent oscillators), we first use a polaron-representation, Markovian master equation for the electron transfer process, in which both the odorant and environment appear in the perturbative terms within the polaron frame. From this we may extract the relevant electron transfer rates, extending previous analyses to a broader set of parameters and looking in more detail at the assumptions required for the Marcus-Jortner

rates to be valid; in fact, these rates arise naturally from our master equation in the high-temperature regime (as compared to the energy scales of the environment).

Moving beyond the perturbative treatment of the odorant, we then look at the dynamics when the odorant mode is regarded as being part of the system (*i.e.* the interaction between it and the donor-acceptor pair is handled non-perturbatively), and explore in which regimes the simpler electron transfer rates can faithfully represent this more accurate evolution. We again do this by deriving a master equation, though in the present case *only* the environment appears in the perturbative terms within the polaron frame. Our results thus differ at various levels of approximation from those previously presented. We find that the dynamics of donor-acceptor populations as predicted by one-way electron transfer rates can differ considerably from those given by this more sophisticated master equation treatment, for a non-negligible set of parameter values. This includes those for which the rates calculated in ref. [151] are assumed to be valid.

Moreover, as the odorant is treated explicitly within our approach, it has the further advantage of allowing us to straightforwardly incorporate the effects of dissipation on the odorant mode. We will show that by introducing sufficiently strong mode dissipation, it is possible to bring the donor-acceptor dynamics derived from our master equation into a simpler exponential form, consistent with irreversible, incoherent transfer between donor and acceptor. However, even within this strongly dissipative regime, our master equation predictions can still differ markedly from the semi-classical Marcus-Jortner theory, depending upon the specific nature of the environment experienced by the donor-acceptor pair. In particular, we show that while in the Marcus-Jortner case the receptor is very sensitive to the presence or absence of the odorant, it is far less sensitive to the specific odorant vibrational frequency. We find, however, that the frequency resolution can be enhanced by considering environments which contain components of similar or larger energy to that set by the ambient temperature, *i.e.* by working outside the semi-classical limit. More generally, we show, when considering dissipation of the odorant mode, that both the sensitivity of the switch to the presence or absence of the odorant, and to the resonance conditions between the odorant and the donor-acceptor pair, can be significantly amplified in comparison to the dissipationless case. We thus find that odorant dissipation plays a constructive role in enhancing the vibrational sensing capabilities of our molecular switch. Once again, to prevent notational clutter, we switch to a system of units in which $\hbar = 1$.

5.2 The vibrationally-assisted electron transfer model for olfaction

Few details are known about the molecular structure of olfactory receptors and their properties [159, 160, 175]. Some possible receptors are metalloproteins — containing metallic cofactors that can act as electron donor and acceptor sites [176] — which may help to explain how the electron transfer process could work in practice [177, 178]. Receptors most likely have rich electronic structures, but here, as in previous work on this model [151, 154, 156], we assume that there exist specific electronic states that can be identified as a donor-acceptor pair, with other levels well separated in energy. We model the vibrationally-assisted electron transfer process using a spin-boson Hamiltonian similar to that used in earlier chapters. The donor-acceptor pair is coupled to an environment represented by a bath of harmonic oscillators (which includes the vibrational degrees of freedom of the receptor and the surrounding protein structure) and to the odorant (when present in the receptor). The odorant is modelled as a single harmonic oscillator mode, though this could also be extended to a set of modes. Our Hamiltonian thus takes the form

$$\begin{aligned}
 H = & \epsilon_D |D\rangle\langle D| + \epsilon_A |A\rangle\langle A| + V(|A\rangle\langle D| + |D\rangle\langle A|) \\
 & + \omega_0 a^\dagger a + (g_{D,0} |D\rangle\langle D| + g_{A,0} |A\rangle\langle A|)(a^\dagger + a) \\
 & + \sum_{\mathbf{k}} [\omega_{\mathbf{k}} b_{\mathbf{k}}^\dagger b_{\mathbf{k}} + (g_{D,\mathbf{k}} |D\rangle\langle D| + g_{A,\mathbf{k}} |A\rangle\langle A|)(b_{\mathbf{k}}^\dagger + b_{\mathbf{k}})]. \quad (5.1)
 \end{aligned}$$

Here, $|D\rangle$ represents the donor electronic state and $|A\rangle$ represents that of the acceptor, these have on-site energies ϵ_D and ϵ_A respectively. V refers to the tunnel-coupling energy between the two states. The odorant molecular mode, with creation operator $a^\dagger$, has frequency ω_0 and is coupled to the donor pair via $g_{D,0}$ and $g_{A,0}$. The environmental oscillators, with creation operators $b_{\mathbf{k}}^\dagger$ for modes of frequency $\omega_{\mathbf{k}}$, couple to the receptor electronic sites via $g_{D,\mathbf{k}}$ and $g_{A,\mathbf{k}}$. Transfer of an electron gives rise to changes in the local electric field and justifies the linear form of the interaction between the oscillators and the donor-acceptor pair as long as the resulting displacements from equilibrium are small [41, 151, 154, 156]. As in chapter 3, the environment is taken to contain a continuum of frequencies whose coupling is described by a spectral density $J(\omega) = \sum_{\mathbf{k}} |g_{D,\mathbf{k}} - g_{A,\mathbf{k}}|^2 \delta(\omega - \omega_{\mathbf{k}})$. A measure of the overall influence of the environment is the reorganisation energy λ defined in eq. (3.4).

In refs. [151, 154], Marcus-Jortner theory was used to derive both elastic electron transfer rates, in the absence of the odorant, and inelastic rates, in its presence. The

basis of these semi-classical derivations is Fermi’s golden rule, wherein the tunnelling term V is treated as a perturbation. This naturally gives rise to a representation of the receptor-odorant-environment basis in terms of displaced oscillator states between which it is assumed that incoherent electron transfer occurs. In ref. [151], typical electron transfer timescales for elastic processes, mediated purely by the environment, were estimated to be around two orders of magnitude longer than for the inelastic processes, as required for discriminating between the presence and the absence of the odorant. Ref. [154] also discusses a wider range of parameters in which a separation of timescales between the elastic and inelastic processes can be obtained.

Here, rather than following the same golden rule calculation, we will look at receptor electron transfer dynamics and issues such as odorant vibrational frequency resolution from the perspective of the master equation formalism. As discussed below, this includes the Marcus-Jortner rate analysis as a limiting case, but can also go well beyond the restricted regime of validity of such an approach.

For consistency with the published literature, we follow the estimation of parameters presented in refs. [151, 154]. As mentioned, the biological receptor’s electronic structure is not known, and neither are the typical energies ϵ_D and ϵ_A . Since we are interested in modelling a receptor that is sensitive to the particular frequency of the odorant mode, we assume that the energy gap $\epsilon_D - \epsilon_A$, which dictates the resonance condition, is of the same order as typical values for ω_0 (since V is taken to be small, $\epsilon_D - \epsilon_A$ is a good approximation the the difference between eigenenergies in the receptor). Typical values for ω_0 are in the range of 70 – 400 meV, and we choose $\epsilon_D - \epsilon_A = 200$ meV for the donor-acceptor energy gap. We shall, however, explore a range of odorant frequencies away from resonance to study the issue of molecular frequency recognition, *i.e.* we are interested in whether the switch is sensitive merely to the presence or absence of the odorant, or to its particular vibrational frequency as well. The receptor binding pocket is thought to be around 5 – 15 Å in size, which leads to an estimate for the donor-acceptor tunnel-coupling energy of $V \simeq 1$ meV [151]. A larger value for V would act to enhance the ET rate in the absence of the odorant in the receptor, which would be disadvantageous as far as the switching mechanism is concerned. Therefore, keeping V small in comparison to other system parameters is well motivated physically. Estimates of the strength of the coupling between the donor-acceptor pair and the odorant mode, and of the reorganisation energy of the multi-mode environment, have been given as $|g_{D,0} - g_{A,0}|^2 / \omega_0^2 \simeq 0.01$ and $\lambda \simeq 30$ meV, respectively.

The detailed properties of the continuous environment, such as the spectral density, do not enter the semi-classical Marcus-Jortner rates and hence have not been discussed in previous work. They are, however, important for our more general analysis. We choose to work with an Ohmic environment, $J(\omega) \propto \omega$ as $\omega \rightarrow 0$, with a characteristic high frequency cut-off ω_c , since in the absence of more detailed information, it straightforwardly reproduces the results of refs. [151, 154] in the correct limit ($\beta\omega_c \ll 1$, where $\beta = 1/k_B T$ is the inverse temperature). We take the cut-off to be exponential, leading to the following spectral density defined also in terms of the reorganisation energy:

$$J(\omega) = \lambda \frac{\omega}{\omega_c} e^{-\omega/\omega_c}. \quad (5.2)$$

Here, we will explore variations in the donor-acceptor-environment coupling strength through the reorganisation energy — focussing on the range $\lambda \sim 10 - 60$ meV — and the cut-off frequency ω_c . In order to explore the effect of widening the range of frequencies within the environment that can interact with the donor-acceptor pair, we will consider regimes in which $\omega_c/k_B T$ is both less than and greater than unity, as well as the intermediate case where the environment frequencies are of the same order as $k_B T$. We assume a temperature of $T = 300$ K throughout

5.3 Incoherent electron transfer rates from a polaron master equation

As noted, for our system to act as an effective molecular switch, the Hamiltonian parameters should be such that unwanted transitions from donor to acceptor are avoided when the odorant is absent. This requires the tunnel-coupling energy V to be small compared to other energy scales in the problem. In this regime, it is convenient to move into a fully-displaced polaron-transformed reference frame to remove the linear coupling terms in eq. (5.1). Provided V is indeed small, perturbative expansions in the transformed basis are valid over a much wider range of system-environment coupling strengths than those in the untransformed case (see the discussion in chapter 3). Let us consider the (unitary) polaron transformation $U = e^{-(G_A + G_B)}$ acting on our Hamiltonian, where

$$G_A = \left(\frac{g_{D,0}}{\omega_0} |D\rangle\langle D| + \frac{g_{A,0}}{\omega_0} |A\rangle\langle A| \right) (a^\dagger - a), \quad (5.3)$$

and

$$G_B = \sum_k \left(\frac{g_{D,\mathbf{k}}}{\omega_{\mathbf{k}}} |D\rangle\langle D| + \frac{g_{A,\mathbf{k}}}{\omega_{\mathbf{k}}} |A\rangle\langle A| \right) (b_{\mathbf{k}}^\dagger - b_{\mathbf{k}}). \quad (5.4)$$

Note that we have transformed with respect to *both* the donor-acceptor-environment and donor-acceptor-odorant interaction terms here. By doing this, we end up with odorant degrees of freedom in the perturbative terms of our subsequent master equation. In sec. 5.4 we take an alternative approach in which the donor-acceptor-odorant interaction is treated fully non-perturbatively.

The polaron transformed Hamiltonian takes the form $\tilde{H} = U^\dagger H U = \tilde{H}_S + \tilde{H}_B + \tilde{H}_I$, where

$$\begin{aligned}\tilde{H}_S &= \epsilon'_D |D\rangle\langle D| + \epsilon'_A |A\rangle\langle A| + \omega_0 a^\dagger a, \\ \tilde{H}_B &= H_B = \sum_{\mathbf{k}} \omega_{\mathbf{k}} b_{\mathbf{k}}^\dagger b_{\mathbf{k}},\end{aligned}$$

and

$$\tilde{H}_I = V(|D\rangle\langle A|\mathcal{A}_+\mathcal{B}_+ + |A\rangle\langle D|\mathcal{A}_-\mathcal{B}_-). \quad (5.5)$$

Here, $\epsilon'_{D(A)} = \epsilon_{D(A)} - |g_{D(A),0}|^2/\omega_0 - \sum_{\mathbf{k}} |g_{D(A),\mathbf{k}}|^2/\omega_{\mathbf{k}}$ is the polaron-shifted on-site energy, and $\mathcal{A}_\pm = \mathcal{D}(\pm(g_{D,0} - g_{A,0})/\omega_0)$ and $\mathcal{B}_\pm = \prod_{\mathbf{k}} \mathcal{D}_{\mathbf{k}}(\pm(g_{D,\mathbf{k}} - g_{A,\mathbf{k}})/\omega_{\mathbf{k}})$ are the new oscillator interaction operators, written in terms of the displacement operators $\mathcal{D}(u) = \exp[ua^\dagger - u^*a]$ and $\mathcal{D}_{\mathbf{k}}(u) = \exp[ub_{\mathbf{k}}^\dagger - u^*b_{\mathbf{k}}]$, respectively. As discussed in chapter 3, the polaron transformation leaves the operators $|D\rangle\langle D|$ and $|A\rangle\langle A|$ — required for calculating donor-acceptor populations — unchanged. Unlike in that chapter however, the bath operators in the transformed interaction Hamiltonian $\tilde{H}_I$ are already traceless, and we do not end up with any renormalised coupling in the system. This is a consequence of our choice of an Ohmic spectral density, for which the traces in eq. (3.8) go to zero.

Tracing out the environment, which we assume to be initially thermal with inverse temperature $\beta = 1/k_B T$, and treating the perturbative term $\tilde{H}_I$ up to second order in the standard Born-Markov approximations (see chapter 2), we obtain a master equation in the polaron frame interaction picture (with respect to $\tilde{H}_S + \tilde{H}_B$), given by

$$\begin{aligned}\frac{d}{dt}\tilde{\rho}_S^I(t) &= -V^2 \int_0^\infty d\tau \left\{ \left([|A\rangle\langle D|\mathcal{A}_-(t), |D\rangle\langle A|\mathcal{A}_+(t-\tau)\tilde{\rho}_S^I(t)]e^{-i\epsilon\tau} \right. \right. \\ &\quad \left. \left. + [|D\rangle\langle A|\mathcal{A}_+(t), |A\rangle\langle D|\mathcal{A}_-(t-\tau)\tilde{\rho}_S^I(t)]e^{i\epsilon\tau} \right) \Lambda(\tau) \right. \\ &\quad \left. + \text{h.c.} \right\}. \quad (5.6)\end{aligned}$$

Here, $\tilde{\rho}_S^I(t)$ is the interaction-picture reduced density operator describing the donor-acceptor pair and odorant mode. The bath correlation function is

$$\Lambda(\tau) = \exp \left[- \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} [(1 - \cos \omega\tau) \coth(\beta\omega/2) + i \sin \omega\tau] \right], \quad (5.7)$$

and $\epsilon = \epsilon'_D - \epsilon'_A$ is the donor-acceptor energy gap in the new frame. We will now use this master equation, to derive incoherent elastic and inelastic electron transfer rates.

5.3.1 Odorant absent

Let us consider the population transfer from donor to acceptor in the absence of an odorant molecule, for which we set $\mathcal{A}_\pm(t) = \mathbb{1}$ in eq. (5.6). We can then easily derive rate equations governing the donor ($p_D(t)$) and acceptor ($p_A(t)$) population dynamics. Our interest lies in the transfer rates that appear in these equations

$$\Gamma(\pm\epsilon) = \int_{-\infty}^\infty d\tau e^{\pm i\epsilon\tau} \Lambda(\tau), \quad (5.8)$$

where, by defining $\Gamma_{D \rightarrow A} = V^2 \Gamma(\epsilon)$ and $\Gamma_{A \rightarrow D} = V^2 \Gamma(-\epsilon)$, we obtain

$$\frac{d}{dt} \begin{pmatrix} p_D(t) \\ p_A(t) \end{pmatrix} = \begin{pmatrix} -\Gamma_{D \rightarrow A} & \Gamma_{A \rightarrow D} \\ \Gamma_{D \rightarrow A} & -\Gamma_{A \rightarrow D} \end{pmatrix} \begin{pmatrix} p_D(t) \\ p_A(t) \end{pmatrix}. \quad (5.9)$$

In the limit that $\Gamma_{D \rightarrow A} \gg \Gamma_{A \rightarrow D}$, these equations define exponential transfer of population from donor to acceptor at (approximately) the rate $\Gamma_{D \rightarrow A}$, which, substituting in for the correlation function $\Lambda(t)$, is

$$\Gamma_{D \rightarrow A} = V^2 \int_{-\infty}^\infty d\tau e^{i\epsilon\tau} e^{-\varphi(\tau)}, \quad (5.10)$$

where

$$\varphi(\tau) = \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} [(1 - \cos \omega\tau) \coth(\beta\omega/2) + i \sin \omega\tau]. \quad (5.11)$$

For a low-frequency environment in which $\omega_c \ll k_B T$, we may derive a simple form for $\Gamma_{D \rightarrow A}$ which turns out to be the same as the Marcus-Jortner rate. Taking the spectral density defined in eq. (5.2) and expanding $\coth(\beta\omega/2) \simeq 2/\beta\omega$ in eq. (5.11), we find

$$\varphi(\tau) \simeq \frac{\lambda}{\beta\omega_c^2} [\omega_c(i\beta + 2\tau) \arctan(\omega_c\tau) - \ln(1 + \omega_c^2\tau^2)]. \quad (5.12)$$

Due to the factor of $\beta\omega_c$ in the denominator of this equation, $e^{-\varphi(\tau)}$ is strongly peaked around $\tau = 0$, such that we may expand $\varphi(\tau)$ to second order in τ to give

$$\varphi(\tau) \simeq i\lambda\tau + \frac{\lambda\tau^2}{\beta}. \quad (5.13)$$

With these assumptions we can write

$$\begin{aligned}\Gamma_{D \rightarrow A} &\simeq V^2 \int_{-\infty}^{\infty} d\tau e^{i(\epsilon - \lambda)\tau} e^{-\lambda\tau^2/\beta} \\ &= 2\pi V^2 \frac{1}{\sqrt{4\pi k_B T \lambda}} \exp \left[-\frac{(\epsilon - \lambda)^2}{4k_B T \lambda} \right],\end{aligned}\quad (5.14)$$

which agrees with the elastic rate (odorant absent) presented in ref. [151] when $g_{D,\mathbf{k}} = -g_{A,\mathbf{k}}$ is assumed, and as a consequence $\epsilon \rightarrow \epsilon_D - \epsilon_A$. We apply this constraint on $g_{D,\mathbf{k}}$ and $g_{A,\mathbf{k}}$ throughout this chapter, although little modification would be required to account for the more general case. Choosing $\lambda = 30$ meV, and other parameters as outlined in sec. 5.2, we obtain $\Gamma_{D \rightarrow A} = 5.67 \times 10^{-6}$ meV from eq. (5.14), which corresponds to $\tau_{D \rightarrow A} = 1/\Gamma_{D \rightarrow A} = 116$ ns as the donor-acceptor transfer time in the absence of the odorant.

Of course, the limit $\omega_c \ll k_B T$ used to derive eq. (5.14) may not always be met, in which case we can use the more general form of eq. (5.10) to define the donor-acceptor elastic transfer rate. Importantly, this allows us to discuss lower temperatures and larger environmental frequencies than those to which the Marcus-Jortner rates apply.

5.3.2 Odorant present

We can derive a similar rate when the odorant is present in the receptor. In this situation, we must deal with a more complex system, as the reduced density operator (after tracing out the environmental degrees of freedom) in eq. (5.6) now encompasses both the two-level donor-acceptor pair and the odorant harmonic oscillator. Obtaining general equations of motion for the donor-acceptor populations becomes significantly more involved. However, this is unnecessary if all we are interested in are electron transfer rates between specific states of the combined donor-acceptor-odorant system. Let us assume that we initialise the system in the state $|D, 0\rangle$, with the electron in the donor state and the odorant in its ground-state $|0\rangle$. We are interested in the rate of electron transfer to a state of the form $|A, n\rangle$, where $|n\rangle$ is an arbitrary Fock (number) state of the odorant. We are therefore considering situations in which the receptor population transfer $|D\rangle \rightarrow |A\rangle$ is accompanied by excitation of the odorant vibrational mode $|0\rangle \rightarrow |n\rangle$, which may or may not act to enhance the rate associated with the process.

We return to the master equation (eq. (5.6)) to derive an expression for the dynamics of the population of the acceptor and a given Fock state $|n\rangle$ of the odorant, $\tilde{\rho}_{AnAn}(t) = \text{tr}\{|A, n\rangle\langle n, A| \tilde{\rho}_S^I(t)\} = \langle n, A| \tilde{\rho}_S^I(t) |A, n\rangle$, where the trace is taken

over both the odorant and the donor-acceptor degrees of freedom. Decomposing the donor-acceptor-odorant density operator as $\tilde{\rho}_S^I(t) = \sum_{X,X',l,m} \tilde{\rho}_{XlX'm}(t) |X, l\rangle \langle X', m|$, where $X, X' \in \{D, A\}$ and l, m are odorant Fock states, allows us to identify the various contributions to the change in population of the state $|A, n\rangle$. In particular, if we assume that the only donor-odorant state of interest is one with no odorant excitations, $|D, 0\rangle$ — valid when we initialise the system in this state and energy splittings are large enough to suppress transitions to any other donor-odorant states — we may then define the transfer rate for the process $|D, 0\rangle \rightarrow |A, n\rangle$ as

$$\Gamma_{D0 \rightarrow An} = \int_0^\infty d\tau \left(e^{i\epsilon\tau} \Lambda(\tau) \langle n | \mathcal{A}_-(t-\tau) | 0 \rangle \langle 0 | \mathcal{A}_+(t) | n \rangle + e^{-i\epsilon\tau} \Lambda^*(\tau) \langle n | \mathcal{A}_-(t) | 0 \rangle \langle 0 | \mathcal{A}_+(t-\tau) | n \rangle \right) V^2. \quad (5.15)$$

Using $\langle n | D(\alpha) | 0 \rangle = (\alpha^n / \sqrt{n!}) e^{-|\alpha|^2/2}$, it is straightforward to calculate the matrix elements of $\mathcal{A}_\pm(t)$. We then arrive at

$$\Gamma_{D0 \rightarrow An} = \frac{V^2 |g_{D,0} - g_{A,0}|^{2n}}{\omega_0^{2n} n!} e^{-(|g_{D,0} - g_{A,0}|/\omega_0)^2} \int_{-\infty}^\infty d\tau e^{i(\epsilon - n\omega_0)\tau} e^{-\varphi(\tau)}, \quad (5.16)$$

which generalises eq. (5.10) in the presence of the odorant ($\Gamma_{D \rightarrow A} = \Gamma_{D0 \rightarrow A0}$). At this point, we can once again take the limit $\omega_c \ll k_B T$, and follow the same steps that led us from eq. (5.10) to eq. (5.14) to find

$$\Gamma_{D0 \rightarrow An} \simeq 2\pi V^2 \frac{|g_{D,0} - g_{A,0}|^{2n} e^{-(|g_{D,0} - g_{A,0}|/\omega_0)^2}}{\omega_0^{2n} n! \sqrt{4\pi k_B T \lambda}} \exp \left[-\frac{(\epsilon - n\omega_0 - \lambda)^2}{4k_B T \lambda} \right]. \quad (5.17)$$

Again, this result for the inelastic electron transfer rates ($n > 0$) agrees with the Marcus-Jortner expressions found in ref. [151] when we assume $g_{D,0} = -g_{A,0}$ and $g_{D,\mathbf{k}} = -g_{A,\mathbf{k}}$, such that $\epsilon \rightarrow \epsilon_D - \epsilon_A$. Using the same parameters as before and $\omega_0 = \epsilon_D - \epsilon_A$, we obtain $\Gamma_{D0 \rightarrow A1} = 4.71 \times 10^{-4}$ meV, which corresponds to a transfer time of $\tau_{D0 \rightarrow A1} = 1/\Gamma_{D0 \rightarrow A1} = 1.4$ ns. This is far shorter than the 116 ns transfer time found above in the absence of the odorant, as required for a viable molecular switch. Furthermore, if we look at the rate for the two-phonon transition we find $\Gamma_{D0 \rightarrow A2} = 1.24 \times 10^{-13}$ meV, and a corresponding time $\tau_{D0 \rightarrow A2} = 5.3$ s, confirming that the single-phonon process is dominant within this treatment. As before, in situations in which the limit $\omega_c \ll k_B T$ does not apply, we may instead use eq. (5.16) to define the inelastic rates, again generalising the Marcus-Jortner rates to a wider range of parameters.

Of course, our master equation also allows us to calculate the reverse rates $\Gamma_{An \rightarrow D0}$ (as well as other rates such as $\Gamma_{Dn \rightarrow Dm}$ and $\Gamma_{An \rightarrow Am}$, which do not play a major role). Following a derivation similar to that leading to eq. (5.16), we find

$$\Gamma_{An \rightarrow D0} = \frac{V^2 |g_{D,0} - g_{A,0}|^{2n} e^{-(|g_{D,0} - g_{A,0}|/\omega_0)^2}}{\omega_0^{2n} n!} \int_{-\infty}^{\infty} d\tau e^{i(\epsilon - n\omega_0)\tau} e^{-\varphi(-\tau)}, \quad (5.18)$$

and, in the limit $\beta\omega_c \ll 1$,

$$\Gamma_{An \rightarrow D0} \simeq 2\pi V^2 \frac{|g_{D,0} - g_{A,0}|^{2n} e^{-(|g_{D,0} - g_{A,0}|/\omega_0)^2}}{\omega_0^{2n} n! \sqrt{4\pi k_B T \lambda}} \exp \left[-\frac{(\epsilon - n\omega_0 + \lambda)^2}{4k_B T \lambda} \right]. \quad (5.19)$$

Notably, the single-phonon reverse transfer rate, $\Gamma_{A1 \rightarrow D0}$, is equal to the donor-to-acceptor rate, $\Gamma_{D0 \rightarrow A1}$, when the odorant is resonant with the receptor ($\omega_0 = \epsilon_D - \epsilon_A$). We will see below that this is also the case in the more exact master equation we derive below, and has important implications for the dynamics of the donor-acceptor pair over a wide range of parameters, often invalidating the treatment of inelastic electron transfer as being a one-way process.

5.4 Treating the odorant mode non-perturbatively

In the previous section, by making use of a polaron representation master equation, we rederived and generalised the Marcus-Jortner electron transfer rates (both in the presence and the absence of the odorant) found in refs. [151, 154]. Both procedures amount to perturbative treatments in a basis of displaced oscillator states representing *both* the odorant and the environment. It is possible, however, to treat the coupling between the odorant vibrational mode and the donor-acceptor pair non-perturbatively and to track the dynamics of the former explicitly. Whilst we could have also tracked the odorant dynamics using the master equation in the previous section — and we would not expect the results to differ drastically in the parameter regime we are considering — we would nevertheless be discarding higher order terms in the (polaron-transformed) receptor-odorant coupling Hamiltonian which could contribute to the dynamics.

The more exact treatment is achieved by again considering a polaron transformation on the original Hamiltonian, this time with respect to only the bath degrees of freedom; the transformed donor-acceptor-odorant Hamiltonian is simply

$$\begin{aligned} \tilde{H}_S = & \epsilon'_D |D\rangle\langle D| + \epsilon'_A |A\rangle\langle A| + \omega_0 a^\dagger a \\ & + (\gamma_D |D\rangle\langle D| + \gamma_A |A\rangle\langle A|)(a^\dagger + a), \end{aligned} \quad (5.20)$$

and the remaining interaction Hamiltonian is now independent of the odorant:

$$\tilde{H}_I = V(|D\rangle\langle A|\mathcal{B}_+ + |A\rangle\langle D|\mathcal{B}_-). \quad (5.21)$$

In order to derive our subsequent master equation, we must move into the interaction picture with respect to $\tilde{H}_S$. It is helpful, therefore, to find the basis in which $\tilde{H}_S$ is diagonal:

$$\tilde{H}_S = \sum_n \tilde{E}_n |\tilde{E}_n\rangle\langle\tilde{E}_n|. \quad (5.22)$$

In practice, this must be found numerically. To do so, we treat the odorant as a finite dimensional system, where the number of Fock basis states used is increased until the master equation dynamics has converged. Then we follow the standard procedure outlined in chapter 2 and write the interaction Hamiltonian in the interaction picture as

$$\tilde{H}_I(t) = S_+(t)\mathcal{B}_+(t) + S_-(t)\mathcal{B}_-(t), \quad (5.23)$$

where

$$S_+(t) = (S_-(t))^\dagger = \sum_{n,m} e^{-i(\tilde{E}_n - \tilde{E}_m)t} V |\tilde{E}_n\rangle\langle\tilde{E}_m| (|D\rangle\langle A| \otimes \mathbb{1}) |\tilde{E}_m\rangle\langle\tilde{E}_m|, \quad (5.24)$$

and $\mathcal{B}_\pm(t) = e^{iH_B t} \mathcal{B}_\pm e^{-iH_B t}$.

Continuing the standard Born-Markov master equation derivation — treating the polaron frame interaction Hamiltonian (eq. (5.23)) to second order, but now keeping the donor-acceptor-odorant interaction to all orders — we end up with, in the Schrödinger picture,

$$\begin{aligned} \frac{d}{dt} \tilde{\rho}_S(t) &= -i[\tilde{H}_S, \tilde{\rho}_S(t)] \\ &- \int_0^\infty d\tau \left\{ ([S_+(0), S_-(-\tau)\tilde{\rho}_S(t)] \right. \\ &\quad \left. + [S_-(0), S_+(-\tau)\tilde{\rho}_S(t)])\Lambda(\tau) + \text{h.c.} \right\}, \end{aligned} \quad (5.25)$$

where the bath correlation function $\Lambda(\tau)$ is again given by eq. (5.7) and $\tilde{\rho}_S$ describes the reduced behaviour of the donor-acceptor pair and odorant mode. Hence, once the master equation has been solved, the dynamics of the donor-acceptor two-level system can be recovered by tracing out the odorant degrees of freedom. Similarly, one can trace out the electronic degrees of freedom to find the explicit dynamics of the odorant mode.

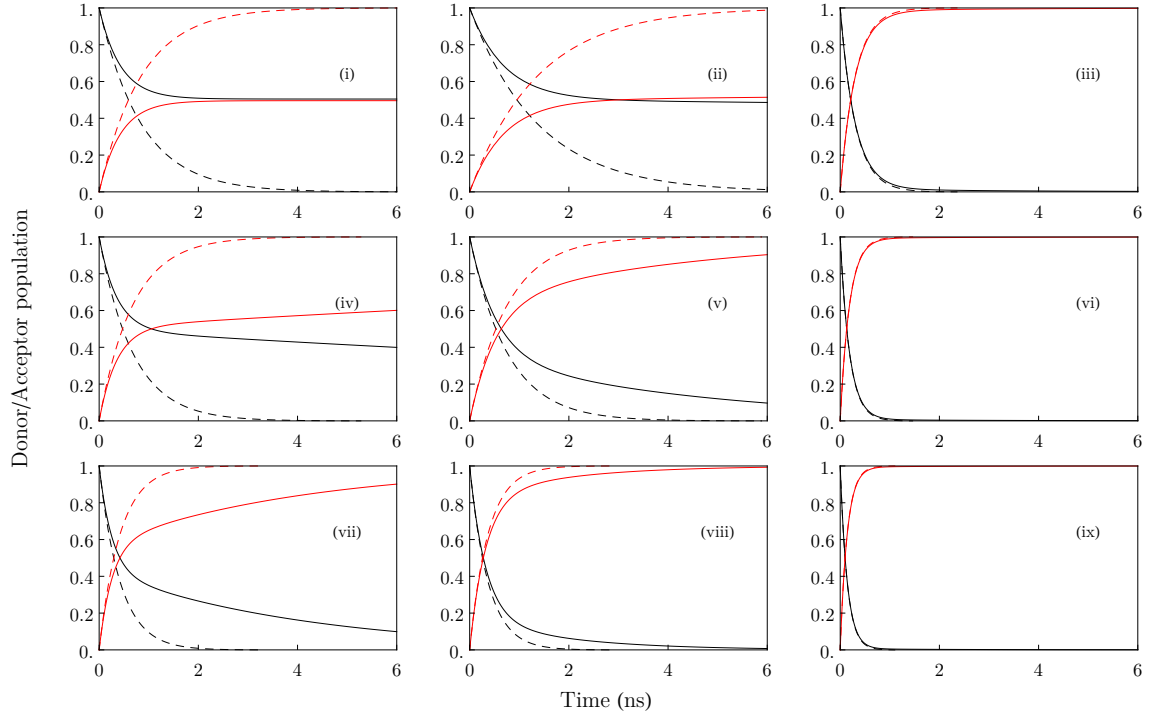


Figure 5.1: Comparison of populations $p_A(t)$ (red) and $p_D(t)$ (black) as predicted by the master equation in eq. (5.25) (solid lines, calculated using N odorant states, where N is chosen to ensure numerical convergence) and by the total (one-way) electron transfer rate $\sum_{n=0}^N \Gamma_{D0 \rightarrow An}$ from eq. (5.16) (dashed lines). The reorganisation energy λ increases from left to right: $\lambda = 15$ meV in the left column, $\lambda = 30$ meV in the middle column and $\lambda = 60$ meV in the right column. The bath cut-off frequency ω_c increases from top to bottom, with $\omega_c = k_B T / 10$ for panels (i - iii), $\omega_c = k_B T$ for panels (iv - vi) and $\omega_c = 2k_B T$ for panels (vii - ix).

5.4.1 Master equation dynamics

We are now in a position to compare the more exact dynamics described above with the simple model of exponential transfer implicitly assumed in refs. [151, 154] (using the incoherent rates derived in sec. 5.3). By investigating various parameter regimes, we hope to identify the regions of validity for the latter approach and to characterise the effect of the odorant mode on the donor-acceptor pair.

Fig. 5.1 shows a comparison between the donor-acceptor population dynamics as calculated using eq. (5.25) and the behaviour assuming pure decay of the donor population with rates given by eqs. (5.16) and (5.17). The dynamics is plotted for various reorganisation energies λ and environmental cut-off frequencies ω_c . In each case, the spectral density is taken to be that in eq. (5.2) and all other parameters are fixed to the values given in sec. 5.2. The initial state of the whole system is taken to be a product state with the electron on the donor site and both the odorant mode and the environment in thermal states with respect to $H_A = \omega_0 a^\dagger a$ and H_B , respectively.

As can be seen in the figure, the donor ($p_D(t)$) and acceptor ($p_A(t)$) population behaviour can deviate significantly from irreversible exponential transfer. The best agreement is found for the highest cut-off frequency and the highest reorganisation energy. However, in the analysis of rates presented in earlier works, the bath was assumed to be of low frequency ($\omega_c \ll k_B T$), which is clearly the case in which the two sets of dynamics differ most (although the electron transfer rates used to calculate the dashed curves in panels (i - iii) do agree with their Marcus-Jortner counterparts). The discussion in sec. 5.3 has already suggested that, without further assumptions, we should not expect exponential-decay like behaviour, due to the fact that the reverse transfer rates are non-negligible. This is especially true when the inelastic process dominates, as the reverse rate in the elastic case is suppressed by a factor $\sim \exp[-(\epsilon_D - \epsilon_A)\lambda/k_B T]$ (*cf.* eqs. (5.17) & (5.19)). The dependence on λ and ω_c of the agreement between the solid and dashed curves agrees with this prediction, and suggests that it is dissipation to the environment that limits the transfer from donor to acceptor in the master equation dynamics. The dissipation rate increases as the reorganisation energy is increased and the characteristic frequency of the environment becomes closer to the energy gap in the donor-acceptor pair.

We can more clearly see what is going on by looking at fig. 5.2, which shows the population dynamics of the first two levels of the odorant mode as predicted by the master equation (other levels are never significantly populated, since the total initial energy is insufficient to further excite the mode). The donor-acceptor pair and the odorant mode quickly become correlated, forming a state where the electron is equally

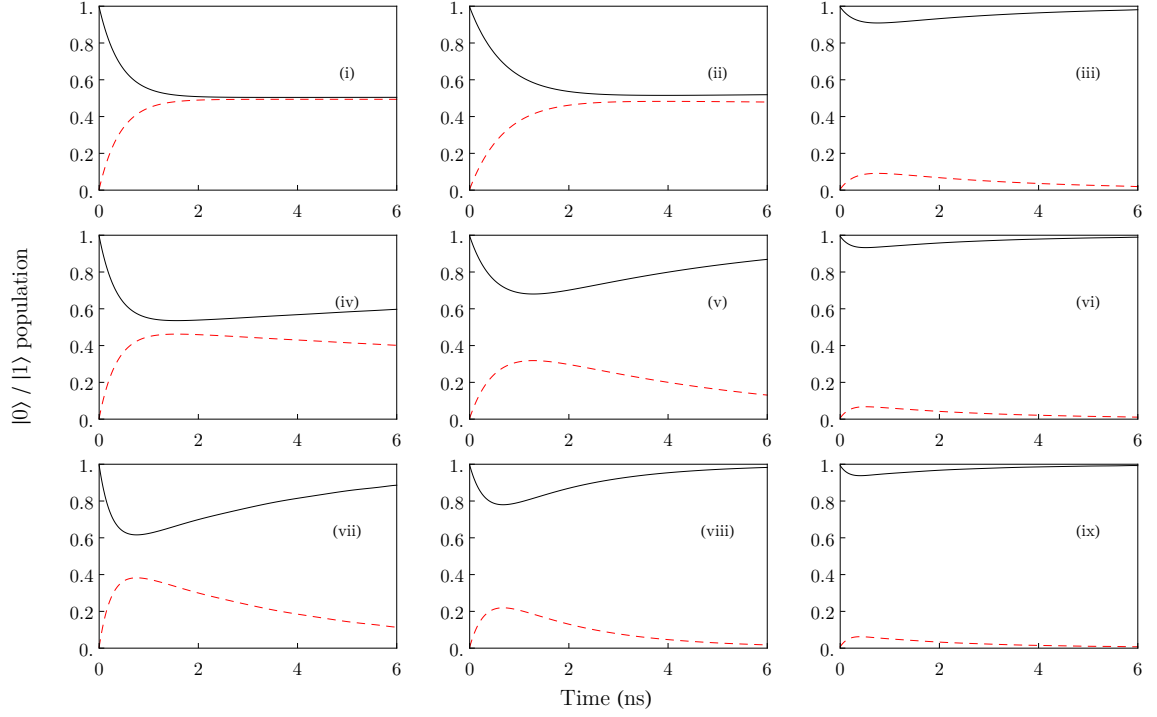


Figure 5.2: Comparison of populations $p_{|0\rangle\langle 0|}(t)$ (solid black) and $p_{|1\rangle\langle 1|}(t)$ (dashed red) as predicted by the master equation in eq. (5.25). Reorganisation energy λ increases from left to right: $\lambda = 15\text{meV}$ in the left column, $\lambda = 30\text{meV}$ in the middle column and $\lambda = 60\text{meV}$ in the right column. Bath cut-off frequency ω_c increases from top to bottom, with $\omega_c = k_B T / 10$ for panels (i - iii), $\omega_c = k_B T$ for panels (iv - vi) and $\omega_c = 2k_B T$ for panels (vii - ix). Populations of higher Fock states are negligible for all times.

likely to be found on the acceptor (having deposited its energy in the odorant mode) as it is on the donor. The only way energy can exit the system (allowing the electron to transfer fully to the acceptor site) is into the bath, leading to the (in some cases) slow relaxation to the acceptor state most clearly seen in panels (v) and (vii - viii).

The transfer-limiting behaviour predicted by the master equation, clearly has the potential to compromise the sensitivity of the olfactory switch, though it could be argued that a less than complete population transfer occurring on a short enough timescale could still lead to detection of the odorant, albeit with a reduced probability. Depending on the details of the olfactory system this may or may not be sufficient to recognise the presence of the odorant, but further exploration of this point is beyond the scope of this chapter.

We will now go on to show that, by introducing dissipation to the mode, we can suppress the population of the excited states of the odorant and restore the agreement between the rate-type behaviour and the master equation dynamics.

5.4.2 Damping the odorant mode

Given that, when present, the odorant is considered to be in the vicinity of the donor-acceptor pair, it is reasonable to assume that it too interacts with the surrounding environment. We may model the effects of the resulting mode dissipation in a straightforward manner by introducing an additional phenomenological Lindblad term (see chapter 2) to the right hand side of our master equation (eq. (5.25)):

$$\begin{aligned}\mathcal{L}_{diss}[\tilde{\rho}_S] = & -\frac{\gamma_0}{2}N_0(aa^\dagger\tilde{\rho}_S - 2a^\dagger\tilde{\rho}_Sa + \tilde{\rho}_Saa^\dagger) \\ & -\frac{\gamma_0}{2}(N_0 + 1)(a^\dagger a\tilde{\rho}_S - 2a\tilde{\rho}_Sa^\dagger + \tilde{\rho}_Sa^\dagger a),\end{aligned}\quad (5.26)$$

where γ_0 is the dissipation rate and $N_0 = (e^{\omega_0/k_B T} - 1)^{-1}$ is the average phonon number in the odorant at temperature T . By modelling dissipation in this way, we are assuming that we can make Born-Markov and secular approximations for the interaction between the odorant and its environment and that neither this nor the donor-acceptor-environment coupling are too strong. When condition the latter condition does not hold, we must treat the dissipation rates of these two subsystems as being dependent upon one another [179]. Additionally, eq. (5.26) only describes a purely dissipative process in the limit where the coupling between the donor-acceptor pair and the odorant is small compared to ω_0 . This is due to the fact that the eigenstates of the donor-acceptor-odorant Hamiltonian do not necessarily coincide with the Fock basis states.

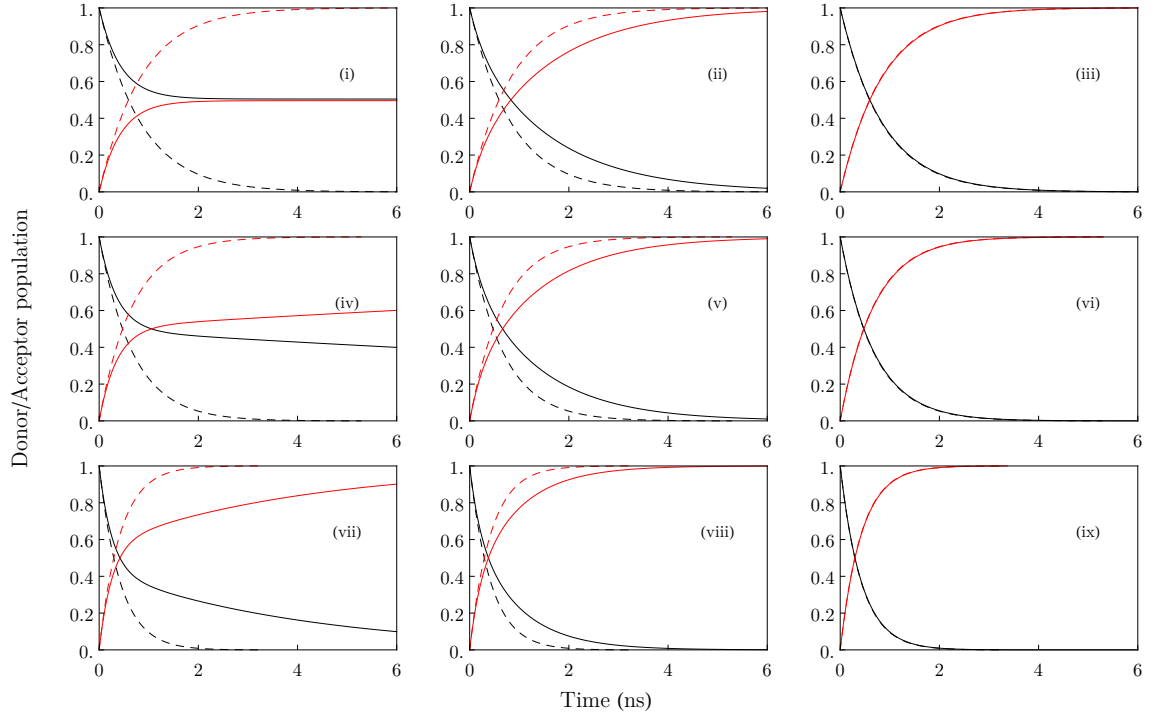


Figure 5.3: Populations $p_A(t)$ (red) and $p_D(t)$ (black) as predicted by the master equation in eq. (5.25) (solid lines) for different odorant dissipation rates γ_0 . The reorganisation energy is $\lambda = 15\text{meV}$ in each case, and exponential transfer with the electron transfer rates derived in sec. 5.3 is plotted for comparison (dashed lines). Dissipation rate γ_0 increases from left to right: $\gamma_0 = 0\text{ns}^{-1}$ in the left column, $\gamma_0 = 1\text{ns}^{-1}$ in the middle column and $\gamma_0 = 1000\text{ns}^{-1}$ in the right column. Bath cut-off frequency ω_c increases from top to bottom, with $\omega_c = k_B T/10$ for panels (i - iii), $\omega_c = k_B T$ for panels (iv - vi) and $\omega_c = 2k_B T$ for panels (vii - ix).

While we do not know the value of the dissipation rate introduced in eq. (5.26), we can investigate its effect by varying γ_0 . Fig. 5.3 shows such a comparison of the dynamics for no dissipation ($\gamma_0 = 0$, left hand column), moderate dissipation ($\gamma_0 \sim \Gamma_{D0 \rightarrow A1}$, middle column) and relatively strong dissipation ($\gamma_0 \gg \Gamma_{D0 \rightarrow A1}$, right hand column). In the limit of large dissipation, we see that the behaviour of the donor-acceptor populations is consistent with the simple transfer rates from eq. (5.16). This means that we can now investigate the effects of different environments based purely on a simple transfer rate approach, provided that the odorant mode is sufficiently damped.

5.5 The dependence of transfer rates on environmental structure

We can think of the olfactory system, as modelled here, in terms of a vibrational spectrometer, and one of the principle figures of merit for any spectroscopic device is its frequency resolution. The more sensitive the individual receptors are to resonance conditions between the donor-acceptor pair and odorant, the better they will be able to distinguish the vibrational spectra of different molecules. To explore the dependence of this resolution on the properties of the environment, in fig. 5.4 we map out the ratio $r = (\Gamma_{\text{tot}} - \Gamma_0)/(\Gamma_{\text{tot}} + \Gamma_0)$ of tunnelling rates as a function of odorant frequency ω_0 and bath reorganisation energy λ . Here, the definition of Γ_{tot} as the tunnelling rate in the presence of the odorant and Γ_0 as the rate in its absence is made possible by the strong mode dissipation, $\gamma_0 = 1000 \text{ ns}^{-1}$, which ensures exponential electron transfer from donor to acceptor as demonstrated in the previous section. Panel (a) corresponds to the regime in which $\omega_c \ll k_B T$, therefore representing the behaviour predicted by the Marcus-Jortner rates of eqs. (5.14) and (5.17), while the other panels encompass parameter ranges outside the Marcus-Jortner limit (larger values of ω_c).

We see that in each plot there exists a frequency window for which the tunnelling rate is significantly enhanced in the presence of the odorant above the background. Furthermore, this window becomes narrower as the environmental cut-off frequency is increased (panels (b) and (c)), suggesting that the structure of the environment can play an important role in tuning the selectivity, and hence frequency resolution, of the receptor's donor-acceptor pair. Crucially, this cannot be predicted by the semi-classical Marcus-Jortner rates, which do not depend on the frequencies present in the environment (they merely assume they are small), and predict a significant

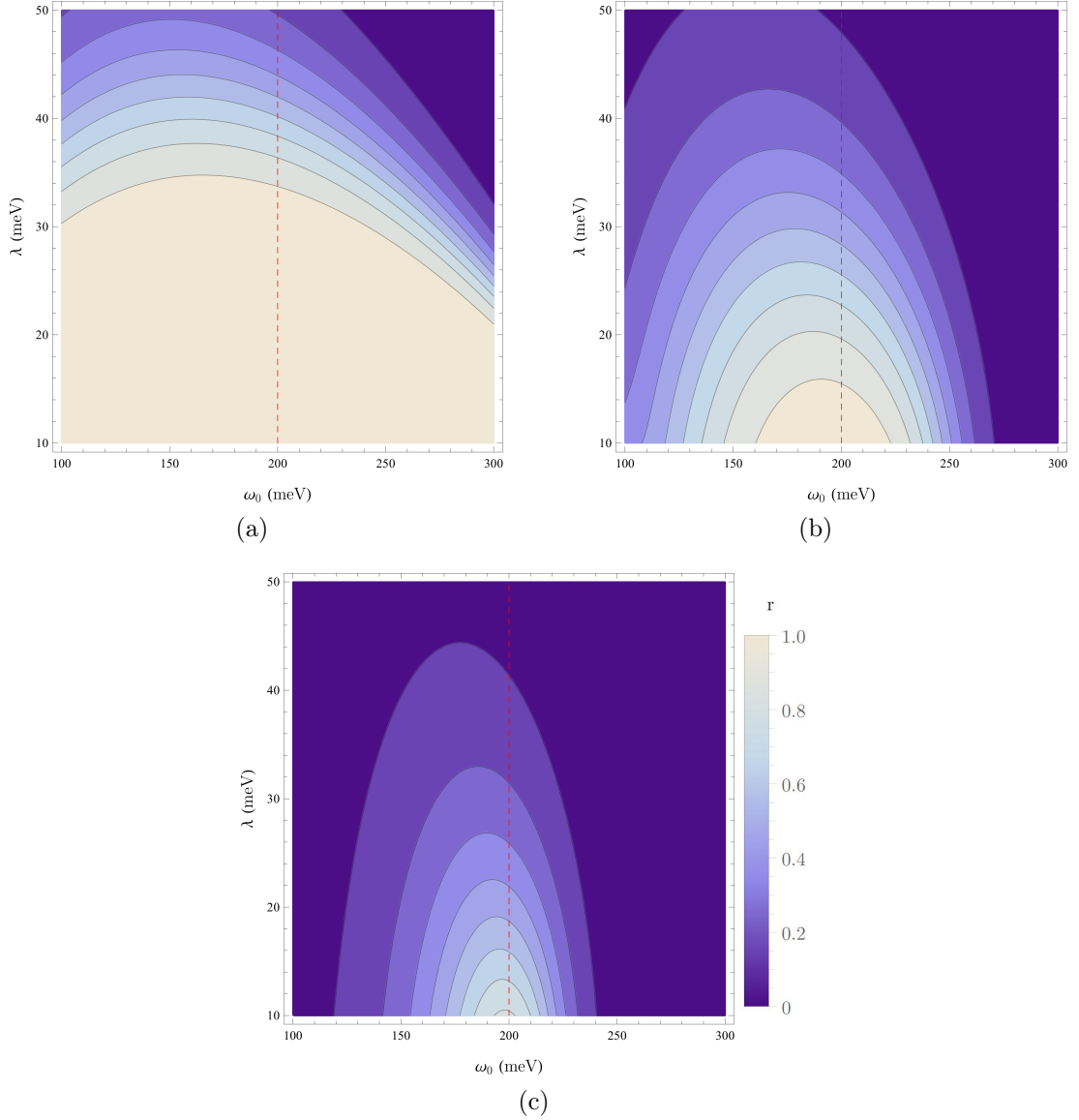


Figure 5.4: Contour plots of the ratio $r = \frac{(\Gamma_{\text{tot}} - \Gamma_0)}{(\Gamma_{\text{tot}} + \Gamma_0)}$ as a function of odorant frequency ω_0 and bath reorganisation energy λ for cut-off frequencies: (a) $\omega_c = k_B T / 10$ (corresponding to the Marcus-Jortner limit), (b) $\omega_c = k_B T$ and (c) $\omega_c = 2 k_B T$. Other parameters are given in sec. 5.2. Light regions correspond to $r \rightarrow 1$ (good odorant discrimination) and the darkest regions correspond to $r \rightarrow 0$ (poor discrimination); contours correspond to steps in r of 0.1. The red dashed lines show the donor-acceptor energy splitting.

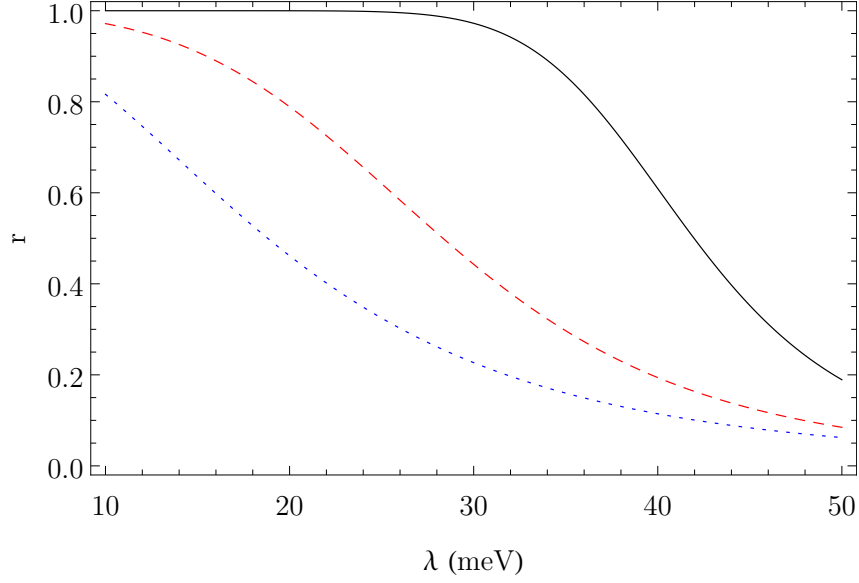


Figure 5.5: The ratio $r = \frac{(\Gamma_{\text{tot}} - \Gamma_0)}{(\Gamma_{\text{tot}} + \Gamma_0)}$ as a function of reorganisation energy λ for three different values of the environmental cut-off frequency: $\omega_c = k_B T / 10$ (solid black), $\omega_c = k_B T$ (dashed red), and $\omega_c = 2 k_B T$ (dotted blue).

enhancement of tunnelling even for odorant vibrational frequencies relatively far off-resonance with the donor-acceptor energy gap of 200 meV (panel (a)). The low-frequency environment regime analysed in previous works — to which we have shown the Marcus-Jortner rates apply under significant mode damping — is thus very sensitive to the presence or absence of the odorant, but not necessarily to the odorant’s specific vibrational spectrum.

It is evident from fig. 5.4, however, that increased frequency resolution comes at a cost. In order to achieve the more selective behaviour apparent with a larger environmental cut-off frequency (and strong odorant dissipation), the coupling to the continuum environment must be reduced — the receptor is only sensitive to the presence of the odorant for smaller reorganisation energies. Furthermore, the switch suffers from intrinsically higher levels of noise, since the peak values of the ratio r also become smaller as the cut-off is increased. This is seen more clearly in fig. 5.5, which shows the ratio r as a function of reorganisation energy when $\omega_0 = \epsilon_D - \epsilon_A$ (along the red lines in fig. 5.4). We can therefore conclude from our analysis that a tradeoff exists, in which the combination of moderate to high frequency components in the environment and a lower reorganisation energy is advantageous for odorant vibrational frequency resolution, though not necessarily for reliable discrimination simply between the presence and the absence of the odorant. It is worth noting also

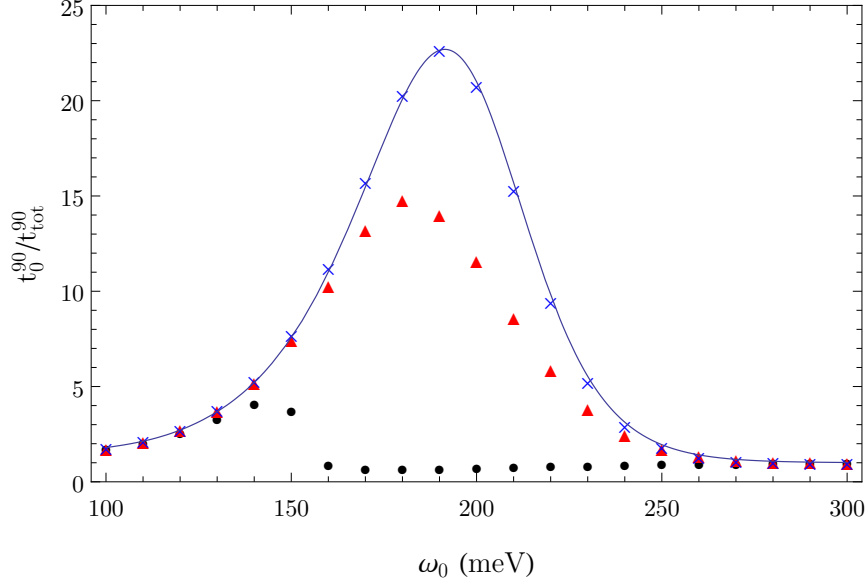


Figure 5.6: The ratio of the electron transfer time (to 90% acceptor population) in the absence of the odorant (t_0^{90}) to that in its presence (t_{tot}^{90}) as a function of odorant frequency, as predicted by eqs. (5.25) & (5.26). We take $\lambda = 15$ meV, $\omega_c = k_B T$, and all other parameters are provided in sec 5.2. The three sets of points correspond to different levels of dissipation on the odorant: $\gamma_0 = 0$ (black dots), $\gamma_0 = 1$ ns⁻¹ (red triangles) and $\gamma_0 = 1000$ ns⁻¹ (blue crosses). The solid curve corresponds to the same ratio calculated using eq. (5.16).

that the validity of the results derived from our polaron transformed Hamiltonians (in both secs. 5.3 & 5.4) rely on the assumption $\lambda \gg V$. It is not possible, therefore, to extrapolate figs. 5.4 & 5.5 to yet lower reorganisation energies within the present analysis.

Finally, we stress that if we move out of the regime of strong odorant dissipation, we find that both the frequency resolution of the receptor and its sensitivity to the presence or absence of the odorant decreases. This is illustrated in fig. 5.6, which shows the ratio of the transfer time (to 90% population on the acceptor site) in the absence of the odorant to that in its presence for different levels of dissipation on the odorant mode. We use the transfer time to allow a meaningful comparison here, since there is no single rate that accurately describes the dynamics outside the strongly dissipative case, and a value of 90% is chosen to represent significant enough transfer for the receptor to consistently register its occurrence. As the dissipation rate is decreased, the height of the peak in the figure also decreases, while its width remains similar (red triangles) until the dissipation ceases to play a role (black dots). Thus, as the mode becomes less damped, the receptor frequency resolution is severely

compromised, as well as its capability to sense the presence of the odorant altogether.

5.6 Conclusions

We have developed a dynamical theory of a molecular switch and applied it to investigate vibrationally-assisted electron transfer in the context of a proposed olfactory mechanism. We have shown that the dynamics of the olfactory receptor, when the model Hamiltonian is treated in isolation, can differ dramatically from that predicted by semi-classical Marcus-Jortner theory, even in the regime of a low-frequency environment, for which it is supposed to do well. The electron transfer dynamics predicted from our master-equation approach can, however, be brought back into agreement with a simpler rate analysis — though not generally the Marcus-Jortner rates unless the semi-classical limit is also taken — provided that strong dissipation is allowed to act on the odorant vibrational mode. This results in an enhanced switching with respect to the dissipationless case. Furthermore, we have found that low-frequency environments, to which the Marcus-Jortner rates apply under strong odorant dissipation, do not provide good odorant frequency resolution in the electron transfer rates. By modifying environmental parameters to move beyond the semi-classical limit, it is nevertheless possible to substantially increase this resolution and thus select for odorant modes of a particular frequency, albeit with an increase in background noise.

In reality, molecular odorants will always have more than the single vibrational mode which we have modelled here. Since these are likely to be of a relatively high frequency and will act as an environment to the receptor, our comparatively simple analysis in this chapter might lead one to the counter-intuitive conclusion that they will increase the receptor’s ability to resolve the frequency of other modes near resonance. It remains to be seen whether this is indeed the case, and one of the next steps in developing the model we have presented would be to include more than one odorant mode simultaneously.

With the aid of more detailed information about environment of real olfactory receptors — either from experimental data or quantum chemical simulations — one could use our results to help determine whether the electron model under discussion would be feasible in a biological setting. For instance, we have come to the general conclusion that having a high-frequency environment aids in the selectivity of the receptor as long as the reorganisation energy is low enough. It may be, however, that in reality the latter is far too high when considering the frequencies present. It may also happen that reduction of the donor-receptor-environment coupling entails

a reduction in damping of the odorant mode — leading again to reduced frequency selectivity.

Nevertheless, while our present model is motivated by the problem of describing olfaction in biological systems, the Hamiltonian in eq. (5.1) can actually correspond to a wide variety of physical settings in which vibrationally-assisted transport processes are important. Examples include nano-mechanical oscillators coupled to two-level systems [180], such as quantum dots [181] and superconducting qubits [182, 183], as well as other biological systems such as the photosynthetic reaction centre in certain organisms [184, 185]. Our results may also be especially relevant for the development of artificial molecular sensors, which could use the principles we have described in their design to aid in distinguishing chemical species based on their vibrational spectra [161, 186, 187].

Bibliography

- [1] Felix A Pollock, Dara P S McCutcheon, Brendon W Lovett, Erik M Gauger, and Ahsan Nazir. A multi-site variational master equation approach to dissipative energy transfer. *New Journal of Physics*, 15(7):075018, 2013.
- [2] N. J. Lambert, M. Edwards, A. A. Esmail, F. A. Pollock, S. D. Barrett, B. W. Lovett, and A. J. Ferguson. Splitting a single Cooper-pair with microwave light. *arXiv/cond-mat.mes-hal*, 1304.5117, 2013.
- [3] N. J. Lambert, M. Edwards, A. A. Esmail, F. A. Pollock, B. W. Lovett, and A. J. Ferguson. The energy landscape of a superconducting double dot. *arXiv/cond-mat.mes-hal*, 1403.6643, 2014.
- [4] A. Chęcińska, F. A. Pollock, L. Heaney, and A. Nazir. Dissipation enhanced vibrational sensing in an olfactory molecular switch. *arXiv/cond-mat.mes-hal*, 1403.6483, 2014.
- [5] James Binney and David Skinner. *The Physics of Quantum Mechanics*. Oxford University Press, 2013.
- [6] Michael A. Nielsen and Isaac I. Chuang. *Quantum Computation and Quantum Information*. Cambridge University Press, 2000.
- [7] H.-P. Breuer and F Petruccione. *The Theory of Open Quantum Systems*. Oxford University Press, 2002.
- [8] Crispin Gardiner and Peter Zoller. *Quantum Noise: A Handbook of Markovian and Non-Markovian Quantum Stochastic Methods with Applications to Quantum Optics*. Springer Science & Business Media, 3rd edition, 2004.
- [9] Ulrich Weiss. *Quantum Dissipative Systems*. World Scientific, 3rd edition, 2008.

- [10] Pieter Kok, W. J. Munro, Kae Nemoto, T. C. Ralph, Jonathan P. Dowling, and G. J. Milburn. Linear optical quantum computing with photonic qubits. *Reviews of Modern Physics*, 79:135–174, 2007.
- [11] Christoph Kloeffel and Daniel Loss. Prospects for Spin-Based Quantum Computing in Quantum Dots. In *Annual Review of Condensed Matter Physics*, volume 4, pages 51–81. Annual Reviews, 2013.
- [12] John Clarke and Frank K. Wilhelm. Superconducting quantum bits. *Nature*, 453(7198):1031–1042, 2008.
- [13] Alexandre Blais, Ren-Shou Huang, Andreas Wallraff, S. M. Girvin, and R. J. Schoelkopf. Cavity quantum electrodynamics for superconducting electrical circuits: An architecture for quantum computation. *Physical Review A*, 69(6):062320, 2004.
- [14] Alexandre Blais, Jay Gambetta, A. Wallraff, D. I. Schuster, S. M. Girvin, M. H. Devoret, and R. J. Schoelkopf. Quantum-information processing with circuit quantum electrodynamics. *Physical Review A*, 75(3):032329, 2007.
- [15] Frank Verstraete, Michael M. Wolf, and J. Ignacio Cirac. Quantum computation and quantum-state engineering driven by dissipation. *Nature Physics*, 5(9):633–636, 2009.
- [16] M. J. Kastoryano, M. M. Wolf, and J. Eisert. Precisely timing dissipative quantum information processing. *Physical Review Letters*, 110:110501, 2013.
- [17] Heinz-Peter Breuer. Foundations and measures of quantum non-markovianity. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 45(15):154001, 2012.
- [18] Á. Rivas, S. F. Huelga, and M. B. Plenio. Quantum Non-Markovianity: Characterization, Quantification and Detection. *arXiv/quant-ph*, 1405.0303, May 2014.
- [19] L Diosi and WT Strunz. The non-Markovian stochastic Schrodinger equation for open systems. *Physics Letters A*, 235(6):569–573, 1997.
- [20] Jan Roden, Alexander Eisfeld, Wolfgang Wolff, and Walter T. Strunz. Influence of complex exciton-phonon coupling on optical absorption and energy transfer of quantum aggregates. *Physical Review Letters*, 103:058301, Jul 2009.

- [21] Jan Roden, Walter T. Strunz, and Alexander Eisfeld. Non-markovian quantum state diffusion for absorption spectra of molecular aggregates. *The Journal of Chemical Physics*, 134(3):034902, 2011.
- [22] A. Fruchtmann, B. W. Lovett, S. C. Benjamin, and E. M. Gauger. Quantum dynamics in a hierarchical non-Markovian environment. *arXiv/quant-ph*, 1406.0468, 2014.
- [23] R. P. Feynman and F. L. Vernon. The theory of a general quantum system interacting with a linear dissipative system. *Annals of Physics*, 24(1):118–173, 1963.
- [24] N. Makri and D. E. Makarov. Tensor propagator for iterative quantum time evolution of reduced density matrices. I. Theory. *The Journal of Chemical Physics*, 102(11):4600–4610, 1995.
- [25] N. Makri and D. E. Makarov. Tensor propagator for iterative quantum time evolution of reduced density matrices. II. Numerical methodology. *The Journal of Chemical Physics*, 102(11):4611–4618, 1995.
- [26] P. Nalbach, A. Ishizaki, G. R. Fleming, and M. Thorwart. Iterative path-integral algorithm versus cumulant time-nonlocal master equation approach for dissipative biomolecular exciton transport. *New Journal of Physics*, 13:063040, 2011.
- [27] A. Ishizaki and G. R. Fleming. Theoretical examination of quantum coherence in a photosynthetic system at physiological temperature. *Proceedings of the National Academy of Sciences of the United States of America*, 106(41):17255–17260, 2009.
- [28] A. Ishizaki and G. R. Fleming. Unified treatment of quantum coherent and incoherent hopping dynamics in electronic energy transfer: Reduced hierarchy equation approach. *The Journal of Chemical Physics*, 130(23):234111, 2009.
- [29] M. Tanaka and Y. Tanimura. Multistate electron transfer dynamics in the condensed phase: Exact calculations from the reduced hierarchy equations of motion approach. *The Journal of Chemical Physics*, 132(21):214502, 2010.
- [30] J. Prior, A. W. Chin, S. F. Huelga, and M. B. Plenio. Efficient simulation of strong system-environment interactions. *Physical Review Letters*, 105:050404, 2010.

- [31] J. M. Dominy, A. Shabani, and D. A. Lidar. A general framework for complete positivity. *arXiv/quant-ph*, 1312.0908, 2013.
- [32] Aharon Brodutch, Animesh Datta, Kavan Modi, Ángel Rivas, and César A. Rodríguez-Rosario. Vanishing quantum discord is not necessary for completely positive maps. *Physical Review A*, 87:042301, 2013.
- [33] Kavan Modi, César A. Rodríguez-Rosario, and Alán Aspuru-Guzik. Positivity in the presence of initial system-environment correlation. *Physical Review A*, 86:064102, 2012.
- [34] K Kraus. General state changes in quantum theory. *Annals of Physics*, 64(2):311 – 335, 1971.
- [35] G. Lindblad. On the generators of quantum dynamical semigroups. *Communications in Mathematical Physics*, 48(2):119–130, 1976.
- [36] Vittorio Gorini, Andrzej Kossakowski, and E. C. G. Sudarshan. Completely positive dynamical semigroups of N-level systems. *Journal of Mathematical Physics*, 17(5):821–825, 1976.
- [37] Sadao Nakajima. On quantum theory of transport phenomena: Steady diffusion. *Progress of Theoretical Physics*, 20(6):948–959, 1958.
- [38] Robert Zwanzig. Ensemble method in the theory of irreversibility. *The Journal of Chemical Physics*, 33(5):1338–1341, 1960.
- [39] Klaus Capelle. A bird’s-eye view of density-functional theory. *Brazilian Journal of Physics*, 36:1318 – 1343, 2006.
- [40] J. D. Whitfield, M.-H. Yung, D. G. Tempel, S. Boixo, and A. Aspuru-Guzik. Computational complexity of time-dependent density functional theory. *arXiv/quant-ph*, 1310.1428, 2013.
- [41] Abraham Nitzan. *Chemical Dynamics in Condensed Phases: Relaxation, Transfer and Reactions in Condensed Molecular Systems*. Oxford University Press, 2006.
- [42] J Kempe. Quantum random walks: An introductory overview. *Contemporary Physics*, 44(4):307–327, 2003.

- [43] Masoud Mohseni, Patrick Rebentrost, Seth Lloyd, and Alán Aspuru-Guzik. Environment-assisted quantum walks in photosynthetic energy transfer. *The Journal of Chemical Physics*, 129(17):174106, 2008.
- [44] F. Caruso, A. W. Chin, A. Datta, S. F. Huelga, and M. B. Plenio. Highly efficient energy excitation transfer in light-harvesting complexes: The fundamental role of noise-assisted transport. *The Journal of Chemical Physics*, 131(10):105106, 2009.
- [45] Torsten Scholak, Fernando de Melo, Thomas Wellens, Florian Mintert, and Andreas Buchleitner. Efficient and coherent excitation transfer across disordered molecular networks. *Physical Review E*, 83:021912, 2011.
- [46] A. J. Leggett, S. Chakravarty, A. T. Dorsey, Matthew P. A. Fisher, Anupam Garg, and W. Zwerger. Dynamics of the dissipative two-state system. *Reviews of Modern Physics*, 59:1–85, 1987.
- [47] S. A. Crooker, J. A. Hollingsworth, S. Tretiak, and V. I. Klimov. Spectrally resolved dynamics of energy transfer in quantum-dot assemblies: Towards engineered energy flows in artificial materials. *Physical Review Letters*, 89:186802, 2002.
- [48] A. Nazir. Correlation-dependent coherent to incoherent transitions in resonant energy transfer dynamics. *Physical Review Letters*, 103:146404, 2009.
- [49] E. Rozbicki and P. Machnikowski. Quantum kinetic theory of phonon-assisted excitation transfer in quantum dot molecules. *Physical Review Letters*, 100:027401, 2009.
- [50] B. D. Gerardot, S. Strauf, M. J. A. de Dood, A. M. Bychkov, A. Badolato, K. Hennessy, E. L. Hu, D. Bouwmeester, and P. M. Petroff. Photon statistics from coupled quantum dots. *Physical Review Letters*, 95:137403, 2005.
- [51] A. Klein, M. Bruderer, S. R. Clark, and D. Jaksch. Dynamics, dephasing and clustering of impurity atoms in bose-einstein condensates. *New Journal of Physics*, 9(11):411, 2007.
- [52] G. S. Engel, T. R. Calhoun, E. L. Read, T-K. Ahn, T. Mancal, Y-C. Cheng, R. E. Blankenship, and G. R. Fleming. Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems. *Nature*, 446:782, 2007.

- [53] G. Panitchayangkoon, D. Hayes, K. A. Fransted, J. R. Caram, E. Harel, J. Wen, R. E. Blankenship, and G. S. Engel. Long-lived quantum coherence in photosynthetic complexes at physiological temperature. *Proceedings of the National Academy of Sciences of the United States of America*, 107:12766, 2010.
- [54] Y.-C. Cheng and G. R. Fleming. Dynamics of light harvesting in photosynthesis. *Annual Review of Physical Chemistry*, 60(241-62), 2009.
- [55] A. W. Chin, S. F. Huelga, and M. B. Plenio. Coherence and decoherence in biological systems: principles of noise-assisted transport and the origin of long-lived coherences. *Philosophical Transactions of the Royal Society A*, 370(1972):3638–3657, 2012.
- [56] D. Tronrud, J. Wen, L. Gay, and R. Blankenship. The structural basis for the difference in absorbance spectra for the FMO antenna protein from various green sulfur bacteria. *Photosynthetic Research*, 100:79–87, 2009.
- [57] G. Ritschel, J. Roden, W. T. Strunz, A. Aspuru-Guzik, and A. Eisfeld. Absence of quantum oscillations and dependence on site energies in electronic excitation transfer in the Fenna-Matthews-Olson trimer. *The Journal of Physical Chemistry Letters*, 2(22):2912–2917, 2011.
- [58] C. Olbrich, T. L. C. Jansen, J. Liebers, M. Aghtar, J. Strümpfer, K. Schulten, J. Knoester, and U. Kleinekathöfer. From atomistic modeling to excitation transfer and two-dimensional spectra of the FMO light-harvesting complex. *The Journal of Physical Chemistry B*, 115(26):8609–8621, 2011.
- [59] Th. Renger and V. May. Ultrafast exciton motion in photosynthetic antenna systems: The FMO-complex. *The Journal of Physical Chemistry A*, 102:4381, 1998.
- [60] M. Mohseni, P. Rebentrost, S. Lloyd, and A. Aspuru-Guzik. Environment-assisted quantum walks in photosynthetic energy transfer. *The Journal of Chemical Physics*, 129:174106, 2008.
- [61] M B Plenio and S F Huelga. Dephasing-assisted transport: quantum networks and biomolecules. *New Journal of Physics*, 10(11):113019, 2008.
- [62] G. D. Scholes and G. R. Fleming. *Energy Transfer and Photosynthetic Light Harvesting*, pages 57–129. John Wiley & Sons, Inc., 2005.

- [63] R. Dorner, J. Goold, L. Heaney, T. Farrow, P.-G. Roberts, J. Hirst, and V. Vedral. Quantum coherent contributions in biological electron transfer. *arXiv/q-bio.BM*, 1111.1646, 2011.
- [64] T. Ritz, S. Adem, and K. Schulten. A model for photoreceptor-based magnetoreception in birds. *Biophysical Journal*, 78(2):707–18, 2000.
- [65] E. M. Gauger, E. Rieper, J. J. L. Morton, S. C. Benjamin, and V. Vedral. Sustained quantum coherence and entanglement in the avian compass. *Physical Review Letters*, 106:040503, 2011.
- [66] C. H. Fleming and N. I. Cummings. Accuracy of perturbative master equations. *Physical Review E*, 83:031117, 2011.
- [67] T. Holstein. Studies of polaron motion: Part I. the molecular-crystal model. *Annals of Physics*, 8(3):325 – 342, 1959.
- [68] T. Holstein. Studies of polaron motion: Part II. the “small” polaron. *Annals of Physics*, 8(3):343 – 389, 1959.
- [69] B. Jackson and R. Silbey. On the calculation of transfer rates between impurity states in solids. *The Journal of Chemical Physics*, 78(6):4193–4196, 1983.
- [70] D. P. S. McCutcheon and A. Nazir. Quantum dot rabi rotations beyond the weak exciton-phonon coupling regime. *New Journal of Physics*, 12(11):113042, 2010.
- [71] D. P. S. McCutcheon and A. Nazir. Coherent and incoherent dynamics in excitonic energy transfer: Correlated fluctuations and off-resonance effects. *Physical Review B*, 83:165101, 2011.
- [72] S. Jang, Y.-C. Cheng, D. R. Reichman, and J. D. Eaves. Theory of coherent resonance energy transfer. *The Journal of Chemical Physics*, 129(10):101104, 2008.
- [73] S. Jang. Theory of coherent resonance energy transfer for coherent initial condition. *The Journal of Chemical Physics*, 131:164101, 2009.
- [74] S. Jang. Theory of multichromophoric coherent resonance energy transfer: A polaronic quantum master equation approach. *The Journal of Chemical Physics*, 135(3):034105, 2011.

- [75] A. Kolli, A. Nazir, and A. Olaya-Castro. Electronic excitation dynamics in multichromophoric systems described via a polaron-representation master equation. *The Journal of Chemical Physics*, 135(15), 2011.
- [76] R. Silbey and R. A. Harris. Variational calculation of the dynamics of a two level system interacting with a bath. *The Journal of Chemical Physics*, 80(6):2615–2617, 1984.
- [77] R. A. Harris and R. Silbey. Variational calculation of the tunneling system interacting with a heat bath. II. dynamics of an asymmetric tunneling system. *The Journal of Chemical Physics*, 83(3):1069–1074, 1985.
- [78] D. P. S. McCutcheon, N. S. Dattani, E. M. Gauger, B. W. Lovett, and A. Nazir. A general approach to quantum dynamics using a variational master equation: Application to phonon-damped rabi rotations in quantum dots. *Physical Review B*, 84:081305, 2011.
- [79] D. P. S. McCutcheon and A. Nazir. Consistent treatment of coherent and incoherent energy transfer dynamics using a variational master equation. *The Journal of Chemical Physics*, 135(11):114501, 2011.
- [80] A. Nazir, D. P. S. McCutcheon, and A. W. Chin. Ground state and dynamics of the biased dissipative two-state system: Beyond variational polaron theory. *Physical Review B*, 85:224301, 2012.
- [81] E. Zimanyi and R. Silbey. Theoretical description of quantum effects in multichromophoric aggregates. *Philosophical Transactions of the Royal Society A*, 370:3620, 2012.
- [82] C. K. Lee, J. Moix, and J. Cao. Accuracy of second order perturbation theory in the polaron and variational polaron frames. *The Journal of Chemical Physics*, 136(20):204120, 2012.
- [83] T. M. Stace, A. C. Doherty, and S. D. Barrett. Population inversion of a driven two-level system in a structureless bath. *Physical Review Letters*, 95:106801, 2005.
- [84] C. Olbrich, J. Strümpfer, K. Schulten, and U. Kleinekathöfer. Quest for spatially correlated fluctuations in the FMO light-harvesting complex. *The Journal of Physical Chemistry B*, 115(4):758–764, 2011.

- [85] Patrick Rebentrost, Masoud Mohseni, and Alán Aspuru-Guzik. Role of quantum coherence and environmental fluctuations in chromophoric energy transport. *The Journal of Physical Chemistry B*, 113(29):9942–9947, 2009.
- [86] Francesca Fassioli, Ahsan Nazir, and Alexandra Olaya-Castro. Quantum state tuning of energy transfer in a correlated environment. *The Journal of Physical Chemistry Letters*, 1(14):2139–2143, 2010.
- [87] Mohan Sarovar, Yuan-Chung Cheng, and K. Birgitta Whaley. Environmental correlation effects on excitation energy transfer in photosynthetic light harvesting. *Physical Review E*, 83:011906, 2011.
- [88] Kenley M Pelzer, Andrew F Fidler, Graham B Griffin, Stephen K Gray, and Gregory S Engel. The dependence of exciton transport efficiency on spatial patterns of correlation within the spectral bath. *New Journal of Physics*, 15(9):095019, 2013.
- [89] Roy J. Glauber. Coherent and incoherent states of the radiation field. *Physical Review*, 131:2766–2788, 1963.
- [90] J. J. Binney, N. J. Dowrick, A. J. Fisher, and M. E. J. Newman. *The Theory of Critical Phenomena*. Oxford Science Publications, 1992.
- [91] P. Nalbach, D. Braun, and M. Thorwart. Exciton transfer dynamics and quantumness of energy transfer in the Fenna-Matthews-Olson complex. *Physical Review E*, 84:041926, 2011.
- [92] Timothy C. Berkelbach, David R. Reichman, and Thomas E. Markland. Reduced density matrix hybrid approach: An efficient and accurate method for adiabatic and non-adiabatic quantum dynamics. *The Journal of Chemical Physics*, 136(3):034113, 2012.
- [93] Timothy C. Berkelbach, Thomas E. Markland, and David R. Reichman. Reduced density matrix hybrid approach: Application to electronic energy transfer. *The Journal of Chemical Physics*, 136(8):084104, 2012.
- [94] J. Iles-Smith, N. Lambert, and A. Nazir. Environmental dynamics, correlations, and the emergence of noncanonical equilibrium states in open quantum systems. *arXiv/quant-ph*, 1311.0016, 2013.

- [95] S. Jesenko and M. Žnidarič. Excitation energy transfer rates: comparison of approximate methods to the exact solution. *arXiv/physics.chem-ph*, 1405.4156, 2014.
- [96] A. W. Chin and M. Turlakov. Coherent-incoherent transition in the sub-ohmic spin-boson model. *Physical Review B*, 73:075311, 2006.
- [97] R. J. Schoelkopf and S. M. Girvin. Wiring up quantum systems. *Nature*, 451(7179):664–669, 2008.
- [98] M. H. Devoret and R. J. Schoelkopf. Superconducting circuits for quantum information: An outlook. *Science*, 339(6124):1169–1174, 2013.
- [99] Jonas Zmuidzinas. Superconducting microresonators: Physics and applications. *Annual Review of Condensed Matter Physics*, 3(1):169–214, 2012.
- [100] Samuel L. Braunstein and Peter van Loock. Quantum information with continuous variables. *Reviews of Modern Physics*, 77:513–577, 2005.
- [101] M. H. Devoret, A. Wallraff, and J. M. Martinis. Superconducting Qubits: A Short Review. *arXiv/cond-mat*, 0411174, 2004.
- [102] J. Männik and J. E. Lukens. Effect of measurement on the periodicity of the coulomb staircase of a superconducting box. *Physical Review Letters*, 92:057004, 2004.
- [103] A. J. Ferguson, N. A. Court, F. E. Hudson, and R. G. Clark. Microsecond resolution of quasiparticle tunneling in the single-cooper-pair transistor. *Physical Review Letters*, 97:106603, 2006.
- [104] N. A. Court, A. J. Ferguson, Roman Lutchyn, and R. G. Clark. Quantitative study of quasiparticle traps using the single-cooper-pair transistor. *Physical Review B*, 77:100501, 2008.
- [105] L. Sun, L. DiCarlo, M. D. Reed, G. Catelani, Lev S. Bishop, D. I. Schuster, B. R. Johnson, Ge A. Yang, L. Frunzio, L. Glazman, M. H. Devoret, and R. J. Schoelkopf. Measurements of quasiparticle tunneling dynamics in a band-gap-engineered transmon qubit. *Physical Review Letters*, 108:230509, 2012.
- [106] Juha Leppäkangas and Michael Marthaler. Fragility of flux qubits against quasiparticle tunneling. *Physical Review B*, 85:144503, 2012.

- [107] M. Lenander, H. Wang, Radoslaw C. Bialczak, Erik Lucero, Matteo Mariantoni, M. Neeley, A. D. O’Connell, D. Sank, M. Weides, J. Wenner, T. Yamamoto, Y. Yin, J. Zhao, A. N. Cleland, and John M. Martinis. Measurement of energy decay in superconducting qubits from nonequilibrium quasiparticles. *Physical Review B*, 84:024501, 2011.
- [108] V. F. Maisi, S. V. Lotkhov, A. Kemppinen, A. Heimes, J. T. Muhonen, and J. P. Pekola. Single quasiparticle excitation dynamics on a superconducting island. *arXiv/cond-mat.supr-con*, 1212.2755, 2012.
- [109] J. Bardeen, L. N. Cooper, and J. R. Schrieffer. Theory of superconductivity. *Physical Review*, 108:1175–1204, 1957.
- [110] James F. Annett. *Superconductivity, Superfluids, and Condensates*. Oxford University Press, first edition, 2004.
- [111] Charles Kittel. *Introduction to Solid State Physics*. Wiley, 8th edition, 2004.
- [112] Michael Tinkham. *The Theory of Superconductivity*. Dover Publications, second edition, 2004.
- [113] F. W. J. Hekking and Yu. V. Nazarov. Subgap conductivity of a superconductor–normal-metal tunnel interface. *Physical Review B*, 49:6847–6852, 1994.
- [114] Gert-Ludwig Ingold and Yu.V. Nazarov. Charge tunneling rates in ultrasmall junctions. In *Single Charge Tunneling*, volume 294 of *NATO ASI Series*, pages 21–107. Springer US, 1992.
- [115] B.D. Josephson. Possible new effects in superconductive tunnelling. *Physics Letters*, 1(7):251 – 253, 1962.
- [116] John M. Martinis. Course 13: Superconducting qubits and the physics of Josephson junctions. In *Quantum Entanglement and Information Processing École d’ été de Physique des Houches Session LXXIX*, volume 79 of *Les Houches*, pages 487 – 520. Elsevier, 2004.
- [117] R. C. Dynes, V. Narayanamurti, and J. P. Garno. Direct measurement of quasiparticle-lifetime broadening in a strong-coupled superconductor. *Physical Review Letters*, 41:1509–1512, 1978.

- [118] R. C. Dynes, J. P. Garno, G. B. Hertel, and T. P. Orlando. Tunneling study of superconductivity near the metal-insulator transition. *Physical Review Letters*, 53:2437–2440, Dec 1984.
- [119] Božidar Mitrović and Lee A Rozema. On the correct formula for the lifetime broadened superconducting density of states. *Journal of Physics: Condensed Matter*, 20(1):015215, 2008.
- [120] W. G. van der Wiel, S. De Franceschi, J. M. Elzerman, T. Fujisawa, S. Tarucha, and L. P. Kouwenhoven. Electron transport through double quantum dots. *Reviews of Modern Physics*, 75:1–22, 2002.
- [121] T. Duty, G. Johansson, K. Bladh, D. Gunnarsson, C. Wilson, and P. Delsing. Observation of quantum capacitance in the cooper-pair transistor. *Physical Review Letters*, 95:206807, 2005.
- [122] K. D. Petersson, C. G. Smith, D. Anderson, P. Atkinson, G. A. C. Jones, and D. A. Ritchie. Charge and spin state readout of a double quantum dot coupled to a resonator. *Nano Letters*, 10(8):2789–2793, 2010.
- [123] G. E. Blonder, M. Tinkham, and T. M. Klapwijk. Transition from metallic to tunneling regimes in superconducting microconstrictions: Excess current, charge imbalance, and supercurrent conversion. *Physical Review B*, 25:4515–4532, 1982.
- [124] V. Palenskis. Drift mobility, diffusion coefficient of randomly moving charge carriers in metals and other materials with degenerated electron gas. *World Journal of Condensed Matter Physics*, 3:73–81, 2013.
- [125] F. W. J. Hekking and Yu. V. Nazarov. Interference of two electrons entering a superconductor. *Physical Review Letters*, 71:1625–1628, 1993.
- [126] P. Lafarge and D. Esteve. Nondivergent calculation of unwanted high-order tunneling rates in single-electron devices. *Physical Review B*, 48:14309–14317, 1993.
- [127] Herbert Schoeller and Gerd Schön. Mesoscopic quantum transport: Resonant tunneling in the presence of a strong coulomb interaction. *Physical Review B*, 50:18436–18452, 1994.

- [128] Heinz-Olaf Müller, Ulrik Hanke, and K A Chao. The influence of incoherent co-tunnelling on single-electron-tunnelling thermometry. *Journal of Physics: Condensed Matter*, 9(3):685, 1997.
- [129] Y. de Wilde, T.M. Klapwijk, A.G.M. Jansen, J. Heil, and P. Wyder. Quasi-particle lifetime broadening in normal-superconductor junctions with {UPt3}. *Physica B: Condensed Matter*, 218(1-4):165 – 168, 1996.
- [130] Leonard Kleinman. Theory of phonon-assisted tunneling in superconductors. *Physical Review*, 132:2484–2489, 1963.
- [131] J. M. Martinis. Quasiparticle tunneling: P(E) theory. *arXiv/cond-mat.mes-hal*, 0904.2035, 2009.
- [132] J. P. Pekola, V. F. Maisi, S. Kafanov, N. Chekurov, A. Kemppinen, Yu. A. Pashkin, O.-P. Saira, M. Möttönen, and J. S. Tsai. Environment-assisted tunneling as an origin of the dynes density of states. *Physical Review Letters*, 105:026803, 2010.
- [133] J.J. Hesse and G. Diener. Andreev reflection in ultrasmall {NSN}-devices with electromagnetic environment. *Physica B: Condensed Matter*, 203(3-4):393 – 396, 1994.
- [134] J. R. Norris. *Markov Chains*. Cambridge University Press, first edition, 1997.
- [135] J. M. Fink, L. Steffen, P. Studer, Lev S. Bishop, M. Baur, R. Bianchetti, D. Bozyigit, C. Lang, S. Filipp, P. J. Leek, and A. Wallraff. Quantum-to-classical transition in cavity quantum electrodynamics. *Physical Review Letters*, 105:163601, 2010.
- [136] Anupam Garg, José Nelson Onuchic, and Vinay Ambegaokar. Effect of friction on electron transfer in biomolecules. *The Journal of Chemical Physics*, 83:4491, 1985.
- [137] C. Olbrich, J. Strümpfer, K. Schulten, and U. Kleinekathöfer. Theory and simulation of the environmental effects on FMO electronic transitions. *The Journal of Physical Chemistry Letters*, 2:1771, 2011.
- [138] Sangwoo Shim, Patrick Rebentrost, Stéphanie Valteau, and Alán Aspuru-Guzik. Atomistic study of the long-lived quantum coherences in the Fenna-Matthews-Olson complex. *Biophysical Journal*, 102:649, 2012.

- [139] Marco del Rey, Alex W. Chin, Susana F. Huelga, and Martin B. Plenio. Exploiting structured environments for efficient energy transfer: The phonon antenna mechanism. *The Journal of Physical Chemistry Letters*, 4(6):903–907, 2013.
- [140] A. W. Chin, J. Prior, R. Rosenbach, F. Caycedo-Soler, S. F. Huelga, and M. B. Plenio. The role of non-equilibrium vibrational structures in electronic coherence and recoherence in pigment-protein complexes. *Nature Physics*, 9(2):113–118, 2013.
- [141] Edward J. O’Reilly and Alexandra Olaya-Castro. Non-classicality of the molecular vibrations assisting exciton energy transfer at room temperature. *Nature Communications*, 5:2041–1723, 2014.
- [142] E. K. Irish, R. Gómez-Bombarelli, and B. W. Lovett. Vibration-assisted resonance in photosynthetic excitation energy transfer. *arXiv/physics.bio-ph*, 1306.6650, June 2013.
- [143] G. Ritschel, J. Roden, W. T. Strunz, and A. Eisfeld. An efficient method to calculate excitation energy transfer in light-harvesting systems: application to the Fenna-Matthews-Olson complex. *New Journal of Physics*, 13:113034, 2011.
- [144] James Lim, Mark Tame, Ki Hyuk Yee, Joong-Sung Lee, and Jinhyoung Lee. Phonon-induced dynamic resonance energy transfer. *New Journal of Physics*, 16(5):053018, 2014.
- [145] A. Kolli, E. J. O’Reilly, G. D. Scholes, and A. Olaya-Castro. The fundamental role of quantized vibrations in coherent light harvesting by cryptophyte algae. *The Journal of Chemical Physics*, 137:174109, 2012.
- [146] Niklas Christensson, Harald F. Kauffmann, T. Pullerits, and Tomas Mančal. Origin of long-lived coherences in light-harvesting complexes. *The Journal of Physical Chemistry B*, 116:7449, 2012.
- [147] Aurélia Chenu, Niklas Christensson, Harald F. Kauffmann, and Tomas Mančal. Enhancement of vibronic and ground-state vibrational coherences in 2D spectra of photosynthetic complexes. *Scientific Reports*, 3:2029, 2013.
- [148] Luca Turin. A spectroscopic mechanism for primary olfactory reception. *Chemical Senses*, 21(6):773–791, 1996.

- [149] Luca Turin. A method for the calculation of odor character from molecular structure. *Journal of Theoretical Biology*, 216(3):367–385, 2002.
- [150] Andreas Keller and Leslie B. Vosshall. A psychophysical test of the vibration theory of olfaction. *Nature Neuroscience*, 7(4):337–338, 2004.
- [151] Jennifer C. Brookes, Filio Hartoutsiou, A. P. Horsfield, and A. M. Stoneham. Could humans recognize odor by phonon assisted tunneling? *Physical Review Letters*, 98(3):038101, 2007.
- [152] Thomas P. Hettinger. Olfaction is a chemical sense, not a spectral sense. *Proceedings of the National Academy of Sciences of the United States of America*, 108(31):E349–E349, 2011.
- [153] Maria Isabel Franco, Luca Turin, Andreas Mershin, and Efthimios M. C. Skoulakis. Molecular vibration-sensing component in drosophila melanogaster olfaction. *Proceedings of the National Academy of Sciences of the United States of America*, 108(9):3797–3802, 2011.
- [154] Ilia A. Solov’yov, Po-Yao Chang, and Klaus Schulten. Vibrationally assisted electron transfer mechanism of olfaction: myth or reality? *Physical Chemistry Chemical Physics*, 14(40):13861–13871, 2012.
- [155] Peter Kovacic. Mechanism of smell: Electrochemistry, receptors and cell signaling. *Journal of Electrostatics*, 70(1):1–6, 2012.
- [156] Eric R. Bittner, Adrian Madalan, Arkadiusz Czader, and Gregg Roman. Quantum origins of molecular recognition and olfaction in drosophila. *The Journal of Chemical Physics*, 137(22):22A551, 2012.
- [157] Simon Gane, Dimitris Georganakis, Klio Maniati, Manolis Vamvakias, Nikitas Ragoussis, Efthimios M. C. Skoulakis, and Luca Turin. Molecular vibration-sensing component in human olfaction. *PLoS ONE*, 8(1):e55780, 2013.
- [158] David J Rowe. *Chemistry and technology of flavors and fragrances*. Blackwell Publishing Ltd, 2005.
- [159] Richard Axel. Scents and sensibility: A molecular logic of olfactory perception. *Angewandte Chemie International Edition*, 44(38):6110–6127, 2005.

- [160] Linda B. Buck. Unraveling the sense of smell (nobel lecture). *Angew. Chem. Int. Ed.*, 44(38):6128–6140, 2005.
- [161] Sang Hun Lee, Oh Seok Kwon, Hyun Seok Song, Seon Joo Park, Jong Hwan Sung, Jyongsik Jang, and Tai Hyun Park. Mimicking the human smell sensing mechanism with an artificial nose platform. *Biomaterials*, 33(6):1722–1729, 2012.
- [162] R. H. Farahi, A. Passian, L. Tetard, and T. Thundat. Critical issues in sensor science to aid food and water safety. *ACS Nano*, 6(6):4548–4556, 2012.
- [163] Richard B. Silverman. *The Organic Chemistry of Enzyme-catalyzed Reactions*. Academic Press, 2002.
- [164] L.J.W Haffenden, V.A Yaylayan, and J Fortin. Investigation of vibrational theory of olfaction with variously labelled benzaldehydes. *Food Chemistry*, 73(1):67–72, 2001.
- [165] G. M. Dyson. The scientific basis of odour. *Chemistry and Industry.*, 57:647–651, 1938.
- [166] R H Wright. Odor and molecular vibration: neural coding of olfactory information. *Journal of Theoretical Biology*, 64(3):473–502, 1977.
- [167] R. H Wright. *The sense of smell*. CRC Press, 1982.
- [168] J. Lambe and R. C. Jaklevic. Molecular vibration spectra by inelastic electron tunneling. *Physical Review*, 165(3):821–832, 1968.
- [169] C. J. Adkins and W. A. Phillips. Inelastic electron tunnelling spectroscopy. *Journal of Physics C*, 18(7):1313, 1985.
- [170] R. A. Marcus. On the theory of Oxidation-Reduction reactions involving electron transfer. I. *The Journal of Chemical Physics*, 24(5):966–978, 1956.
- [171] R A Marcus. Chemical and electrochemical electron-transfer theory. *Annual Review of Physical Chemistry*, 15(1):155–196, 1964.
- [172] R. A. Marcus. On the theory of Electron-Transfer reactions. VI. unified treatment for homogeneous and electrode reactions. *The Journal of Chemical Physics*, 43(2):679–701, 1965.

- [173] R.A. Marcus and Norman Sutin. Electron transfers in chemistry and biology. *Biochimica et Biophysica Acta - Bioenergetics*, 811(3):265–322, 1985.
- [174] M. Bixon and Joshua Jortner. Electron transfer - from isolated molecules to biomolecules. *Advances in Chemical Physics*, 106:35–202, 1999.
- [175] Linda Buck and Richard Axel. A novel multigene family may encode odorant receptors: A molecular basis for odor recognition. *Cell*, 65(1):175–187, 1991.
- [176] Harry B. Gray and Jay R. Winkler. Electron flow through metalloproteins. *Biochimica et Biophysica Acta - Bioenergetics*, 1797(9):1563 – 1572, 2010.
- [177] Jiangyun Wang, Zaida A. Luthey-Schulten, and Kenneth S. Suslick. Is the olfactory receptor a metalloprotein? *Proceedings of the National Academy of Sciences of the United States of America*, 100(6):3035–3039, 2003.
- [178] Xufang Duan, Eric Block, Zhen Li, Timothy Connelly, Jian Zhang, Zhimin Huang, Xubo Su, Yi Pan, Lifang Wu, Qiuyi Chi, Siji Thomas, Shaozhong Zhang, Minghong Ma, Hiroaki Matsunami, Guo-Qiang Chen, and Hanyi Zhuang. Crucial role of copper in detection of metal-coordinating odorants. *Proceedings of the National Academy of Sciences of the United States of America*, 109(9):3492–3497, 2012.
- [179] H J Carmichael and D F Walls. Master equation for strongly interacting systems. *Journal of Physics A: Mathematical, Nuclear and General*, 6(10):1552, 1973.
- [180] Laura G. Remus and Miles P. Blencowe. Damping and decoherence of fock states in a nanomechanical resonator due to two-level systems. *Physical Review B*, 86(20):205419, 2012.
- [181] Neill Lambert and Franco Nori. Detecting quantum-coherent nanomechanical oscillations using the current-noise spectrum of a double quantum dot. *Physical Review B*, 78:214302, 2008.
- [182] A. D. Armour and M. P. Blencowe. Probing the quantum coherence of a nanomechanical resonator using a superconducting qubit: I. echo scheme. *New Journal of Physics*, 10(9):095004, 2008.

- [183] M P Blencowe and A D Armour. Probing the quantum coherence of a nanomechanical resonator using a superconducting qubit: Ii. implementation. *New Journal of Physics*, 10(9):095005, 2008.
- [184] D. Xu and K. Schulten. Coupling of protein motion to electron transfer in a photosynthetic reaction center: investigating the low temperature behavior in the framework of the spin-boson model. *Chemical Physics*, 182:91, 1994.
- [185] Robert E Blankenship. *Molecular mechanisms of photosynthesis*. Blackwell Science, 2002.
- [186] Sang Hun Lee, Hye Jun Jin, Hyun Seok Song, Seunghun Hong, and Tai Hyun Park. Bioelectronic nose with high sensitivity and selectivity using chemically functionalized carbon nanotube combined with human olfactory receptor. *Journal of Biotechnology*, 157(4):467–472, 2012.
- [187] Liping Du, Chunsheng Wu, Qingjun Liu, Liquan Huang, and Ping Wang. Recent advances in olfactory receptor-based biosensors. *Biosensors and Bioelectronics*, 42:570–580, 2013.