Algorithms and Platforms for
Quantum Science and Technology

A dissertation presented
by

DOMINIK SEBASTIAN WILD

to
The Department of Physics
in partial fulfillment of the requirements
for the degree of
Doctor of Philosophy
in the subject of
Physics

Harvard University
Cambridge, Massachusetts
April 2020
Algorithms and Platforms for
Quantum Science and Technology

Abstract

The field of quantum science and technology has seen tremendous recent progress. Despite this, building large-scale quantum devices remains daunting as fault tolerance is a distant goal in all current experimental platforms. This dissertation discusses two complementary avenues towards practically relevant quantum technologies.

In the first part, we explore physically inspired quantum algorithms that run on near-term devices without quantum error correction. We investigate the robustness of adiabatic quantum algorithms, placing stringent requirements on noise induced by the environment. In addition, we construct quantum algorithms that sample from classical Gibbs distributions. These algorithms elucidate connections between computational complexity and phase transitions and provide physical insight into the origin of quantum speedup.

The second part focuses on novel platforms and optical interfaces for quantum applications. We demonstrate that optical resonances in ordered arrays of atoms and atomically thin semiconductors offer a powerful tool to control and manipulate light at both the classical and single-photon level. We further study interactions between optical excitations and charge carriers in two-dimensional semiconductors, which give rise to complex quantum many-body dynamics in a largely unexplored regime.
Contents

Acknowledgments .................................................. viii
Citations to previously published work ....................... xii

1 Introduction .................................................... 1
  1.1 Background .................................................. 1
  1.2 Overview of this dissertation ............................... 5

2 Adiabatic quantum computing in the presence of noise .... 8
  2.1 Introduction .................................................. 8
  2.2 Summary of results ......................................... 10
  2.3 Model .......................................................... 13
    2.3.1 Closed system .......................................... 13
    2.3.2 Environment ........................................... 14
  2.4 Renormalized tunneling rate ................................ 15
    2.4.1 Single-boson processes .............................. 15
    2.4.2 Two-boson processes ............................... 18
  2.5 Outlook ..................................................... 20

3 Quantum sampling algorithms for near-term devices ... 22
  3.1 Introduction .................................................. 22
  3.2 Parent Hamiltonian ......................................... 25
  3.3 Sampling from the 1D Ising model ......................... 26
  3.4 Weighted independent set problem ......................... 32
    3.4.1 Chain graph .......................................... 35
    3.4.2 Star graph ........................................... 37
  3.5 Outlook ..................................................... 39

4 Light–matter interaction .................................... 41
  4.1 Introduction .................................................. 41
  4.2 Classical Green’s function formalism ...................... 42
    4.2.1 One classical dipole ................................ 42
4.2.2 Many classical dipoles .............................................. 47
4.3 Quantum formalism .................................................. 48

5 Ordered arrays of atoms ............................................. 57
5.1 Band structure ....................................................... 57
5.2 Reflection and transmission ....................................... 63
5.3 Deterministic interaction with a single atom ................. 68

6 Two-dimensional semiconductors .................................. 74
6.1 Introduction .......................................................... 74
6.2 Excitons .............................................................. 75
6.3 Transition metal dichalcogenide monolayers .................. 81
   6.3.1 Basic properties .............................................. 81
   6.3.2 Selection rules ............................................... 82
6.4 Reflection spectrum ............................................... 87

7 Quantum nonlinear optics in atomically thin materials ...... 95
7.1 Introduction .......................................................... 95
7.2 Linear response ..................................................... 98
7.3 Quantum nonlinear response ..................................... 101
7.4 Antibunching ....................................................... 104
7.5 Experimental parameters ......................................... 107
7.6 Outlook ............................................................. 108

8 Rotons in optical excitation spectra of monolayer semicon-
ductors ........................................................................... 110
8.1 Introduction .......................................................... 110
8.2 Exciton dispersion ................................................... 112
8.3 Polaron formation .................................................... 117
8.4 Optical spectra ....................................................... 120
8.5 Outlook ............................................................. 122

A Supporting material for Chapter 2 ................................. 124
A.1 Derivation of the effective Hamiltonian ......................... 124
A.2 Adiabatic renormalization ......................................... 132
   A.2.1 Single-boson processes ....................................... 134
   A.2.2 Two-boson processes ......................................... 138
   A.2.3 Combined effects ............................................. 141
A.3 Thermalization rates ............................................... 142
   A.3.1 Incoherent regime ............................................. 142
   A.3.2 Coherent regime .............................................. 144
A.4 Diagonalization of quadratic Hamiltonians .......................... 145

B Supporting material for Chapter 3 ...................................... 148
B.1 Upper bound on total variation distance ......................... 148
B.2 Ising chain .......................................................... 150
B.2.1 Parent Hamiltonian .............................................. 150
B.2.2 Free fermion solution ........................................... 151
B.2.3 Numerical details ............................................... 156
B.2.4 Adiabatic path length ......................................... 159
B.3 Weighted independent set problem ................................. 162
B.3.1 Parent Hamiltonian .............................................. 162
B.3.2 Chain graph .................................................... 163
B.3.3 Star graph ....................................................... 167

C Supporting material for Chapter 5 .................................... 174
C.1 Regularization of the Green’s function ......................... 174

D Supporting material for Chapter 6 .................................... 177
D.1 Selection rules ...................................................... 177
D.2 Transfer matrix method ........................................... 183

E Supporting material for Chapter 7 .................................... 186
E.1 Linear response ..................................................... 186
E.2 Heisenberg–Langevin equation ................................. 187
E.3 Photon statistics .................................................. 193
E.4 Anharmonic oscillator ........................................... 194
E.5 Pure dephasing ..................................................... 196

F Supporting material for Chapter 8 .................................... 198
F.1 Computational details ............................................. 198
F.2 Optical decay rates ............................................... 199

Bibliography ................................................................. 204
To my parents.
Acknowledgments

The past seven years have been an incredible experience. Incredibly challenging, incredibly rewarding, and incredibly fun. I have been fortunate to share this time with incredibly wonderful people.

First and foremost, I would like to thank Professor Mikhail Lukin for being a tremendous advisor and mentor, one who leads with patience and enthusiasm. Misha’s passion and deep desire to further science for the benefit of society will continue to inspire me. I am also indebted to the two other members of my committee, Professor Eugene Demler and Professor Philip Kim. Much of what I know about condensed matter physics and cold atoms comes from Eugene’s excellent courses. Philip allowed me to peek into the world of experimental condensed matter physics and I thank him for letting me collaborate with his group.

I am particularly grateful for Misha’s active encouragement of collaboration. From the very beginning, I had the privilege to learn from brilliant people, many of whom have become good friends. Professor Norman Yao—at the time not even Dr. Norm—took me under his wing and taught me among many other things how to get the most out of a meeting with Misha (be prepared). During my first research project, Michael Knap and Sarang Gopalakrishnan
turned a vague idea into a tangible research question. Ephraim Shahmoon taught me that much of what people call quantum optics is in fact classical but that makes it neither trivial nor less interesting. Hannes Pichler has been a well of wisdom for all matters quantum. Quantum skeptic extraordinaire Dries Sels convinced me that qubits should not be compared to classical bits. Richard Schmidt explained to me how polarons differ from trions. Janos Peczela helped me take my first steps with dipole–dipole interactions. I thank all of them for being so generous with their time.

I thank the groups who shared their research with me. Professor Susanne Yelin allowed me to join a number of her group’s projects, resulting most recently in a fruitful collaboration with Taylor Patti. Professor Ataç İmamoğlu hosted me at ETH Zurich to explore the world of polarons together with Ovidiu Cotlet. Professor Peter Zoller and Alexander Glaetzle let me contribute to their “spin lens” project. Professor Ignacio Cirac and Johannes Knörzer kindly considered my thoughts concerning optical readout of Wigner crystals. I am privileged to have had the opportunity to work with so many talented people.

An exceptionally exciting series of projects emerged from collaboration with experimental groups, in particular those of Professor Hongkun Park and Professor Philip Kim. I thank Alex High, You Zhou, Kristiaan de Greve, Luis Jauregui, Alan Dibos, Jiho Sung, Giovanni Scuri, Trond Andersen, Andrey Sushko, Ryan Gelly, Hyobin Yoo, Rob Devlin, and Kate Pistunova for sharing their data with me and for the stimulating discussions. I was constantly impressed by the ingenuity and hard work that went into each experiments.

I would like to extend a special thank you to Soonwon Choi, who was a
collaborator, companion, and confidant through most of graduate school. His creativity and keen observations, not to forget his shared love for topological lasers, helped me overcome numerous obstacles in research and beyond. I thank Ruffin Evans for being a close friend and the best officemate imaginable. We may never settle whether a yurt is a house, but my house plants have never been healthier. It has been a great pleasure to share many insightful and entertaining conversations with all other members of the Lukin group and the physics department, including Leo Zhou, Shiang Fang, Xun Gao, Sheng-Tao Wang, Wen Wei Ho, Valentin Walther, Harry Zhou, Rivka Bekenstein, Martin Schuetz, Péter Kómár, Johannes Borregaard, Iris Cong, Nathan Leitao, Emil Khabiboulline, Nishad Maskara, Maddie Cain, Bihui Zhu, Leigh Martin, Mihir Bhaskar, Alp Siphigil, Erik Knall, Elana Urbach, Bo Dwyer, David Levonian, Aditya Venkatramani, Alexei Bylinskii, Alex Keesling, Harry Levine, Tamara Dordevic, Tamara Sumarac, Christian Nguyen, Emma Rosenfeld, Joonhee Choi, Paloma Ocola, Arthur Safira, Jan Gieseler, Ahmed Omran, Ralf Riedinger, Po Samutpraphoot, Denis Sukachev, Georg Kucsko, Shimon Kolkowitz, Jeff Thompson, Nathalie de Leon, Javier Sanchez-Yamagishi, Alex Sushkov, Manuel Endres, Hannes Bernien, Renate Landig, Aavishkar Patel, Henry Wilkin, Christie Chiu, and Daniel Greif. I am also grateful to the competent and hard-working staff at the physics department, including Lisa Cacciaabando, Jacob Barandes, Samantha Dakoulas, Clare Ploucha, and Silke Exner.

I will remember my time in graduate school as much for the academic environment as for the memorable times spent away from work. I am lucky to have had great friends accompanying me on this journey. Several of them de-
serve a special mention. Matt was there from the beginning of this adventure. I hope we will one day turn our treasure chest of digital records into a rock opera. Michael’s excellent sense of humor and love of doughnuts and chicken wings filled many evenings with deliciousness and laughter. Louis helped me widen my horizon when it comes to beer, although I count it as my win when we shared PBR shandies on the Fourth of July. Neel’s informed opinions and great taste in music make him a great companion at any time of the day. I thank the rest of the “crew”, Rachel, Midas, Erin, Will, and Nick, for the fun times, from camping trips to kiddie pool parties. I am grateful to Sean for letting me view the world through a lens other than my own. I spent a significant portion of my non-working time climbing and much of that with Will. I could not wish for a better climber partner. I also thank Melinda for soft catches and all the members of the Harvard Mountaineering Club for many adventures. My friends in Europe supported me over the years even though we were separated by an ocean for most of the time. Notably, Ivan, Dave, Lukas, Sandro, and Mathias always warmly welcomed me back on me on my brief trips to Switzerland. Visar, Andrew, Jack, Simon, Matthieu, and Max did the same for me in London. Caroline helped me finish this thesis with excitement about the times ahead. Thank you.

Most importantly, I thank my family for their unconditional support. My parents, my brother, and my sister have always helped me accomplish my dreams and have encouraged me to follow my own path even if it meant moving to a city 6000 km away. This dissertation is dedicated to them.
Citations to previously published work

Chapter 2, in its entirety, has been published as


Chapter 3 forms the basis of a manuscript currently being prepared.

Elements of Chapter 5 have been published as


Elements of Chapter 6 have been published as


Chapter 7, in its entirety, has been published as


Chapter 8, in its entirety, has been published as

Chapter 1

Introduction

1.1 Background

The 20\textsuperscript{th} century was an age of scientific and technological revolution. The development of quantum mechanics in particular has had far reaching consequences. Despite its oft-noted “weirdness”, quantum mechanics has been tremendously successful at explaining the world surrounding us as well as at predicting previously undiscovered phenomena. For example, the newly gained understanding of materials enabled the development of the transistor, an essential component of the semiconductor chips now found in every electronic device. Yet, quantum mechanics is usually hidden from plain view. Once we take the correct functioning of transistors for granted—they essentially act as electrically controlled switches—we may forget about quantum mechanics and describe any process inside a conventional electronic device within the framework of classical physics.

It was not until the 1980s that someone asked what happens when the computation itself proceeds according to the laws of quantum mechanics. While
this question may seem obvious from a modern perspective, it required profound insight at a time when quantum mechanics and computer science resided in largely distinct corners of the academic world. In a now famous keynote speech at the 1st Conference on Physics and Computation at MIT, Richard Feynman argued that simulating the dynamics of a quantum system posed a formidable challenge for a classical computer [9]. At the same time, he showed that a computer that obeyed the laws of quantum mechanics could solve this problem efficiently.

Feynman’s results suggested a quantum speedup: It is now widely believed that quantum computers can perform certain tasks much more efficiently than classical computers. To compare the run time of algorithms independent of the detailed specifics of a particular implementation such as the clock speed of a CPU, computer scientists introduced the concept of time complexity. The time complexity of an algorithm tells us how the time required to solve a given problem depends on the input size. For instance, the time to find the prime factors of a number with \( d \) digits using the fastest known classical algorithm is roughly\(^1\) proportional \( \exp(\alpha d^{1/3}) \), where \( \alpha \) is an unimportant constant. Shor’s algorithm, a quantum algorithm constructed by Peter Shor in 1994 to solve the same problem, achieves a time complexity of \( d^2 \), representing a significant speedup [10]. Implementing Shor’s algorithm would constitute much more than a mathematical curiosity since many encryption protocols rely on the practical intractability of factoring large integers.

Why then, if these ideas date more than 25 years back, are we still not carrying quantum computers in our pockets? The main reason is that the

\(^1\)We ignore logarithmic corrections for both the classical and quantum time complexity.
quantum states required for computation are extremely fragile. The slightest interaction between the computer and an uncontrolled environment destroys the delicate quantum superpositions that enable a speedup over classical computers. The adverse effects of the environment can be mitigated by means of quantum error correction, whose practical overhead is however prohibitively high for current technology. State-of-the-art error correcting schemes require several millions of qubits, each of them still isolated from the environment to an exquisite degree, to implement Shor’s algorithm for a sufficiently large integer to break common encryption protocols [11]. This is a long way from the 10s to 100s of qubits available in cutting edge experiments that fill up entire laboratories [12–14].

It would be incorrect to conclude from the above discussion that we live in quantum computing stone age. Technology has developed at a staggering pace over the past years and we have entered an era which John Preskill has aptly described as NISQ: noisy, intermediate scale, quantum [15]. Noisy refers to the unavailability of quantum error correction, intermediate scale stands for 100 or so qubits, and quantum means, well, quantum. It may seem arbitrary to single out 100 qubits as a special number. The choice is motivated by the size of the systems whose dynamics can be simulated on classical computers in a sensible amount of time. While the exact numbers depend on the specific application, it is generally possible to simulate up to 20 qubits even on a laptop, 50 qubits can sometimes be simulated with heavy lifting by a supercomputer [16], while 100 qubits are well out of reach in most cases. Because the computation time depends exponentially on the number of qubits, we do not expect these numbers to dramatically change over the
coming years even as the power of classical computers continues to increase.

The existence of NISQ devices prompts the question whether there are problems that offer a quantum speedup without the need for error correction. The physicist’s answer to this question is yes, of course, the device can simulate its own evolution, which is intractable on a classical computer. This may seem almost tautological but this so-called quantum simulation is arguably the most significant current application of NISQ devices. The large degree of control available in NISQ devices allows us to study quantum many-body dynamics in a manner that is difficult to replicate in more natural settings as the properties of real materials cannot be modified at will. The insights gained are not only of academic interest but may lead to new technology by an improved understanding of phenomena such as high-temperature superconductivity [17–19]. The answer is less clear when considering computational tasks of the kind preferred by computer scientists, namely ones that can be stated in a device-independent manner. An advantage of quantum devices over classical computers for such problems is often referred to as quantum supremacy or quantum advantage [20, 21]. Sampling algorithms have emerged as an important class of algorithms in this context. In essence, the task is to sample from a probability distribution that is defined abstractly in terms of a quantum circuit. In 2019, a team at Google reported on the implementation of such an algorithm on a device comprising 53 qubits, claiming it would take a classical supercomputer 10,000 years to run the task completed by the quantum device in 200 seconds [14, 16]. The drawback of these algorithms is that they have no known practical application.

Understanding the power and limitation of NISQ devices remains a highly
active area of research. This dissertation approaches this vast field from a number of angles, including algorithmic considerations as well as technological ones. In fact, technological progress has been a major driving force behind recent progress in the field. NISQ devices have already led to numerous unexpected discoveries while simultaneously pushing forward the development of new theoretical tools. To harness the full power of NISQ devices, experimental and theoretical communities will have to closely work together to identify the approaches that are most robust against noise. Progress thus far has been astounding but many obstacles remain to successfully make the leap from the age of quantum science into an age of quantum technology.

1.2 Overview of this dissertation

This dissertation consists of two parts. The first two chapters are concerned with abstract questions related to quantum algorithms, while the remaining chapters 4–8 focus on more practical considerations. Most of the chapters are accompanied by an appendix that provides technical details unessential to the understanding of the main results.

In Chapter 2, we shed light on the mechanisms by which quantum computers fail in the presence of noise. Using the concrete example of the adiabatic quantum search algorithm, we show that the environment renormalizes the spectral gap of the system, resulting in an increase of the computation time.

\footnote{One might add that the same is true for fully fledged, fault-tolerant quantum computers. There are few known algorithms such as Shor’s with a quantum speedup and practical use. Even fewer algorithms exhibit a provable quantum speedup as the exact relation between classical and quantum complexity classes remains unknown. While deemed unlikely by most people in the field, it is even possible that Shor’s algorithm offers no quantum speedup and we have simply not yet found the fastest classical algorithm for factoring.}
In Chapter 3, we propose a method to construct quantum algorithms for classical sampling problems.\textsuperscript{3} We provide a physical explanation for the observed quantum speedup by establishing a novel relation to quantum phase transition. Both chapters are self-contained.

Light is a central theme for the remainder of the dissertation. Light is used to probe and manipulate quantum states in many quantum computing platforms. It can also serve to transmit quantum information for the purposes of quantum cryptography or to connect distant quantum devices. The latter is a promising avenue in the pursuit of increasing the number of qubits. In Chapter 4, we review the basics of light–matter interaction using a Green’s function formalism. We apply the formalism in Chapter 5 to two-dimensional arrays of atoms, demonstrating that they interact strongly with light despite the diluteness and vanishing thickness of the array. The effect is explained in terms of the collective behavior of the atoms: they are synchronized to form what is effectively an antenna. The antenna can be engineered to deterministically focus an incoming photon onto a single atom, which is a key ingredient in many schemes for quantum communication.

We explore related effects in an entirely different platform in Chapters 6 and 7. Chapter 6 introduces the basic optical properties of two-dimensional semiconductors, drawing close analogies with arrays of atoms. The theoretical discussion is accompanied by experimental data from the groups of Professor Hongkun Park and Professor Philip Kim at Harvard University. The experimental results demonstrate the strong interaction of light with monolayers of transition metal dichalcogenides, a class of two-dimensional semiconductors.

\textsuperscript{3}These sampling problems are distinct from the ones mentioned above.
We describe how the optical properties of these materials can be modified by engineering the electromagnetic environment and we propose a number of applications. These ingredients are combined in Chapter 7, where we show theoretically that a conventional mirror can enhance the quantum nonlinear response of a two-dimensional semiconductor. Finally, in Chapter 8 we delve deeper into the material properties of two-dimensional semiconductors, analyzing the implications of interactions between optical excitations and charge carriers. The results highlight the role the complex many-body body dynamics in two-dimensional materials.
Chapter 2

Adiabatic quantum computing in the presence of noise

2.1 Introduction

The adiabatic theorem provides a powerful tool to characterize the evolution of a quantum system under a time-dependent Hamiltonian. It underlies theoretical concepts ranging from Landau-Zener transitions [22] to Berry phase accumulation and experimental techniques such as adiabatic passage [23]. Adiabatic evolution can also serve as a platform for quantum information processing [24–29]. This paradigm bears some resemblance to simulated annealing: computation proceeds via smoothly varying a parameter to hone in on a solution encoded in the ground state of a specific Hamiltonian. Thus, a generic adiabatic quantum computation (AQC) proceeds in three steps. A physical system is first prepared in the known ground state of a simple initial Hamiltonian. The Hamiltonian is then adiabatically transformed into
the desired one. Finally, the state of the system is measured and, assuming adiabaticity, represents the solution to the encoded question.

Nearly a decade ago, it was shown that AQC and the canonical circuit model of quantum computation are equivalent in computational power [30–32]. While the two models can provably solve the same problems, their physical implementation and thus their susceptibility to errors differ significantly. For instance, imperfections of individual gates will reduce the fidelity of a computation in the circuit model. In AQC, by contrast, errors may arise due to non-adiabatic transitions. Furthermore, AQC is affected by noise present in any realistic implementation. It has been suggested that AQC may be inherently robust against noise [33, 34] and that the presence of an environment may even improve performance [35]. Adiabatic evolution is particularly susceptible to noise when the gap between the ground state and the excited states is small. A thorough understanding of the effect of noise on small gaps is therefore desirable. In this chapter, we study the effect of an environment on the adiabatic quantum search (AQS) algorithm [24, 36], the adiabatic equivalent of Grover’s algorithm [37]. While the AQS algorithm in open systems has been the subject of numerous studies, a complete understanding of its scalability is missing [35, 38–46].

Although the AQS algorithm involves a highly non-local Hamiltonian, we utilize it as a convenient example of an algorithm exhibiting a single avoided level crossing. In realistic systems with $k$-local interactions ($k \leq 2$ typically), small gaps often arise due to avoided level crossings between macroscopically distinct states. In this case, an environment that also acts locally is incapable of inducing transitions between the two states involved in the crossing, and
it predominantly leads to dephasing. To this end, in our model for the AQS algorithm, the environment only couples to the dephasing channel. We show that under these assumptions, the problem of determining the scalability of the algorithm can be cast into an implementation-independent form, parameterized by the minimum gap at the avoided level crossing. Thus, we expect our conclusions to generalize beyond the AQS algorithm.

2.2 Summary of results

To understand the main result of our work, it is helpful to consider the different ways in which the environment influences the algorithm. One naively expects that a thermal bath will degrade performance whenever the temperature exceeds the smallest gap encountered during the computation. However, this is not necessarily the case if the number of thermally accessible states is small [35]. In the AQS algorithm, there exist two low-energy states, separated by a large gap from higher excited states. These two low-lying states undergo an avoided level crossing (see inset of Figure 2.1). It is thus natural to assume that the environment can thermally mix these two states but does not give rise to higher excitations. Thermalization may then reduce the success probability by at most 50%, which can be compensated for by repeating the algorithm multiple times [35].

Apart from leading to thermalization, the environment also renormalizes the gap at the avoided crossing. The effect is best understood by appealing to an analogy with a double-well system. In this picture, the two low-energy states of the AQS algorithm are spanned by the ground states of two wells,
Figure 2.1: Qualitative dynamics of the adiabatic quantum search algorithm in an open system. The evolution of the system is coherent below the critical temperature $T^*$ (indicated by the solid curves) and a quantum speedup is available in this regime. The three curves correspond to different sizes $N$ of the search space. The parameter $\eta$ characterizes the noise spectral density at low frequency $\propto \omega^\eta$, with $\eta = 1$ corresponding to an ohmic bath. The dependence of $T^*$ on $\eta$ changes qualitatively at $\eta_c$ due to scattering processes contributing significantly when $\eta > \eta_c$. The inset shows the spectrum of the AQS Hamiltonian for $N = 256$.

which are detuned from each other by a bias $\varepsilon$ and connected by a tunneling rate $\Delta$. The avoided crossing occurs at zero bias ($s = 1/2$ in Figure 2.1), for which the energy gap is equal to the tunneling rate. As mentioned above, a local environment predominantly gives rise to dephasing between the wells, whereas environment-induced transitions from one well to another are negligible. This dephasing suppresses coherent tunneling, which in turn results in a decrease of the minimum gap. Equivalently, this mechanism may be viewed as a consequence of the quantum Zeno effect, where the environment tends to localize the system in one of the wells by gaining information about its
current state \cite{47}. Coherent tunneling may vanish entirely if the coupling to the environment is sufficiently strong. We refer to this as the incoherent regime, as opposed to the coherent regime, where tunneling persists. The terminology reflects the fact that coherent Rabi oscillations can, in principle, be observed in the coherent regime, whereas the oscillations are overdamped if the system is incoherent. Any potential quantum speedup is lost in the incoherent regime, as discussed in detail below. Conversely, a quantum speedup is always available in the coherent regime provided the gap retains the same scaling with problem size as in a closed system.

In order to identify the relevant regimes, we compare the tunneling rate with the coupling rate to the environment. At zero temperature, the coupling rate is given by the noise spectral density of the environment, $J(\omega)$, evaluated at the gap frequency. The noise spectral density is assumed to obey a power law at low frequencies, $J(\omega) \propto \omega^\eta$, where we distinguish between sub-ohmic ($\eta < 1$), ohmic ($\eta = 1$), and super-ohmic ($\eta > 1$) environments. For a sub-ohmic environment, the ratio $J(\Delta)/\Delta$ diverges in the limit $\Delta \to 0$, suggesting that the system is incoherent at the avoided level crossing for large search spaces. If the environment is super-ohmic, the same reasoning predicts that even large systems remain coherent. This simple argument is indeed correct at zero temperature, while at finite temperature, bosonic enhancement and two-boson processes lead to significant modifications. We demonstrate that even for a super-ohmic environment, a quantum speedup can only be achieved below a certain critical temperature, whose dependence on $\eta$ and the size of the search space is summarized in Table 2.1 and Figure 2.1. Notably, the critical temperature decays as a power law with the size of the search space,
such that the AQS algorithm offers no improvement over a classical algorithm for large search spaces at finite temperature.

<table>
<thead>
<tr>
<th></th>
<th>single-boson processes</th>
<th>two-boson processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta &lt; 1$</td>
<td>$\alpha T^* = 0$</td>
<td></td>
</tr>
<tr>
<td>$\eta &gt; 1$</td>
<td>$\alpha T^* = O(N^{(\eta-2)/2})$</td>
<td>$\alpha^{2/(2\eta+1)} T^* = O(N^{-1/(4\eta+2)})$</td>
</tr>
</tbody>
</table>

Table 2.1: Scaling of the critical temperature $T^*$ with the size of the search space $N$ for a given coupling strength $\alpha$ between the system and the environment. The scaling of $T^*$ is evaluated separately for processes involving one and two bosons of the bath. For a sub-ohmic environment, the one-boson processes render the dynamics incoherent even at zero temperature such that two-boson processes are never relevant.

2.3 Model

2.3.1 Closed system

We now proceed with detailed calculations. The AQS algorithm in a closed system is described by the Hamiltonian $H(s) = E_0(1 - s)(\mathbb{1} - |\psi_0\rangle\langle\psi_0|) + E_0 s (\mathbb{1} - |m\rangle\langle m|)$, where $E_0$ sets the energy scale of the system, the state $|\psi_0\rangle = \frac{1}{\sqrt{N}} \sum_{x=1}^{N} |x\rangle$ is an equal superposition of all states in the search space, and $|m\rangle$ denotes the marked element to be found. The parameter $s$ is increased monotonically from its initial value $s = 0$ to its final value $s = 1$. The Hamiltonian $H(s)$ can be exactly diagonalized in the two-level subspace spanned by $|m\rangle$ and $|m_\perp\rangle = \frac{1}{\sqrt{N-1}} \sum_{x \neq m} |x\rangle$, where

$$H(s) = \frac{E_0}{2} \mathbb{1} - \frac{1}{2} [\varepsilon(s) \tau^z + \Delta(s) \tau^x].$$

(2.1)
Here, $\tau^i$ are the Pauli matrices acting on $\{|m\rangle, |m_\perp\rangle\}$, $\varepsilon(s)/E_0 = 2s-1+2(1-s)/N$, and $\Delta(s)/E_0 = 2\sqrt{N-1}/N(1-s)$. The orthogonal subspace is degenerate with constant energy $E_0$ (see inset of Figure 2.1). The spectrum exhibits an avoided level crossing at $s = 1/2$, where the gap is of order $O(N^{-1/2})$ for large $N$. As anticipated, the low-energy Hamiltonian is equivalent to one describing two wells connected by a tunneling rate $\Delta$ and detuned from each other by a bias $\varepsilon$. Classically, the computation time scales linearly with the size of the search space $N$, whereas both Grover’s algorithm and the AQS algorithm achieve a quadratic quantum speedup, scaling as $O(N^{1/2})$. The latter scaling, set by the inverse of the minimum gap, is provably optimal [36].

2.3.2 Environment

To specify the environment, we envision that the AQS Hamiltonian is implemented using $L$ qubits, where $N = 2^L$. Each qubit is coupled to an independent, bosonic bath. We assume throughout that the temperature $T \ll E_0/L$, which ensures that the dynamics of the system are restricted to the two lowest-lying levels. As derived in Appendix A.1, the environment couples to the low-energy subspace under these conditions through an effective interaction of the form

$$V = \tau^z \sum_k g_k (b_k + b_k^\dagger) + \tau^z \sum_{k,l} \frac{g_k g_l}{E}(b_k + b_k^\dagger)(b_l + b_l^\dagger),$$

where $b_k$ and $b_k^\dagger$ are bosonic annihilation and creation operators, $g_k$ is a coupling strength, and $E$ an energy scale proportional to $E_0$. The first term in

\footnote{The proof of optimality in reference [36] straightforwardly generalizes to open systems, assuming that the environment contains no information about the marked state.}
Equation (2.2) describes absorption or emission of a single boson, while the second term corresponds to two-boson processes, such as two-boson emission or boson scattering. Higher-order terms, which depend on specifics of the higher excited states, have been neglected since they do not affect our results qualitatively. We have also dropped terms that couple to $\tau^{x,y}$, representing environment induced transitions between $|m\rangle$ and $|m_{\perp}\rangle$, as they are strongly suppressed in the limit of large $N$. Both approximations are formally justified in Appendix A.1.

The bath is characterized by the noise spectral density $J(\omega) = \sum_k g_k^2 \delta(\omega - \omega_k)$, which follows a power law at low frequencies, $J(\omega) = \alpha \omega^\eta$. The parameter $\alpha$ sets the coupling strength to the environment. Our analysis is restricted to $\eta > 0$ because the effective two-level description breaks down otherwise (see Appendix A.1). Furthermore, we assume that the weak-coupling condition $J(\omega) \ll E_0$ is satisfied for all $\omega$. We emphasize that coupling is only weak compared to the overall energy scale of the system but may be strong compared to the gap between the low-energy states.

### 2.4 Renormalized tunneling rate

#### 2.4.1 Single-boson processes

In order to explore the coherence properties of the system, we employ a procedure known as adiabatic renormalization, which has been widely put to use in the context of the spin–boson model [48]. The method is particularly powerful as it is valid even for non-perturbative and non-Markovian environments. Adiabatic renormalization proceeds by eliminating modes of the environment
that are fast compared to the tunneling rate. To a good approximation these
oscillators adiabatically follow the system thereby reducing the bare tunneling
rate $\Delta$ to a renormalized tunneling rate $\tilde{\Delta}$. The case $\tilde{\Delta} = 0$ corresponds to
the incoherent regime introduced above, while in the coherent regime $\tilde{\Delta} > 0$.

To compute $\tilde{\Delta}$, we first determine the energy eigenstates in the absence of
tunneling. For the moment, we only consider single-boson processes and limit
ourselves to the region near the avoided crossing, where $\varepsilon(s) \approx 0$. The eigen-
states are given by $|\tau, n\rangle = e^{-i\tau S_1} |\tau\rangle \prod_k |n_k\rangle$, where $S_1 = i \sum_k \frac{\omega_k}{\omega_k} (b_k - b_k^\dagger)$,
$\tau = m, m_\perp$ (corresponding to $\tau^z = \pm 1$), and $n_k$ are the occupation numbers of
the bosonic modes. Physically speaking, the system is dressed by oscillators,
whose displacements depend on the state of the system. Oscillators with fre-
quencies much greater than the tunneling rate will adjust to the state of the
system almost instantaneously, while slower oscillators must be accounted for
more carefully. We hence define the renormalized tunneling rate between the
states $|m, n\rangle$ and $|m_\perp, n\rangle$ as $\tilde{\Delta}_n = \Delta \langle m, n | \tau^x | m_\perp, n \rangle'$, where the prime de-
notes that only oscillators with frequencies satisfying $\omega_k > \Omega$ should be taken
into account. Here, $\Omega$ is a low-frequency cutoff, which may be self-consistently
determined as $\Omega = p \tilde{\Delta}_n$. The exact value of $p$ is irrelevant in what follows,
provided that $p \gg 1$. Due to the dependence of $\tilde{\Delta}_n$ on the occupation num-
bers, it is only possible to define a unique renormalized tunneling rate at zero
temperature. Nevertheless, we can define a typical rate $\tilde{\Delta}$ by taking a thermal
expectation value, yielding

$$\tilde{\Delta} = \Delta \exp \left[-2 \int_\Omega^\infty d\omega \frac{J(\omega)}{\omega^2} \coth \frac{\omega}{2T} \right].$$

(2.3)
We first consider the above expression at $T = 0$. For a super-ohmic environment, the integral in the exponent remains finite as $\Omega \to 0$. For large $N$, we may set $\Omega$ to zero to a very good approximation such that $\tilde{\Delta}$ is proportional to $\Delta$. If the environment is ohmic or sub-ohmic, the integral exhibits an infrared divergence. There exists a critical coupling strength $\alpha^* \propto \Delta^{1-\eta}$ such that $\tilde{\Delta} = 0$ for all $\alpha > \alpha^*$. For $\alpha < \alpha^*$, the renormalized tunneling rate remains finite as shown in Appendix A.2. The critical coupling strength tends to zero as $N \to \infty$, showing that the dynamics are incoherent in the limit of large search spaces consistent with the discussion above.

The results at finite temperature can be obtained by very similar arguments. In short, one obtains that $\tilde{\Delta}$ is always finite and proportional to $\Delta$ for $\eta > 2$, while for $1 < \eta \leq 2$ there exists a critical coupling strength of the form $\alpha^* \propto \Delta^{2-\eta}/T$, where we assumed that $T \gg \tilde{\Delta}$. If the coupling constant is fixed, the expression can be interpreted as an expression for a critical temperature

$$T^* \propto \frac{\Delta^{2-\eta}}{\alpha} = O(N^{(\eta-2)/2}). \tag{2.4}$$

This is consistent provided $\eta > 1$. In the sub-ohmic regime, $T^*$ cannot be taken much greater than $\tilde{\Delta}$ and we find instead that the dynamics are always incoherent for a fixed $\alpha$ in the limit of large search spaces. At $\eta = 1$, the existence of a non-zero critical temperature depends on the value of $\alpha$. We note that these results, summarized in the first column of Table 2.1, are in agreement with previous work by Tiersch and Schützhold [43].
2.4.2 Two-boson processes

Two-boson processes may be treated similarly although they affect the system in a qualitatively different manner [49]. There are two kinds of two-boson processes: those in which a pair of bosons is absorbed or emitted, and those in which a boson is scattered between two modes. Conservation of energy requires that in two-boson emission/absorption processes both modes have energies $\lesssim \Delta$. By contrast, the scattering processes can involve pairs of modes with arbitrarily high energy, provided their energy difference is small. Crucially, the phase space for boson scattering is independent of $\Delta$ for large $N$ and remains non-zero as $\Delta \to 0$. The two-boson coupling strength at finite temperature is thus expected to be always large compared to $\Delta$ for large $N$.

To support this argument, we again perform adiabatic renormalization, the detailed steps of which are provided in Appendix A.2. We focus on super-ohmic environments since single-boson processes already prevent a quantum speedup in the sub-ohmic case. We further extend the weak coupling approximation to include bosonic enhancement, i.e., $J(\omega)(1 + N(\omega)) \ll E_0$ for all $\omega$, where $N(\omega)$ is the Bose–Einstein distribution. Under these assumptions, two-boson processes only weakly renormalize the tunneling rate at zero temperature and do not render the dynamics incoherent. If $T > 0$, there exists a critical coupling strength, which is given by $\alpha^* \propto E \Delta^{1/2} / T^{\eta + 1/2}$, such that the dynamics are incoherent for any $\alpha > \alpha^*$. Clearly, $\alpha^*$ vanishes as $N \to \infty$ regardless of $\eta$. This is in stark contrast to the renormalization due to single-boson processes alone, where the system remains coherent if $\eta > 2$. At fixed
coupling strength, we thus predict a critical temperature

\[ T^* \propto \frac{\Delta^{1/(2\eta+1)}}{\alpha^{2/(2\eta+1)}} = O(N^{-1/(4\eta+2)}) \]  

(2.5)

for two-boson processes.

In addition to coherent tunneling, there exist incoherent transitions, during which the system exchanges energy with the environment and thermalizes. We argued above that in the case of the AQS algorithm, these processes merely give rise to constant overhead. In fact, thermalization may even improve the performance if it occurs sufficiently fast [35]. By letting the system thermalize, one can obtain the ground state with a probability of at least 50% since only the lowest two energy states may be significantly populated. In order to exclude the possibility of a quantum speedup in the incoherent regime, it is therefore necessary to ensure that the thermalization rate decreases with system size at least as fast as \(O(N^{-1})\). Indeed, we verify in Appendix A.3 that the thermalization rate always scales as \(O(N^{-1})\) in the incoherent regime.

In the coherent regime, the thermalization rate can exceed this scaling near the avoided level crossing. This is an intriguing result since it implies that quantum computation can proceed through thermalization alone. This may be accomplished, for instance, by initializing the system in its ground at \(s = 0\) (large bias) before rapidly decreasing the bias to zero. The system is then left to thermalize before being measured in the computational basis. Repeating this procedure several times will yield the ground state with high probability. We note, however, that this approach does not lead to an improved scaling.
compared to adiabatic evolution, which always offers a quantum speedup in the coherent regime.

2.5 Outlook

We summarize our results by discussing the combined effect of single-boson and two-boson processes. We show in Appendix A.2 that for the parameter regime considered here, the two processes decouple and their combined effect can be deduced from the results presented above. In particular, for the dynamics to be incoherent it is sufficient that one of the processes renormalizes the tunneling rate to zero. We thus conclude that the system is always incoherent at finite temperature in the limit of large \( N \) and the algorithm does not provide a quantum speedup. We observe that the critical temperature associated with the coherent–incoherent transition scales differently for the two processes, see Figure 2.2. Only the smaller critical coupling is physically significant; thus, two-boson processes dominate for \( \eta > \eta_c \), and single-boson processes otherwise. At \( \eta_c = (3 + \sqrt{17})/4 \) the critical temperatures scale identically and model-dependent pre-factors determine which process dominates.

Owing to the generic nature of the system–bath interaction discussed here, we expect that our results extend to a wide range of adiabatic algorithms involving avoided level crossings. The interaction Hamiltonian in Equation (2.2), involving only dephasing, arises naturally in such situations because small gaps generically correspond to macroscopically distinct states that are not connected by a local environment. The non-local interactions in the AQS algorithm lead to a spectrum in which the \( N - 2 \) states not involved
Figure 2.2: Dependence of the critical temperature $T^*$ on the search space size $N$. The critical temperature follows a power law $T^* = O(N^\delta)$. Above $T^*$, the system evolves incoherently, while below, quantum coherence is retained. The qualitative change at $\eta_c$ is due to competition between single and two-boson processes. For $\eta < 1$, the dynamics are incoherent even at zero temperature in the limit of large $N$.

in the level crossing are extensively separated in energy (i.e., their excitation gap is proportional to the full energy bandwidth of the system). A more realistic model with few-body interactions will instead have an intensive excitation gap. As long as the temperature is much lower than this excitation gap, our reduced model of the avoided crossing continues to apply, and so do our conclusions. Moreover, our findings should be broadly relevant for adiabatic quantum algorithms that involve many-body tunneling [50–52]. For the AQS algorithm we were able to draw a direct correspondence between tunneling and speedup, whereas the general significance of tunneling in AQC algorithms is an open question. Future work may explore the applicability of our results to algorithms offering an exponential speedup, where the role of many-body tunneling is particularly unclear [53]. Finally, our work highlights the need for quantum error correction to render AQC scalable at finite temperature [54–61].
Chapter 3

Quantum sampling algorithms for near-term devices

3.1 Introduction

Efficient solutions of Gibbs sampling problems are of broad practical importance. The Gibbs distribution is not only at the heart of statistical physics [62], but it also plays a significant role in a wide variety of other areas such as optimization algorithms [63] and machine learning [64]. Quantum systems are naturally suited for encoding sampling problems: According to the Born rule, a projective measurement of a quantum state $|\psi\rangle$ in a given orthonormal basis $\{|s\rangle\}$ yields a random sample drawn from the probability distribution $p(s) = |\langle s | \psi \rangle|^2$. This observation underpins recent work aiming to demonstrate quantum advantage over classical computers by sampling from a probability distribution defined in terms of a quantum gate sequence [65, 66] or an optical network [67]. While these efforts have led to impressive experimental
demonstrations [14, 68], they have limited implications for practically relevant problems.

Here, we introduce a family of quantum algorithms for sampling from classical Gibbs distributions. We illustrate our approach with three specific examples: sampling from the Gibbs distribution corresponding to the Ising chain and sampling from weighted independent sets of two different graphs. Sampling from independent sets at low temperature encompasses computationally hard problems since approximating the size of the maximum independent set on a random graph is NP hard [69]. Problems of this type appear in diverse applications including computer vision [70], biochemistry [71], and social networks [72]. Before proceeding, we note that various pioneering quantum algorithms for Gibbs sampling have been developed [73–83]. In contrast to many of these proposals, our approach does not require a large-scale, universal quantum computer and may be realized and tested on relatively near-term quantum devices.

The key ideas for our approach are summarized in Figure 3.1. We consider a system of $n$ classical bits, labeling a complete bit string by $s$. We focus on spin models, where $s = s_1 s_2 \ldots s_n$ with each spin being either up ($s_i = +1$) or down ($s_i = -1$). The desired Gibbs distribution $p_\beta(s) = e^{-\beta H_c(s)}/Z$ is defined in terms of energies $H_c(s)$ and the inverse temperature $\beta$, with $Z = \sum_s e^{-\beta H_c(s)}$ denoting the partition function. Sampling from a classical Gibbs distribution can be reduced to preparing the quantum state

$$|\psi (\beta )\rangle = \frac{1}{\sqrt{Z}} \sum_s e^{-\beta H_c(s)/2} |s\rangle,$$

(3.1)
followed by a projective measurement in the orthonormal \{ |s \rangle \} basis. Although the construction applies more generally, we focus on classical Hamiltonians that can be written as a sum of one- and two-body terms, in which case \( | \psi(\beta) \rangle \) is a projected entangled pair state with bond dimension \( D = 2 \) [84].

\[ p_\beta(s) = \frac{1}{Z} e^{-\beta H_\beta(s)} \]

\[ | \psi(\beta) \rangle \]

\[ H_{q(\beta)} \]

\[ H_0 \]

\[ H_{q(\beta)} \]

**Figure 3.1:** Construction of quantum algorithms to sample from a Gibbs distribution. The green boxes constitute the sampling procedure, which is carried out on a quantum computer.

In order to prepare the Gibbs state, Equation (3.1), we start from a classical Markov chain Monte Carlo algorithm for sampling from the Gibbs distribution. Any such Markov chain can be mapped onto a so-called parent Hamiltonian \( H_{q(\beta)} \), whose unique ground state is \( | \psi(\beta) \rangle \). This construction directly relates the mixing time of the Markov chain to the ground state gap of the parent Hamiltonian. For hard problems, where the Markov chain mixes slowly, the gap vanishes in the thermodynamic limit such that \( H_{q(\beta)} \) describes either a gapless phase or a system at a quantum phase transition.

To prepare the state \( | \psi(\beta) \rangle \), adiabatic evolution can be used. In this approach, we identify a sufficiently simple Hamiltonian \( H_0 \), whose ground state can be readily prepared. Next, we adiabatically deform \( H_0 \) into the target Hamiltonian \( H_{q(\beta)} \). However, in contrast to prior work [79], we do not restrict the adiabatic evolution to the one-parameter family of Hamiltonians defined by \( H_{q(\beta)} \) for arbitrary \( \beta \). Instead, as shown below, more general paths exist.
that outperform adiabatic evolution along the one-parameter family and give rise to an asymptotic speedup over the classical Markov chain. The speedup can be traced to the distinct nature of the phase transitions encountered by different paths. The origin of the speedup is quantum mechanical in the sense that there exists no simple reverse mapping to a classical Markov chain algorithm.

3.2 Parent Hamiltonian

Our construction of the parent Hamiltonian follows the prescription in reference [84] (see references [85–87] for related earlier work). We first define a Markov chain that samples from the desired Gibbs distribution \( p_\beta(s) \). The Markov chain is specified by the generator matrix \( M_\beta \), where the probability distribution \( q_t(s) \) at time \( t \) evolves according to \( q_{t+1}(s) = \sum_{s'} q_t(s') M_\beta(s', s) \).

By assumption, \( p_\beta(s) \) is a stationary distribution of the Markov chain and it therefore constitutes a left eigenvector of \( M_\beta \) with eigenvalue unity. We assume in addition that the Markov chain satisfies detailed balance, which can be expressed as

\[
e^{-\beta H_c(s')} M_\beta(s', s) = e^{-\beta H_c(s)} M_\beta(s, s').
\]

This property implies that

\[
H_q(\beta) = n \left( I - e^{-\beta H_c/2} M_\beta e^{\beta H_c/2} \right)
\]

is a real, symmetric matrix. It can be viewed as a quantum Hamiltonian with the Gibbs state \( |\psi(\beta)\rangle \) being its zero-energy eigenstate. The Gibbs state is a ground state because the spectrum of \( H_q(\beta) \) is bounded from below by 0. For every eigenvalue \( n(1 - \lambda) \) of \( H_q(\beta) \), there exists an eigenvalue \( \lambda \) of \( M_\beta \), where \( \lambda \leq 1 \) because \( M_\beta \) is a stochastic matrix. If the Markov chain is fully
mixing and aperiodic, the Perron–Frobenius theorem [88] guarantees that all other eigenvalues are strictly less than 1 in magnitude such that \( |\psi(\beta)\rangle \) is in fact the unique ground state of \( H_\beta(\beta) \). The factor of \( n \) in the Equation (3.2) ensures that the spectrum of the parent Hamiltonian is extensive. To account for the natural parallelization in adiabatic quantum computation, we divide the mixing time of the Markov chain by \( n \) for a fair comparison, denoting the result by \( t_m \). The correspondence between the spectra of \( M_\beta \) and \( H_\beta(\beta) \) establishes the bound \( t_m \geq 1/\Delta(\beta) \), where \( \Delta(\beta) \) is the gap between the ground state and first excited state of the parent Hamiltonian [89].

3.3 Sampling from the 1D Ising model

We now illustrate this procedure by considering a ferromagnetic Ising model composed of \( n \) spins in one dimension. The classical Hamiltonian is given by

\[
H_c = -\sum_{i=1}^{n} \sigma_i^z \sigma_{i+1}^z \quad \text{with periodic boundary conditions, letting } \sigma_{n+1}^z = \sigma_1^z \text{ and } \sigma_0^z = \sigma_n^z.
\]

We choose Glauber dynamics as the Markov chain, where at each time step, a spin is selected at random and its value is drawn from a thermal distribution with all other spins fixed [90]. Up to a constant, the parent Hamiltonian takes the form

\[
H_\beta(\beta) = -\sum_{i=1}^{n} \left[ h(\beta) \sigma_i^x + J_1(\beta) \sigma_i^z \sigma_{i+1}^z + J_2(\beta) \sigma_{i-1}^z \sigma_i^x \right],
\]

where \( 4h(\beta) = 1 + 1/\cosh(2\beta), \ 2J_1(\beta) = \tanh(2\beta), \) and \( 4J_2(\beta) = 1 - 1/\cosh(2\beta) \) (see Appendix B.2 for details and references [91, 92] for early derivations of this result). At infinite temperature \( (\beta = 0) \), we have \( J_1 = J_2 = 0 \) and \( h = 1 \). The ground state is a paramagnet aligned along the
$x$-direction, which corresponds to an equal superposition of all classical spin configurations consistent with the Gibbs distribution at infinite temperature. When the temperature is lowered, the parameters move along a segment of a parabola in the two-dimensional parameter space $(J_1/h, J_2/h)$ shown by the red curve (ii) in Figure 3.2a. The segment terminates at $(J_1/h, J_2/h) = (2, 1)$ for $\beta \to \infty$. We highlight that any point along the segment can be viewed as a generalized Rokhsar-Kivelson point [86, 93], where the Hamiltonian is by construction stoquastic and frustration free [87, 94].

To find the optimal adiabatic path with a potential quantum speedup, it is instructive to determine the quantum phase diagram of the Hamiltonian in Equation (3.3) for arbitrary values of $h$, $J_1$, and $J_2$. As shown in Appendix B.2, the Hamiltonian can be diagonalized by performing a Jordan-Wigner transformation that maps it onto a free fermion model. The resulting quantum phases are displayed in Figure 3.2a, with the black lines indicating phase transitions. The model reduces to the transverse field Ising model on the $J_2/h = 0$ axis, where a phase transition from a paramagnet to a ferromagnet occurs at $J_1/h = 1$. Along the $J_1/h = 0$ axis, the ground state undergoes a symmetry-protected topological phase transition at $J_2/h = \pm 1$ from the paramagnet to a cluster-state-like phase [95, 96]. We note that the tricritical point between the distinct phases describes the parent Hamiltonian corresponding to zero temperature.

For the adiabatic preparation of the Gibbs state $|\psi(\beta)\rangle$, one may start from the Hamiltonian $H_q(0)$, preparing its ground state of all spins aligned along the $x$ axis. The parameters $(h, J_1, J_2)$ are then smoothly varied to transform the Hamiltonian into its final form at the desired inverse temperature $\beta$. States
Figure 3.2: (a) Quantum phase diagram of the Hamiltonian corresponding to the Ising chain. The black lines indicate the boundaries between paramagnetic (PM), ferromagnetic (FM), and cluster-state-like (CS) phases. The curves labeled (i)–(iv) show four different choices of adiabatic paths. (b) The time dependence of the parameters for a chain of \( n = 100 \) spins according to Equation (3.4). (c) Fidelity as a function of the total sweep time along these trajectories. (d) The time \( t_a \) required to reach a fidelity exceeding \( 1 - 10^{-3} \) as a function of the number of spins, \( n \). The black lines are guides to the eye showing the expected linear, quadratic, and quartic dependencies of \( t_a \) on \( n \).
with finite $\beta$ can be connected to the infinite temperature state by a path that lies fully in the paramagnetic phase, where the parent Hamiltonian is gapped. We expect both adiabatic state preparation and the Markov chain to be efficient in this case. Indeed, it has been shown that there exists a general quantum algorithm with run time $\sim \log n$ [83] for gapped parent Hamiltonians, which is identical to the Markov mixing time $t_m$ for the Ising chain [97]. For the sampling problem at zero temperature, we consider the four different paths in Figure 3.2a. As shown below, adiabatic state preparation along path (ii), corresponding to the one-parameter family $H_q(\beta)$, requires a time $t_a \sim n^2$. The mixing time of the Markov chain at zero temperature is similarly bounded by $t_m \sim n^2$. The quadratic scaling with system size is a consequence of the diffusive dynamics of domain walls. By contrast, domain walls propagate ballistically at the quantum phase transition between the paramagnetic and ferromagnetic phases, which results in a quadratic speedup of paths (iii) and (iv) over path (ii) and the classical Markov chain.

To evaluate the dynamics quantitatively, we choose the rate of change with the aim of satisfying the adiabatic condition at every point along the path [98, 99]. For general set of parameters $\lambda_\mu$, we let

$$\sum_{\mu,\nu} g_{\mu\nu} \frac{d\lambda_\mu}{dt} \frac{d\lambda_\nu}{dt} = \varepsilon^2,$$

(3.4)

where $\varepsilon$ is a small, dimensionless number and

$$g_{\mu\nu} = \sum_{k \neq 0} \frac{\langle \partial_{\mu} 0 | k \rangle \langle k | \partial_{\nu} 0 \rangle}{(E_k - E_0)^2}.$$

(3.5)

Here the $|k\rangle$ and $E_k$ label the eigenstates and corresponding eigenenergies of
the system with $k = 0$ denoting the ground state. The notation $\partial_\mu$ is a short-hand for $d/d\lambda_\mu$. Equations (3.4) and (3.5) ensure that the parameters change slowly when the gap is small, while simultaneously taking into account the matrix elements $\langle k|\partial_\mu|0\rangle$, which determine the coupling strength of nonadiabatic processes to a particular excited state $|k\rangle$. The solution of Equation (3.4) for $\lambda_1 = J_1/h$ is shown in Figure 3.2b. We fix $h = 1$ since rescaling the entire Hamiltonian does not induce transitions between the eigenstates and numerically integrate the Schrödinger equation with the initial state $|\psi(0)\rangle$ to obtain $|\phi(t_{\text{tot}})\rangle$ after total evolution time $t_{\text{tot}}$, which can be adjusted by varying $\varepsilon$. Figure 3.2c shows the resulting fidelity $F = |\langle \phi(t_{\text{tot}})|\psi(\infty)\rangle|^2$ for a chain of $n = 100$ spins. As expected, the fidelity is close to zero at short evolution times and approaches unity for all paths at late times.

To determine the dependence on the number of spins, we extract the time $t_a$ at which the fidelity exceeds $1 - 10^{-3}$, Figure 3.2d. (We show in Appendix B.1 that the total variation distance $d = ||p - q||$ between the desired Gibbs distribution and the prepared distribution $q(s) = |\langle s|\phi(t_{\text{tot}})\rangle|^2$ is bounded by $d \leq \sqrt{1 - F}$.) We find three different scalings of the time $t_a$: along path (i), it roughly scales as $t_a \sim n^3$, along (ii) as $t_a \sim n^2$, while (iii) and (iv) exhibit a scaling close to $t_a \sim n$. As shown in Appendix B.2, the above scalings follow from the singular properties of $g_{\mu\nu}$ at the tricritical point assuming that a constant fidelity is reached at a value of $\varepsilon$ independent of $n$.

The origin of the different scalings can be understood by considering the nature of the phase transitions. The dynamical critical exponent at the tricritical point is $z = 2$, meaning that the gap closes with system size as $\Delta \sim 1/n^2$, which is consistent with the time required along path (ii). The dynamical crit-
ical exponent at all phase transitions away from the tricritical point is $z = 1$ and the gap closes as $\Delta \sim 1/n$. The paramagnetic to ferromagnetic phase transition can be crossed adiabatically in a time proportional to $n$ since quantum coherence allows for ballistic propagation of domain walls as opposed to diffusive propagation in the Markov chain. There is no quadratic slowdown as paths (iii) and (iv) approach the tricritical point, which we attribute to the large overlap of the final state with ground states in the ferromagnetic phase.

Path (i) performs worse than path (ii) because the gap between the paramagnetic and cluster-state-like phases vanishes exactly for certain parameters even in a finite-sized system (see Appendix B.2). To further support the statement that the speedup is of quantum mechanical origin, we note that the half-chain entanglement entropy of the ground state diverges logarithmically with the number of spins when paths (iii) and (iv) cross from the paramagnetic into the ferromagnetic phase. Thus it is impossible to find a representation for the ground state at the phase transition in the form of Equation (3.1) with a local, classical Hamiltonian $H_c$ since any such representation is a matrix product state with constant bond dimension and bounded entanglement entropy.

While the example of the Ising chain illustrates a mechanism for quantum speedup, it has two shortcomings. First, sampling becomes hard only at zero temperature in the asymptotic limit of infinite system size. This is due to the absence of long-range correlations at nonzero temperature, which implies that a Markov chain with local updates mixes fast [100]. Sampling at zero temperature is equivalent to optimization, for which there may exist more suitable algorithms. Secondly, the parent Hamiltonian Equation (3.3) does not have a simple physical realization. The three-body terms can in principle
be implemented using Hamiltonian simulation [101, 102] but this might be challenging with near-term devices.

3.4 Weighted independent set problem

We address the above limitations by considering the weighted independent set problem. An independent set of a graph is any subset of vertices in which no two vertices share an edge, see Figure 3.3a. We say vertex $i$ is occupied if it is in the independent set and assign the occupation number $n_i = 1$. All other vertices are unoccupied with $n_i = 0$. In the weighted independent set problem, each vertex is in addition assigned a weight $w_i$ and we seek to maximize $\sum_i w_i n_i$ or equivalently minimize the energy $H_c = -\sum_i w_i n_i$ subject to the independent set constraint. The corresponding Gibbs distribution has been studied extensively in probability theory and computer science [103] as well as in statistical physics [104–106], where the model is known as the hard-core lattice gas.

To construct a quantum algorithm, each vertex is associated with a spin variable $\sigma^z_i = 2n_i - 1$. Single spin flips with the Metropolis–Hastings update rule [107] yield the parent Hamiltonian

$$H_q(\beta) = \sum_i P_i [V_{e,i}(\beta)n_i + V_{g,i}(\beta)(1 - n_i) - \Omega_i(\beta)\sigma^z_i],$$  \hspace{1cm} (3.6)

where we only consider the subspace spanned by the independent sets. In Equation (3.6), $P_i = \prod_{j \in N_i} (1 - n_j)$ projects onto states in which the nearest neighbors $N_i$ of vertex $i$ are all unoccupied. The remaining parameters are given by $V_{e,i}(\beta) = e^{-\beta w_i}$, $V_{g,i}(\beta) = 1$, and $\Omega_i(\beta) = e^{-\beta w_i/2}$. 

32
Figure 3.3: (a) Example of an independent set (red vertices) on a unit disk graph. Two vertices are connected if and only if they are separated by a distance less than $R$. (b) Physical realization of the parent Hamiltonian Equation (3.6) using Rydberg blockade. The Hamiltonian parameters are determined by the drive amplitudes $E_i$ and $E'_i$ as well as their detuning from resonance. (c) Parameter space and order parameter of the parent Hamiltonian for a chain of length $n = 30$. The order parameter $|M_2| + |M_3|$ distinguishes the disordered phase from the $\mathbb{Z}_2$ and $\mathbb{Z}_3$ ordered phases. The red curve (i) indicates the one-parameter family $H_q(\beta)$, while the blue curve (ii) is an alternative adiabatic path crossing into the $\mathbb{Z}_2$ phase. (d) Adiabatic state preparation time $t_a$ along the two paths in (c). Path (i) terminates at $\beta_c = 2 \log n$ while (ii) continues to $\beta \to \infty$. The threshold fidelity is set to $\mathcal{F} = 1 - 10^{-3}$. The black lines are guides to the eye, showing the scalings $t_a \sim n$ and $t_a \sim n^4$. 
The projectors $P_i$ involve up to $d$-body terms, where $d$ is the degree of the graph. Nevertheless, they can be implemented with minimal experimental overhead for certain classes of graphs. For example, in the case of so-called unit disk graphs, these operators are naturally realizable using highly excited Rydberg states of neutral atoms [108]. A unit disk graph is formed by a set of vertices arranged in a two-dimensional plane where any pair of vertices is connected by an edge if and only if they are separated by a distance less than $R$. As illustrated in Figure 3.3b, the ground state $|g_i\rangle$ of an atom $i$ encodes the unoccupied state of a given vertex $i$. Similarly, the occupied state is encoded in a Rydberg state $|r_i\rangle$. We implement the first and last term in Equation (3.6) by driving a transition from $|g_i\rangle$ to $|r_i\rangle$. The value of $V_{e,i}$ is determined by the detuning of the drive, whereas $\Omega_i$ is proportional to the amplitude of the drive, $\mathcal{E}_i$. The projectors $P_i$ arise due to Rydberg blockade. If an atom is excited to the Rydberg state, the strong van der Waals interaction $U_{vdW}$ shifts the Rydberg states of all neighboring atoms out of resonance, effectively turning off the drive and thereby enforcing the independent set constraint. The remaining second term in Equation (3.6) can be realized using a similar approach, combining the Rydberg blockade with an AC Stark shift induced by an off-resonant drive from the ground state to an auxiliary Rydberg state $|r'_i\rangle$. The Rydberg interaction contributes additional terms to the Hamiltonian that decay as $1/r^6$ with the distance $r$ between two atoms. We neglect these terms in what follows, noting that a strategy to mitigate their role has been proposed in a related context [109].
3.4.1 Chain graph

As a simple example of a unit disk graph, we again consider a chain of length \( n \) and choose equal weights \( w_i = 1 \). The resulting parent Hamiltonian has been studied both theoretically [110, 111] and experimentally using Rydberg atoms [12]. Its quantum phases can be characterized by the staggered magnetization \( M_k = (1/n) \sum_{j=1}^{n} e^{2\pi ij/k} \sigma_j^z \), with \( k \) a positive integer. Figure 3.3c shows the ground state expectation value of \( |M_2| + |M_3| \) for \( n = 30 \), clearly indicating the presence of three distinct phases. For large \( \Omega/V_g \) or large, positive \( V_e/V_g \), assuming \( V_g > 0 \) throughout, the ground state respects the full translational symmetry of the Hamiltonian such that \( |M_k| \) vanishes for all \( k > 1 \). When \( V_e/V_g \) is sufficiently small, the ground state orders into a state where every other site is occupied, known as the \( \mathbb{Z}_2 \) ordered phase. Translational symmetry is broken, resulting in \( |M_2| \neq 0 \). Owing to next-to-nearest neighbor repulsive terms in the Hamiltonian, there further exists a \( \mathbb{Z}_3 \) ordered phase, in which \( |M_3| \neq 0 \) and the ground state is invariant only under translations by three lattice sites or multiples thereof.

The one-parameter family \( H_q(\beta) \) is indicated by the red curve (i) in Figure 3.3c. We note that \( |\psi(0)\rangle \) is not a product state. However, the Hamiltonian \( H_q(0) \) can be adiabatically connected to \( \Omega/V_g = 0 \) and \( V_e/V_g > 3 \), where the ground state is a product state of all sites unoccupied. Since such a path may lie fully in the disordered phase, adiabatic state preparation of the zero temperature Gibbs state is efficient. Similarly, the Markov chain at infinite temperature is efficient as the quantum Hamiltonian is gapped. More generally, we show numerically in Appendix B.3 that the gap is proportional to \( e^{-2\beta} \) at high temperature and \( e^{-\beta}/n^2 \) at low temperature. The crossover
between these scalings occurs at around $\beta_c = 2 \log n$, corresponding to the temperature at which the correlation length is comparable to the system size. In contrast to the Ising chain, the gap vanishes as $\beta \to \infty$ even for finite sized systems. The physical reason is that defects in the $\mathbb{Z}_2$ ordering must overcome a potential barrier to propagate. Therefore, the Markov chain is not ergodic at zero temperature and cannot be used to sample from the Gibbs distribution. It is nevertheless possible to sample approximately from the ground state by running the Markov chain at a nonzero temperature $\beta > \beta_c$. The gap of the parent Hamiltonian bounds the mixing time by $t_m \gtrsim e^{2\beta_c} \sim n^4$. As shown in Figure 3.3d, the adiabatic state preparation time along the one-parameter family $H_\beta(\beta)$ appears to follow the same scaling.

A quantum speedup is obtained by choosing a different adiabatic path, along which $|\psi(0)\rangle$ can be prepared in finite time. For example, an approximately linear scaling $t_a \sim n$, is observed along path (ii) in Figure 3.3c, where the sweep rate was set according to Equation (3.4). In analogy with the Ising chain, we attribute the linear scaling to the dynamical critical exponent $z = 1$ at the phase transition between the disordered and the $\mathbb{Z}_2$ ordered phases. Note that for the independent set problem the quantum speedup is quartic owing to the more slowly mixing Markov chain. We remark that it is possible to improve the performance of the Markov chain by adding simultaneous spin flips on neighboring sites. Such an update allows defects of two adjacent, unoccupied sites to diffuse without an energy barrier, resulting in a gap $\Delta \sim 1/n^2$ without the factor $e^{-\beta}$ at low temperature. In the parent Hamiltonian, these pair updates give rise to nearest-neighbor hopping, which could also be implemented by means of a Förster resonance between Rydberg
states [112]. However, the pair updates are not expected to parametrically improve the quantum algorithm as the linear scaling obtained without them is limited by the time required to spread correlations across the entire system.

### 3.4.2 Star graph

Finally, we consider a graph for which it is hard to sample from its independent sets even at nonzero temperature. The graph takes the shape of a star with $b$ branches and two vertices per branch. The weight of the vertex at the center is $b$, while all other weights are set to 1. Even though this is not a unit disk graph, the parent Hamiltonian could potentially be implemented using anisotropic interactions between Rydberg states [113, 114]. When the central vertex is unoccupied, each branch can have either zero occupied vertices or one occupied vertex, leading to $3^b$ allowed configurations. This number is reduced to $2^b$ when the center is occupied because the independent set constraint forces the inner vertices of each branch to be unoccupied. The exponential separation leads to a discontinuous phase transition at $\beta_c = \log \varphi \approx 0.48$, where $\varphi$ is the golden ratio (see Appendix B.3). Above the phase transition temperature, the free energy is dominated by the entropic contribution from the $3^b$ states with the center unoccupied. Below the transition temperature, it is more favorable to decrease the potential energy by occupying the center at the cost of reducing the entropy (see Figure 3.4a).

The Markov chain on this graph is severely kinetically constrained. In order to change the central vertex from unoccupied to occupied, all neighboring vertices must be unoccupied. Assuming that each individual branch is in thermal equilibrium, the probability of accepting such a move is given
Figure 3.4: (a) Entropy per branch, \( S/b \), of the Gibbs distribution corresponding to the weighted independent set problem on a star graph with two vertices per branch. The system exhibits a discontinuous phase transition at \( \beta_c \approx 0.48 \) (dashed, vertical line). The blue curves were obtained for finite-sized systems, while the black curve indicates the thermodynamic limit. (b) The mixing of the Markov chain is limited at low temperature by the probability \( p_{0 \rightarrow 1} \) to change central vertex from unoccupied to occupied. The quantum algorithm achieves a quadratic speedup over the Markov chain by tunneling between such configurations.

by \( p_{0 \rightarrow 1} = \left[ \frac{1 + e^{\beta}}{1 + 2e^{\beta}} \right]^b \). Similarly, the reverse process is energetically suppressed with an acceptance probability \( p_{1 \rightarrow 0} = e^{-b\beta} \). The central vertex can thus become trapped in the thermodynamically unfavorable configuration, resulting in a mixing time of the Markov chain that increases exponentially with \( b \) at any finite temperature. At high temperature, the Markov chain will nevertheless sample efficiently as the probability of initializing the chain with the central vertex occupied is exponentially small. By the same argument, the Markov chain almost certainly starts in the wrong configuration in the low temperature phase and convergence to the Gibbs distribution requires a time \( t_m \gtrsim 1/p_{0 \rightarrow 1} \).

Even though the quantum dynamics are subject to the same kinetic constraints, tunneling enables a quadratic speedup (see Figure 3.4b). As shown in Appendix B.3, the quantum dynamics are captured by a two-state model
formed by $|\psi_0(\beta)\rangle$ and $|\psi_1(\beta)\rangle$, which are Gibbs states with the central vertex fixed to be respectively unoccupied or occupied. The tunneling rate between these states, i.e. the matrix element $\langle \psi_0 | H_q | \psi_1 \rangle$, is given by $J = \Omega_{\text{cen}} \sqrt{p_0 \rightarrow 1}$, where $\Omega_{\text{cen}}$ denotes the coefficient $\Omega_i$ in Equation (3.6) associated with the central vertex. The time required to adiabatically cross the phase transition is bounded by $t_a \gtrsim 1/J$ with $J$ evaluated at the phase transition. Along the one-parameter family $H_q(\beta)$, we have $\Omega_{\text{cen}} = \sqrt{p_{1 \rightarrow 0}}$ as well as $p_{0 \rightarrow 1} = p_{1 \rightarrow 0}$ at the phase transition such that $t_a \gtrsim 1/p_{0 \rightarrow 1}$, yielding the same time complexity as the Markov chain that samples at the phase transition. However, the square-root dependence of the tunneling rate on $p_{0 \rightarrow 1}$ immediately suggests that a quadratic speedup may be attainable by crossing the phase transition with $\Omega_{\text{cen}} = 1$. An example of such a path is provided in Appendix B.3.

3.5 Outlook

Our new approach to quantum sampling algorithms unveils a connection between computational complexity and phase transitions and provides physical insight into the origin of quantum speedup. The quantum Hamiltonians appearing in the construction are guaranteed to be local given that the Gibbs distribution is derived from a local, classical Hamiltonian and that the Markov chain updates are local. Consequently, time evolution under these quantum Hamiltonians can be implemented using Hamiltonian simulation [101, 102]. Moreover, a hardware efficient implementation in near-term devices may be possible for certain cases such as the independent set problem. While the proposed realization utilizing Rydberg blockade is restricted to unit disk graphs,
a wider class of graphs may be accessible using anisotropic interactions [113, 114] and individual addressing with multiple atomic sublevels [108]. To address practically relevant sampling problems, our analysis should be extended to disordered systems in two or more dimensions, where it may be challenging to identify an efficient adiabatic path. Hybrid algorithms that combine quantum evolution with classical optimization offer a potential solution to this problem. For instance, the energy of the parent Hamiltonian $H_q(\beta)$ could be minimized using a variational quantum algorithm, similar to previous proposals that directly minimize the free energy [115, 116], without requiring complex measurements of the entanglement entropy. Apart from testing such algorithms on near-terms quantum devices, their novel applications in areas ranging from physical science to machine learning should be explored.
Chapter 4

Light–matter interaction

4.1 Introduction

Light is one of the main tools to probe and manipulate matter. Classically, light–matter interaction is governed by Maxwell’s equations combined with equations of motion that capture the forces acting on the material. As the charges in the system produce electromagnetic fields, the coupled dynamics can give rise to interesting effects even in simple systems such as the single dipole discussed in Section 4.2.1. Effects such as radiation reaction [117] necessitate a careful, self-consistent solution, for which the Green’s function formalism introduced below is ideally suited. The electromagnetic Green’s function is the field produced by a point source, in the present case an oscillating point dipole. This classical object also features in the description of the quantized electromagnetic field as we will see in Section 4.3. In fact, the Green’s function formalism offers a particularly transparent way of quantizing fields in the presence of matter. Applications of the formalism are discussed in Chapters 5 and 6.
4.2 Classical Green’s function formalism

4.2.1 One classical dipole

To introduce our formalism, we consider a single classical dipole. We adopt the Lorentz oscillator model \[118\], where the dipole is represented by a point charge \( q \) with mass \( m \) attached to a spring. Newton’s equation of motion for the position \( \mathbf{r} \) of the charge is given by

\[
\frac{d^2 \mathbf{r}}{dt^2} + \gamma_m \frac{d\mathbf{r}}{dt} + \omega_0^2 \mathbf{r} = \frac{q}{m} \mathbf{E}(\mathbf{r}, t),
\]

(4.1)

where \( \gamma_m \) is the damping rate of the spring, \( \omega_0 \) its resonance frequency, and \( \mathbf{E}(\mathbf{r}, t) \) the electric field at position \( \mathbf{r} \) and time \( t \). We note that \( \gamma_m \) only includes the intrinsic damping of the spring, “nr” standing for nonradiative. There is no need to account for damping due to the energy lost via radiation, so-called radiation reaction \[117\], as it will emerge naturally at a later stage.

For a small dipole close to the origin, we may approximate \( \mathbf{E}(\mathbf{r}, t) \approx \mathbf{E}(0, t) \). The equation of motion is readily solved by a Fourier transform in time:

\[
\mathbf{r}(\omega) = \frac{q}{m(\omega_0^2 - \omega^2 - i\gamma_\text{nr}\omega)} \mathbf{E}(0, \omega).
\]

(4.2)

Defining the dipole moment \( \mathbf{p} = q\mathbf{r} \), this result may be written as

\[
\mathbf{p}(\omega) = \alpha(\omega) \mathbf{E}(0, \omega),
\]

(4.3)

where \( \alpha(\omega) \) is the polarizability of the dipole. If the frequency range of interest as well as \( \gamma_\text{nr} \) are small compared to \( \omega_0 \), we can let \( \omega_0^2 - \omega^2 \approx 2\omega_0(\omega_0 - \omega) \).
and approximate the polarizability by the complex Lorentzian

$$\alpha(\omega) \approx -\frac{q^2}{2m\omega_0} \frac{1}{\omega \omega_0 + i\gamma_{\text{nr}}/2}.$$ \hspace{1cm} (4.4)

While it is straightforward to proceed without this approximation, it conveniently simplifies the discussion. In addition, the approximation is equivalent to the rotating-wave approximation typically employed in quantum mechanical treatments and thereby facilitates comparison between the classical and the quantum result.

Solving for the dynamics of the dipole is rather subtle as the dipole interacts with the field produced by itself, giving rise to radiation reaction as mentioned above. A direct approach to ensure self-consistency is to formally solve the wave equation

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}, \omega) - \frac{\omega^2}{c^2} \mathbf{E}(\mathbf{r}, \omega) = \frac{1}{\varepsilon_0} \frac{\omega^2}{c^2} \mathbf{P}(\mathbf{r}, \omega),$$ \hspace{1cm} (4.5)

where $\mathbf{P}(\mathbf{r}, \omega)$ is the electric polarization. In the present case of a single point dipole, we have $\mathbf{P}(\mathbf{r}, \omega) = \mathbf{p}(\omega)\delta(\mathbf{r})$. For simplicity, we focus on free space, although the approach readily generalizes to arbitrary dielectric environments.

The solution of Equation (4.5) can be written as

$$\mathbf{E}(\mathbf{r}, \omega) = \mathbf{E}_0(\mathbf{r}, \omega) + \frac{1}{\varepsilon_0} \frac{\omega^2}{c^2} \int d\mathbf{r}' \mathcal{G}(\mathbf{r}, \mathbf{r}'; \omega) \mathbf{P}(\mathbf{r}', \omega),$$ \hspace{1cm} (4.6)

where $\mathbf{E}_0(\mathbf{r}, \omega)$ is a homogeneous solution of the wave equation and $\mathcal{G}(\mathbf{r}, \mathbf{r}'; \omega)$ is the dyadic Green’s function. The Green’s function solves the wave equation
with a source term. Explicitly,\[\begin{align} &\left[\partial_\alpha \delta_\rho - \partial_\rho \partial_\alpha \delta_\rho - \frac{\omega^2}{c^2} \delta_\rho\right] G_{\rho\beta}(\mathbf{r}, \mathbf{r}'; \omega) = \delta_{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}'). \tag{4.7}\end{align}\]

Here, $\partial_\alpha$ denotes the derivative with respect to the $\alpha$ component of $\mathbf{r}$ and repeated indices are summed over. We further made use of the identity $\nabla \times \nabla \times \mathbf{E} = \nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E}$. In physical terms, $G_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; \omega)$ is proportional to the $\alpha$ component of the electric field at position $\mathbf{r}$ produced by a point dipole at position $\mathbf{r}'$ oscillating with frequency $\omega$ along the $\beta$ direction. In a translationally invariant environment, the Green’s function only depends on $\mathbf{r}$ and $\mathbf{r}'$ through $\mathbf{r} - \mathbf{r}'$ but we will keep the dependence on both parameters for generality. The differential equation can be solved analytically in free space to obtain

\[
G_{\alpha\beta}(\mathbf{r}, 0; \omega) = \frac{e^{i k r}}{4 \pi r} \left[ \left( 1 + \frac{i}{k r} - \frac{1}{k^2 r^2} \right) \delta_{\alpha\beta} - \left( 1 + \frac{3 i}{k r} - \frac{3}{k^2 r^2} \right) \frac{r_\alpha r_\beta}{r^2} \right]
- \frac{1}{3 k^2} \delta_{\alpha\beta} \delta(\mathbf{r}), \tag{4.8}\]

where $k = \omega/c$ and $r = |\mathbf{r}|$.

Returning to the point dipole, the electric field can now be written as

\[
\mathbf{E}(\mathbf{r}, \omega) = \mathbf{E}_0(\mathbf{r}, \omega) + \frac{1}{\varepsilon_0} \frac{\omega^2}{c^2} \mathcal{G}(\mathbf{r}, r; 0; \omega) \alpha(\omega) \mathbf{E}(0, \omega). \tag{4.9}\]

The term $\mathbf{E}_0(\mathbf{r}, \omega)$ is determined boundary conditions. In practice, it is often specified as an input field used to drive the dipole. We emphasize that the second term involves the total field $\mathbf{E}(0, \omega)$ such that the self-interaction of the dipole is fully taken into account. By evaluating the above equation at
\[ \mathbf{r} = 0, \text{ we can solve for } \mathbf{E}(0, \omega) \text{ and thus obtain the dipole moment } \]

\[ \mathbf{p}(\omega) = -\frac{q^2}{2m\omega_0} \left[ \left( \omega - \omega_0 + \frac{i}{2} \gamma_{nr} \right) \mathbb{I} + \frac{q^2 \omega^2}{2\varepsilon_0 mc^2 \omega_0} \mathcal{G}(0, 0; \omega) \right]^{-1} \mathbf{E}_0(0, \omega). \]

(4.10)

The isotropy of free space implies that \( \mathcal{G}(0, 0; \omega) \) is proportional to the identity, allowing us to replace the term in brackets by a scalar. To simplify the result, we ignore the frequency dependence of the last term between the brackets, setting \( \omega = \omega_0 \). This is known as the Markov approximation, the validity of which will be discussed below. We introduce the effective polarizability

\[ \alpha_{\text{eff}}(\omega) = -\frac{q^2}{2m\omega_0} \frac{1}{\omega - (\omega_0 + \Delta) + i(\gamma_{nr} + \gamma_{r})/2}, \]

(4.11)

where

\[ \Delta = -\frac{q^2 \omega_0}{2\varepsilon_0 mc^2} \text{ Re } \mathcal{G}(0, 0; \omega_0), \quad \gamma_{r} = \frac{q^2 \omega_0}{\varepsilon_0 mc^2} \text{ Im } \mathcal{G}(0, 0; \omega_0), \]

(4.12)

such that \( \mathbf{p}(\omega) = \alpha_{\text{eff}}(\omega)\mathbf{E}_0(0, \omega) \). Comparing with Equation (4.3), we can see that the total field \( \mathbf{E}(0, \omega) \) has been replaced by the input field \( \mathbf{E}_0(0, \omega) \) and all effects due to self-interaction have been absorbed into the effective polarizability.

Self-interaction affects the dipole in two ways: they shift the resonance frequency by \( \Delta \) and induce radiative decay at rate \( \gamma_{r} \). However, the real part of \( \mathcal{G}(\mathbf{r}, 0; \omega) \) diverges as \( r \to 0 \) such that \( \Delta \) is ill defined. This is not particularly surprising as this term corresponds to the energy of a point dipole interacting with itself. We should not be disturbed by this since working with a point dipole is merely a mathematical convenience with which we approximate a
finite sized system. We may therefore simply deal with this issue by ignoring \( \Delta \) entirely and setting \( \omega_0 \) to the experimentally observed resonance frequency.

The decay rate \( \gamma_r \), on the other hand, is well defined. One can show from Equation (4.8) that in free space

\[
\text{Im} \mathcal{G}(0, 0; \omega) = \frac{1}{6\pi} \frac{\omega}{c} \tag{4.13}
\]

and hence

\[
\gamma_r = \frac{q^2 \omega_0^2}{6\pi \varepsilon_0 mc^3}. \tag{4.14}
\]

This rate is in perfect agreement with the Larmor formula [117]. The dipole loses energy with rate \( \gamma_r \) due to radiation, resulting in the radiated power

\[
P = \gamma_r m \omega_0^2 x_0^2 / 2 = q^2 \langle a^2 \rangle / 12\pi \varepsilon_0 c^3,
\]

where \( x_0 \) is the amplitude of oscillation and \( \langle a^2 \rangle \) the square of the acceleration averaged over one cycle.

To conclude this section, we comment on the validity of the approximations made above. First, we let \( \omega + \omega_0 \approx 2\omega_0 \), which can be justified when the frequency ranged explored is small compared to \( \omega_0 \). Since the oscillator is broadened by \( \gamma_{nr} + \gamma_r \), this leads us to the condition \( \gamma_{nr} + \gamma_r \ll \omega_0 \). Next, we made the Markov approximation, which requires that \( \omega^2 \mathcal{G}(0, 0; \omega) \) can be taken to be a constant. In free space, this is again leads to the constraint \( \gamma_{nr} + \gamma_r \ll \omega_0 \). However, in a more complex dielectric environment such as a cavity, the Markov approximation can give rise to more stringent conditions as the Green’s function may depend strongly on the frequency. Finally, the discussion is of course only valid for systems that are sufficiently small to be indistinguishable from a point dipole. This implies that the wavelength \( 2\pi c / \lambda \) must be much greater than the largest length scale of the physical dipole.
4.2.2 Many classical dipoles

We next generalize the approach to multiple dipoles located at positions $\mathbf{r}_n$. As a slight extension of the above discussion, we take the dipoles to be polarizable only along the unit vector $\hat{\mathbf{d}}_n$. While the orientation may differ from dipole to dipole, we assume that all their other properties are identical. The polarizability of dipole $n$, which is now a tensor, is given by

$$\alpha_n(\omega) = -\frac{q^2}{2m\omega_0} \frac{1}{\omega - \omega_0} \hat{\mathbf{d}}_n \hat{\mathbf{d}}_n^T. \quad (4.15)$$

The isotropic case can be readily recovered by placing three dipoles with mutually orthogonal polarizations at the each location.

Following the same steps as for the single dipole and making the same approximations, we find the polarization of the dipole $m$ to be given by

$$\mathbf{p}_m(\omega) = -\frac{q^2}{2m\omega_0} \hat{\mathbf{d}}_m \sum_n [\omega - H]^{-1}_{mn} \hat{\mathbf{d}}_n^T \mathbf{E}_0(\mathbf{r}_n, \omega), \quad (4.16)$$

where the matrix $H$ is defined by its matrix elements

$$H_{mn} = \omega_0 \delta_{mn} - \frac{q^2 \omega_0}{2\varepsilon_0 mc^2} \hat{\mathbf{d}}_m \mathbf{G}(\mathbf{r}_m, \mathbf{r}_n; \omega_0) \hat{\mathbf{d}}_n. \quad (4.17)$$

For simplicity, we set the $\gamma_{nr} = 0$ throughout this section.

Equation (4.16) shows that the polarization of dipole $m$ depends not only on the field at position $\mathbf{r}_m$ but also at the positions of all other dipoles. This is of course expected as the dipoles scatter radiation and thereby interact with each other. The interactions are quantitatively captured by the second term.

47
in Equation (4.17), which can be separated into a Hermitian part,

\[ \Delta_{mn} = -\frac{q^2\omega_0}{2\varepsilon_0 mc^2} \hat{d}^\dagger_m \text{Re} \mathcal{G}(\mathbf{r}_m, \mathbf{r}_n; \omega_0) \hat{d}_n, \]  

(4.18)

and an anti-Hermitian part,

\[ \Gamma_{mn} = \frac{q^2\omega_0}{\varepsilon_0 mc^2} \hat{d}^\dagger_m \text{Im} \mathcal{G}(\mathbf{r}_m, \mathbf{r}_n; \omega_0) \hat{d}_n. \]  

(4.19)

As in the case of a single dipole, we should ignore the divergent terms \( \Delta_{nn} \), which simply renormalize the transition frequency.

Before proceeding to the quantum treatment, we note that the case of multiple dipoles requires an additional assumption. For the Markov approximation to be valid when \( \mathbf{r}_m \neq \mathbf{r}_n \), we need the time for radiation to travel between the atoms to be small compared to all other time scales. This results in the condition \( (\gamma_m + \gamma_n)|\mathbf{r}_m - \mathbf{r}_n|/c \ll 1 \).

### 4.3 Quantum formalism

So far, our discussion has been entirely classical. A common first step in a quantum mechanical treatment is to make a semi-classical approximation, where the matter degrees of freedom are quantized while the electromagnetic field remains classical. However, as the electromagnetic field mediates interactions between different dipoles, it may become entangled with them. The Markov approximation, which already featured in the classical formalism, turns out to be crucial to be able to neglect this entanglement and to separate the matter and electromagnetic degrees of freedom.
Most approaches to derive the semi-classical equations of motion start from fully quantized fields before eliminating the photonic degrees of freedom [119–122]. Such an approach has the advantage that the starting point is completely rigorous and that all approximations can be stated formally. Below, we present an alternative derivation that emphasizes physical intuition over rigor. We are able to replicate many steps from the classical formalism by applying the Markov approximation before quantizing the field. By contrast, approaches based on quantized electromagnetic modes often lack a transparent connection to standard classical electromagnetism.

We again consider a set of point dipoles located at positions $\mathbf{r}_n$. We showed above that the classical electromagnetic field for some input field $\mathbf{E}_0(\mathbf{r}, \omega)$ satisfies

$$
\mathbf{E}(\mathbf{r}, \omega) = \mathbf{E}_0(\mathbf{r}, \omega) + \frac{1}{\varepsilon_0 c^2} \sum_n G(\mathbf{r}, \mathbf{r}_n; \omega) \mathbf{p}_n(\omega). \quad (4.20)
$$

The fact that $\mathbf{E}(\mathbf{r}, t)$ is real implies that $\mathbf{E}(\mathbf{r}, -\omega) = \mathbf{E}(\mathbf{r}, \omega)^*$. Therefore, it suffices to consider the positive frequency part

$$
\mathbf{E}^+(\mathbf{r}, \omega) = \mathbf{E}(\mathbf{r}, \omega) \Theta(\omega) = \mathbf{E}_0^+(\mathbf{r}, \omega) + \frac{1}{\varepsilon_0 c^2} \sum_n G(\mathbf{r}, \mathbf{r}_n; \omega) \mathbf{p}_n^+(\omega), \quad (4.21)
$$

where $\Theta(\omega)$ is the Heaviside step function and $\mathbf{E}_0^+(\mathbf{r}, \omega)$ and $\mathbf{p}_n^+$ are defined in an analogous manner. We again assume that the dipoles all have the same resonance frequency $\omega_0$. In this case, the polarization $\mathbf{p}_m(\omega)$ is expected to be sharply peaked around $\omega_0$, as long as the decay rates and the interactions between dipoles are both small compared to $\omega_0$. Assuming that the Green’s function is roughly constant over the relevant frequency range close to $\omega_0$, we
can approximate the real-time dynamics by
\[ E^+(r, t) \approx E_0^+(r, t) + \frac{1}{\varepsilon_0 c^2} \sum_n G(r, r_n; \omega_0) p_n^+(t). \] (4.22)

This is yet again the Markov approximation, valid under the conditions discussed in the previous sections.

Equation (4.22) can be readily quantized by promoting the electric field and the dipole moments to operators in the Heisenberg picture. For this section only, we will put hats on all operators to make clear the distinction from the classical formalism. The term \( \hat{E}^+_0(r, t) \) describes the free evolution of the input field, as would be the case in the absence of the dipoles. The dipole moments can further be expressed in terms of the transition dipole moments \( d_n \) and the lowering operators \( \hat{\sigma}_n \) as
\[ \hat{p}_n^+(t) = d_n \hat{\sigma}_n(t). \] (4.23)

There is no need to make any further assumptions about the nature of the lowering operators. They could for instance, be associated with a single transition in an atom or with the entire ladder of states of a harmonic oscillator. While we consider only a single transition per site, the generalization to multiple degenerate transitions with differently aligned dipoles is straightforward.

Eq. (4.22) allows us to determine the electric field everywhere, provided the evolution of the atomic polarization is known. In order to derive an equation of motion for the atoms, we start from the full Hamiltonian
\[ \hat{H} = \hat{H}_d + \hat{H}_{ph} - \sum_n \left[ d_n^+ \hat{E}^+(r_n) \hat{\sigma}_n^+ + h.c. \right], \] (4.24)
where $\hat{H}_d$ and $\hat{H}_{ph}$ describe the free evolution of the dipoles and the electric field (photons), respectively. Even though the exact form of these Hamiltonians is irrelevant for the present discussion, we should let $\hat{H}_d = \omega_0 \sum_n \hat{\sigma}_n^\dagger \hat{\sigma}_n$ to be consistent with the assumption that all dipoles have the same resonance frequency $\omega_0$. The interaction term is the standard Hamiltonian for a dipole interacting with the electric field, where we already made the rotating-wave approximation. The rotating-wave approximation amounts to neglecting terms that oscillate with frequency $2\omega_0$ and is equivalent to setting $\omega^2 - \omega_0^2 \approx 2\omega_0(\omega - \omega_0)$ in Equation (4.4).

The Heisenberg equation of motion for any dipole operator $\hat{Q}$, that is any operator that commutes with all photonic operators, is given by (we set $\hbar = 1$ everywhere except for definitions of physically significant quantities)

$$\frac{d}{dt} \hat{Q} = -i \left[ \hat{Q}, \hat{H}_a \right] + i \sum_n \left[ \hat{Q}, \hat{\sigma}_n^\dagger \right] \mathbf{d}_n \hat{E}_n^+(\mathbf{r}_n) + i \sum_n \hat{\mathbf{E}}_n^+(\mathbf{r}_n) \dagger \mathbf{d}_n \left[ \hat{Q}, \hat{\sigma}_n \right]. \quad (4.25)$$

We have arranged the terms in such a way that the dipole operators stand to the left of photonic annihilation operators and to the right of creation operators. This form of normal ordering proves convenient as we substitute in from Eq. (4.22) to obtain

$$\frac{d}{dt} \hat{Q} = -i \left[ \hat{Q}, \hat{H}_a + \sum_{m,n} \Delta_{mn} \hat{\sigma}_m^\dagger \hat{\sigma}_n \right] + \sum_{m,n} \Gamma_{mn} \left( \hat{\sigma}_m^\dagger \hat{\sigma}_n - \frac{1}{2} \left\{ \hat{\sigma}_m^\dagger \hat{\sigma}_n, \hat{Q} \right\} \right) + i \sum_n \left[ \hat{Q}, \hat{\sigma}_n^\dagger \right] \mathbf{d}_n \hat{E}_n^+(\mathbf{r}_n) + i \sum_n \hat{\mathbf{E}}_n^+(\mathbf{r}_n) \dagger \mathbf{d}_n \left[ \hat{Q}, \hat{\sigma}_n \right]. \quad (4.26)$$
where we defined

\begin{align}
\Delta_{mn} &= -\frac{\omega_0^2}{\varepsilon_0 \hbar c^2} d_m^\dagger \text{Re} \mathcal{G}(r_m, r_n; \omega_0) d_n, \\
\Gamma_{mn} &= \frac{2\omega_0^2}{\varepsilon_0 \hbar c^2} d_m^\dagger \text{Im} \mathcal{G}(r_m, r_n; \omega_0) d_n.
\end{align}

(4.27)  

(4.28)

While these expressions are already starting to look a lot like their classical counterparts, we have one final nontrivial step to make before we discuss the result. In particular, we would like to separate the classical part of the electric field from its quantum fluctuation. We assume that the dipoles and the electromagnetic field are initially uncorrelated, i.e. they are in a product state. Furthermore, the photons are assumed to be in a coherent state. These assumptions are necessary for the dipoles and the field to remain largely uncorrelated at later times, which is commonly referred to as the Born approximation. To implement these steps, we let

\[
\hat{E}_0^+(r, t) = E_0^+(r, t) + \delta \hat{E}_0^+(r, t).
\]

(4.29)

Here \( E_0^+(r, t) \) is the positive frequency component of the freely evolving classical field as set by the initial conditions. The term \( \delta \hat{E}_0^+(r, t) \) captures the quantum fluctuations. With these definitions, the Heisenberg equation be-
\[
\frac{d}{dt} \hat{Q} = -i \left[ \hat{Q}, \hat{H}_a + \sum_{m,n} \Delta_{mn} \hat{\sigma}_m^+ \hat{\sigma}_n - \sum_n \left( \hat{d}_n^\dagger \hat{E}_0^+(\mathbf{r}_n,t) \hat{\sigma}_n^+ + \text{h.c.} \right) \right] \\
+ \sum_{m,n} \Gamma_{mn} \left( \hat{\sigma}_m^+ \hat{Q} \hat{\sigma}_n - \frac{1}{2} \left\{ \hat{\sigma}_m^+ \hat{\sigma}_n, \hat{Q} \right\} \right) \\
+ i \sum_n \left[ \hat{Q}, \hat{\sigma}_n^+ \right] \hat{d}_n^\dagger \delta \hat{E}_0^+(\mathbf{r}_n) + i \sum_n \delta \hat{E}_0^+(\mathbf{r}_n) \hat{d}_n \left[ \hat{Q}, \hat{\sigma}_n \right]
\]

(4.30)

The first two lines only depend on classical properties of the electric field. The third line may be viewed as quantum noise. It is important to remember that \( \delta \hat{E}_0^+(\mathbf{r}_n) \) is an operator evolving in the Heisenberg picture under the free Hamiltonian \( \hat{H}_\text{ph} \). Given that the photons are initially in a coherent state, \( \delta \hat{E}_0^+(\mathbf{r}_n) \) annihilates the state of the entire system at any time. If we trace out over the photons entirely, the last line in Equation (4.30) will vanish, leaving us with an equation of motion for the dipoles driven by a classical field. Nevertheless, these terms are important when computing correlation functions and are in fact an inevitable consequence of the fluctuation–dissipation theorem that states that any damping is necessarily accompanied by noise. In analogy with classical damped systems, the quantum noise terms are often referred to as Langevin noise and the full equation of motion is known as the Heisenberg–Langevin equation [123].

Since the Heisenberg–Langevin equation holds for any atomic operator \( \hat{Q} \), we can translate it back into the Schrödinger picture. For the density matrix \( \hat{\rho}(t) \) in the Schrödinger picture, we have \( \text{tr} \left[ \hat{Q}(t) \hat{\rho}(0) \right] = \text{tr} \left[ \hat{Q}(0) \hat{\rho}(t) \right] \). Hence,
\[ \dot{\rho}(t) \text{ evolves according to the master equation} \]

\[
\frac{d}{dt}\dot{\rho}(t) = -i \left[ \hat{H}, \dot{\rho}(t) \right] + \mathcal{D}[\dot{\rho}(t)], \tag{4.31}
\]

where the unitary dynamics are determined by the Hamiltonian

\[
\hat{H} = \hat{H}_u + \sum_{m,n} \Delta_{mn} \hat{\sigma}_m^\dagger \hat{\sigma}_n - \sum_n \left[ d_n^\dagger \mathbf{E}_0^\dagger(\mathbf{r}_n, t) \hat{\sigma}_n^\dagger + \text{h.c.} \right], \tag{4.32}
\]

and the dissipator is given by

\[
\mathcal{D}[\dot{\rho}] = \sum_{m,n} \Gamma_{mn} \left( \hat{\sigma}_n \hat{\sigma}_m^\dagger - \frac{1}{2} \left\{ \hat{\sigma}_m^\dagger \hat{\sigma}_n, \dot{\rho} \right\} \right). \tag{4.33}
\]

We are now in the position to provide a physical interpretation for the quantities \( \Delta_{mn} \) and \( \Gamma_{mn} \). The physical picture emerges more naturally than in the classical discussion because we have succeeded in clearly separating the dipole degrees of freedom from the photonic degrees of freedom. The off-diagonal element \( \Delta_{mn} \) is the rate of an excitation hopping from dipole \( n \) to dipole \( m \) as mediated by the exchange of a photon. The diagonal element \( \Delta_{nn} \) corresponds to a shift of the resonance frequency of dipole \( n \). The shifts are divergent as in the classical case for the same reasons. We will ignore them in what follows. The term involving \( \Gamma_{nn} \) describes spontaneous emission from dipole \( n \), while the off-diagonal elements account for interference between dipoles, which can enhance or reduce the emission rate.

Comparing the classical expressions Equation (4.18) and Equation (4.19) for \( \Delta_{mn} \) and \( \Gamma_{mn} \) with their quantum counterparts, Equation (4.27) and Equa-
tion (4.28), we observe that they are in perfect agreement when

\[ |d_n|^2 = \frac{\hbar}{2m\omega_0} q^2. \]  

(4.34)

This is indeed the correct expression for the transition dipole moment of a quantum harmonic oscillator with mass \( m \), frequency \( \omega_0 \), and charge \( q \). For more general quantum mechanical systems, this relation prescribes how to choose the properties of the Lorentz model that will yield the same decay rates and interaction strengths between the dipoles. Indeed, the ratio between the two sides of the equation can be related to the so-called oscillator strength \([124]\) that quantifies how closely an atomic transition resembles a classical, harmonic oscillator. More conventionally, the oscillator is defined in terms of the ratio between the radiative decay rates of the classical and quantum systems. The classical rate was given in Equation (4.14), while the quantum result reads

\[ \gamma_r = \frac{\omega_0^2 |d_n|^2}{3\pi \varepsilon_0 \hbar c^3}. \]  

(4.35)

We conclude this section by outlining the general steps to solve a problem within the quantum framework. First one computes the Green’s function \( G(r, r'; \omega) \) for the dielectric environment of interest, which immediately yields the quantities \( \Delta_{mn} \) and \( \Gamma_{mn} \). We emphasize that this first step is a purely classical solution of Maxwell’s equations. Before proceeding, one should verify that all conditions required for the Markov approximation are satisfied. Next, one solves for the system dynamics using either the Heisenberg–Langevin equation, Equation (4.30), or the master equation, Equation (4.31), given the desired input field. In applications where the scattered field is of interest,
one finally plugs this result into Equation (4.22) to obtain the (quantized) total field $\hat{E}^+(r, t)$. 
Chapter 5

Ordered arrays of atoms

5.1 Band structure

As a first application of the formalism developed in Chapter 4, we consider the optical properties of an ordered array of atoms. For concreteness, we focus on a square lattice with lattice constant $a$ although the results can be readily generalized to other lattices. At each lattice site, we place an atom with an isotropic response to the electric field. This can be realized by preparing the atoms in a $J = 0$ state and probing close to the resonance of a transition to a $J = 1$ state. Hence, there will be three transitions per site with dipole moments $d_\alpha$, $\alpha = 1, 2, 3$. Isotropy requires that all dipole moments have the same magnitude $d$ and that $\sum_\alpha d_\alpha d_\alpha^\dagger = d^2 \mathbb{I}$. We note that we will only consider linear response such that one could obtain the same results with classical dipoles instead of atoms.

We assume that all atoms are identical with resonance frequency $\omega_0$. Instead of the full master equation, we will work with a non-Hermitian Hamiltonian. This approach is exactly equivalent when quantum jumps are in-
cluded [125]. However, quantum jumps are negligible in linear response and we will therefore not discuss them further. For a monochromatic drive with frequency $\omega_d$, the non-Hermitian Hamiltonian in the rotating frame is given by

$$
H = \sum_{m,n,\alpha,\beta} \left[ (\omega - \omega_d) \delta_{mn} \delta_{\alpha\beta} + \Delta_{\alpha\beta}(r_m, r_n) - \frac{i}{2} \Gamma_{\alpha\beta}(r_m, r_n) \right] \sigma^\dagger_{m\alpha}\sigma_{n\beta} - \sum_{m,\alpha} \left[ d^\dagger_\alpha E^\dagger_0(r_m, 0) \sigma^\dagger_{m\alpha} + \text{h.c.} \right], 
$$

where the sums over $m$ and $n$ run over all lattice sites with corresponding position vectors $r_m, r_n$. The incident field $E^\dagger_0(r, z)$ is evaluated in the plane of the array, taken to be $z = 0$. Expressions for the Hermitian matrices $\Delta$ and $\Gamma$ were derived in Chapter 4. Concisely,

$$
\Delta_{\alpha\beta}(r_m, r_n) - \frac{i}{2} \Gamma_{\alpha\beta}(r_m, r_n) = -\frac{3\pi c\gamma_0}{\omega_0} d^\dagger_\alpha G(r_m, r_n; \omega_0) \hat{d}_\beta, 
$$

where $\gamma_0 = d^2 \omega_0^3 / 3\pi \varepsilon_0 hc^3$ is the free-space decay rate of the atoms.

Owing to the discrete translational invariance of the lattice, the Hamiltonian is diagonal in momentum space. We define the operators

$$
\sigma_{k\alpha} = \frac{1}{\sqrt{N}} \sum_m \sigma_{m\alpha} e^{-i k \cdot r_m}, 
$$

where $N$ is the number of atoms, which will be taken to infinity at the end. Momenta that differ by a reciprocal lattice vector yield the same operator (up to a phase). Unless noted otherwise, we will assume that $k$ is confined to the first Brillouin zone. The normalization is chosen such that $[\sigma_{m\alpha}, \sigma^\dagger_{n\beta}] = \delta_{mn} \delta_{\alpha\beta}$.
\( \delta_{mn} \delta_{\alpha\beta} \) implies \( \left[ \sigma_{k\alpha}, \sigma_{k'\beta}^\dagger \right] = \delta_{kk'} \delta_{\alpha\beta}. \) The inverse Fourier transform is given by

\[
\sigma_{m\alpha} = \frac{1}{\sqrt{N}} \sum_k \sigma_{k\alpha} e^{ikr_m}. \tag{5.4}
\]

Substituting this expression into Equation (5.1) yields

\[
H = \sum_{k,\alpha,\beta} \left[ (\omega_0 - \omega_\alpha) \delta_{\alpha\beta} + \Delta_{\alpha\beta}(k) - \frac{i}{2} \Gamma_{\alpha\beta}(k) \right] \sigma_{k\alpha}^\dagger \sigma_{k\beta} - \sum_{k,\alpha} \left[ \Omega_{\alpha}(k) \sigma_{k\alpha}^\dagger + \text{h.c.} \right], \tag{5.5}
\]

where

\[
\Omega_{\alpha}(k) = \frac{1}{\sqrt{N}} \mathbf{q}^\dagger_{\alpha} \sum_m \mathbf{e}_{0m}^+ (r_m, 0) e^{-ikr_m} \tag{5.6}
\]

and

\[
\Delta_{\alpha\beta}(k) - \frac{i}{2} \Gamma_{\alpha\beta}(k) = -\frac{3\pi\gamma_0}{(\omega_0/c)} \mathbf{d}^\dagger_{\alpha} \sum_{\mathbf{R}} \mathcal{G}(\mathbf{R}, 0; \omega_0) e^{-ik \mathbf{R}} \mathbf{d}_{\beta}. \tag{5.7}
\]

Here, \( \mathbf{R} \) are lattice vectors and we made use of the fact that because of translational invariance \( \mathcal{G}(\mathbf{r}, \mathbf{r}'; \omega) \) only depends on the positions through their difference, \( \mathbf{r} - \mathbf{r}' \).

We can see from Equation (5.5) that the eigenvalues of the \( 3 \times 3 \) matrix \( \Delta_{\alpha\beta}(k) \) determine the energies of the eigenmodes with momentum \( k \). Similarly, the eigenvalues of \( \Gamma_{\alpha\beta}(k) \) tell us about the dissipative eigenmodes. We note that \( \Delta_{\alpha\beta}(k) \) and \( \Gamma_{\alpha\beta}(k) \) do in general not commute and may therefore not have the same eigenvectors. While Equation (5.7) can be evaluated numerically, it is more convenient to carry out the computation in momentum

\footnote{In linear response, it is justified to use the commutation relations of a harmonic oscillator even for atoms with a single excited state.}
space. We define the Fourier transformed Green’s function

$$G(k; z, z'; \omega) = \int d^2 r \ G(r, z; 0, z'; \omega)e^{-ik r}. \quad (5.8)$$

The inverse transform is given by

$$G(r, z; 0, z'; \omega) = \frac{1}{NA} \sum_B \sum_k G(k + B; z, z'; \omega)e^{i(k+\text{B} \cdot r)}, \quad (5.9)$$

where $A$ is the area a unit cell and $B$ are the reciprocal lattice vectors. The introduction of reciprocal lattice vectors is convenient as it allows us to again restrict $k$ to the first Brillouin zone. Equation (5.7) becomes

$$\Delta_{\alpha \beta}(k) - \frac{i}{2} \Gamma_{\alpha \beta}(k) = -\frac{3\pi\gamma_0}{(\omega_0/c)A} \hat{d}_\alpha \sum_B G(k + B; 0, 0; \omega_0)\hat{d}_\beta. \quad (5.10)$$

One can show that in free space

$$G(k; z, z'; \omega) = \frac{i}{2k_z}e^{ik_z|s|}$$

$$-\frac{i}{2k_z(\omega/c)^2}e^{ik_z|s|} \begin{pmatrix}
  k_x^2 & k_x k_y & k_x k_z \text{sgn}(s) \\
  k_x k_y & k_y^2 & k_y k_z \text{sgn}(s) \\
  k_x k_z \text{sgn}(s) & k_y k_z \text{sgn}(s) & k_z^2 + 2ik_z \delta(s)
\end{pmatrix}, \quad (5.11)$$

where $s = z - z'$ and $k_z = \sqrt{(\omega/c)^2 - k^2}$ along with the convention that $\text{sgn}(0) = 0$. We note that $k_z$ is in general complex: The Green’s function describes propagating modes when $k < \omega/c$ and evanescent modes otherwise. Dropping the delta function, which corresponds to an infinite energy shift of
the out-of-plane polarized mode, yields

\[
G(k; 0, 0; \omega) = \frac{i}{2k_z (\omega/c)^2} \begin{pmatrix}
(\omega/c)^2 - k_x^2 & -k_x k_y & 0 \\
-k_x k_y & (\omega/c)^2 - k_y^2 & 0 \\
0 & 0 & k^2
\end{pmatrix}.
\tag{5.12}
\]

We can see that \(G(k; 0, 0; \omega)\) is anti-Hermitian when \(k < \omega/c\) and Hermitian otherwise. To proceed, we assume that the lattice constant \(a\) is smaller than \(\lambda_0/2\), with \(\lambda_0 = 2\pi c/\omega_0\) the resonant wavelength. This condition ensures that there is only a single Bragg scattering order for any incident angle. The Brillouin zone is separated into two regions by the circle of radius \(\omega_0/c\), the so-called light cone, as shown in Figure 5.1. Modes with momenta outside the light cone do not couple to propagating modes and therefore exhibit no spontaneous decay.

![Figure 5.1: First Brillouin zone of a square lattice showing the location of the high-symmetry points \(\Gamma = (0, 0)\), \(X = (\pi/a, 0)\), \(M = (\pi/a, \pi/a)\), where \(a\) is the lattice constant. The dashed circle with radius \(2\pi/\lambda_0\) indicates the light cone. The light cone is fully contained within the first Brillouin zone when \(a < \lambda_0/2\).](image)

To verify this statement formally, we observe that all terms in Equation (5.10) with \(B \neq 0\) are Hermitian for any value of \(k\) inside the first
Brillouin zone. Hence, only the $B = 0$ term contributes to $\Gamma(k)$, giving

$$\Gamma(k) = \frac{3\pi\gamma_0}{k_z(\omega_0/c)^3a^2} \Theta \left( \frac{\omega_0}{c} - k \right) \begin{pmatrix}
(\omega_0/c)^2 - k_x^2 & -k_xk_y & 0 \\
-k_xk_y & (\omega_0/c)^2 - k_y^2 & 0 \\
0 & 0 & k^2
\end{pmatrix}.$$  \hspace{1cm} (5.13)

The step function $\Theta((\omega_0/c) - k)$ shows that indeed modes outside the light cone do not decay. Inside the light cone, the three eigenvalues are

$$\Gamma_{\parallel}(k) = \frac{3\pi\gamma_0}{(\omega_0/c)^2a^2} \cos \theta,$$  \hspace{1cm} (5.14)

$$\Gamma_{\perp}(k) = \frac{3\pi\gamma_0}{(\omega_0/c)^2a^2} \frac{1}{\cos \theta},$$  \hspace{1cm} (5.15)

$$\Gamma_{\pi}(k) = \frac{3\pi\gamma_0}{(\omega_0/c)^2a^2} \frac{\sin^2 \theta}{\cos \theta},$$  \hspace{1cm} (5.16)

where $\cos \theta = ck_z/\omega_0$ and $\sin \theta = ck/\omega_0$. The subscripts refer to the polarizations of the respective eigenmodes. The eigenmodes associated with $\Gamma_{\parallel}(k)$ and $\Gamma_{\perp}(k)$ are polarized in the $xy$ plane, parallel and perpendicular to $k$, respectively. The subscript $\pi$ refers to an out-of-plane polarized mode, along the $z$ axis.

In physical terms, $\theta$ is the angle between the $z$ axis and the direction of propagation of the emitted light. The dependence of the three decay rates on $\theta$ has a simple geometric interpretation. At $\theta = 0$ ($k = 0$), we have $\Gamma_{\parallel} = \Gamma_{\perp}$ as required by the four-fold rotational symmetry of the square lattice.\textsuperscript{2} Furthermore $\Gamma_{\pi} = 0$ since a dipole polarized along the $z$ axis may not radiate upwards. An analogous argument explains why $\Gamma_{\parallel} = 0$ when $\theta = \pi/2$. The

\textsuperscript{2}The polarizations $\parallel$ and $\perp$ are ill defined when $k = 0$. One may adopt an arbitrary convention for this case, e.g. $\parallel$ along the $x$ axis and $\perp$ along $y$. 

62
rates $\Gamma_\perp$ and $\Gamma_\parallel$ diverge as $\theta$ approaches $\pi/2$, which is explained by the constructive interference of all atoms with the emitted light propagating parallel to the array.

The expression for $\Delta(k)$ involves a sum over an infinite number of lattice vectors, either in real or reciprocal space, which cannot be evaluated analytically. In both cases, we have to subtract the divergent self-interaction term. In real space this is trivially accomplished by dropping the $R = 0$ term. To evaluate the sum in momentum space, Equation (5.10), which often converges faster, it is necessary to regularize the Green’s function. We show in Appendix C.1 how this can be done using a Gaussian regulator that cuts off high momenta.

The numerical results for the three eigenvalues of $\Delta$ are plotted for a square lattice with $a = 0.2\lambda_0$ in Figure 5.2. The $\pi$-polarized mode is decoupled from the in-plane modes since the Green’s function is block diagonal. The in-plane modes are degenerate at the high-symmetry points $\Gamma$ and $M$ (see Figure 5.1). For most points in the Brillouin zone, the in-plane eigenmodes are roughly, but not exactly, equal to the eigenmodes derived from $\Gamma(k)$, that is parallel and perpendicular to $k$.

5.2 Reflection and transmission

Having described the internal dynamics of the array, we proceed to its optical properties. After a Fourier transform, the total electric field can be written as

$$E^+(k, z) = E^+_0(k, z) + \frac{\sqrt{N}}{\varepsilon_0} \frac{\omega_0^2}{c^2} G(k, z; 0; \omega_0) \sum_\alpha d_\alpha \sigma_{k+\mathbf{B}_\alpha}. \quad (5.17)$$
Figure 5.2: Band structure: Eigenvalues of the matrix $\Delta$ as a function of momentum for a square lattice with lattice constant $a = 0.2\lambda_0$. The momentum follows straight line segments connecting the high symmetry points shown in Figure 5.1. The vertical dashed lines indicate the location of the light cone.

Since the electric field is defined in the continuum of space, $k$ can take any value. The reciprocal lattice vector $B$ is chosen such that $k + B$ is in the first Brillouin zone.

For a monochromatic input field with frequency $\omega_d$, the steady state expectation value of $\sigma_{k\alpha}$ is found from the Heisenberg–Langevin equations to be given by

$$
\langle \sigma_{k\alpha} \rangle = \sum_{\beta} \left[ (\omega_0 - \omega_d) I + \Delta(k) - \frac{i}{2} \Gamma(k) \right]^{-1} \langle \Omega_{\beta}(k) \rangle.
$$

(5.18)

We can now eliminate the atomic operators to obtain an expression for the total electric field in terms of the input field. Continuing to assume that the response of the atoms is isotropic, we obtain

$$
\langle \mathbf{E}^+(k, z) \rangle = \langle \mathbf{E}_0^+(k, z) \rangle + \frac{1}{\varepsilon_0 A} \frac{\omega_0^2}{c^2} \mathcal{G}(k; z, 0; \omega_0)
$$

$$
\times \left[ (\omega_0 - \omega_d) I + \Delta(k) - \frac{i}{2} \Gamma(k) \right]^{-1} \sum_B \langle \mathbf{E}_0^+(k + B, 0) \rangle.
$$

(5.19)
We only consider the scattered light in the far field such that \( k \) can be assumed to be inside the light cone. Since the wavevector of the incident light is also restricted to the light cone, we only have to include the \( B = 0 \) term when \( a < \lambda/2 \).

The Green’s function appearing in Equation (5.19) can be concisely written as

\[
G(k; z, z'; \omega) = \frac{i}{2k} e^{ik|z-z'|} \left( \mathbf{s}s^\dagger + \mathbf{p}_\rho \mathbf{p}_\rho^\dagger \right),
\]

where \( \rho = \text{sgn}(z - z') \) and

\[
\mathbf{s} = \begin{pmatrix} -\sin \varphi \\ \cos \varphi \\ 0 \end{pmatrix}, \quad \mathbf{p}_\rho = \begin{pmatrix} \rho \cos \theta \cos \varphi \\ \rho \cos \theta \sin \varphi \\ -\sin \theta \end{pmatrix}.
\]

Here, \( \theta \) is the angle of propagation relative to the \( z \) axis, as defined above, and \( \varphi \) denotes the angle between \( k \) and the \( x \) axis. These unit vectors define the transverse polarizations of the field as shown in Figure 5.3. The \( s \) polarization is perpendicular (“senkrecht”) to the plane of incidence, whereas the \( p \) polarization is parallel. The orientation of the \( p \) polarization depends on the direction of propagation in the \( z \) direction.

For an incident field that propagates in the negative \( z \) direction, the total field can now be written as

\[
\langle E^+(k, z) \rangle = \left( e^{-ikz} + e^{ik|z|} S_\rho \right) \langle E^+_0(k, 0) \rangle,
\]
where we recognize the quantity

\[
S_\rho = \frac{i}{2} \Gamma_s(k) \left( \hat{s}\hat{s}^\dagger + \hat{p}_-\hat{p}_-^\dagger \right) \left[ (\omega_0 - \omega_{id})I + \Delta(k) - \frac{i}{2} \Gamma(k) \right]^{-1} \left( \hat{s}\hat{s}^\dagger + \hat{p}_-\hat{p}_-^\dagger \right)
\]

(5.23)

as a scattering matrix. We were allowed to insert the projector \( \hat{s}\hat{s}^\dagger + \hat{p}_-\hat{p}_-^\dagger \) on the right because the incident field is contained in the transverse plane. The amplitude reflection and transmission coefficients are obtained by projecting the matrices

\[
r = S_+, \quad t = \hat{s}\hat{s}^\dagger + \hat{p}_-\hat{p}_-^\dagger + S_-
\]

(5.24)

onto the polarizations of interest. Since the dynamics are linear, the intensity reflection and transmission coefficient are found by taking the absolute value squared.\(^3\)

We conclude this section by considering the special case of normal incidence, \( k = 0 \). We then have \( \hat{s}\hat{s}^\dagger + \hat{p}_-\hat{p}_-^\dagger = \hat{s}\hat{s}^\dagger + \hat{p}_-\hat{p}_-^\dagger = \hat{x}\hat{x}^\dagger + \hat{y}\hat{y}^\dagger \) such that the out of plane polarized mode does not contribute to the scattering. The

\(^3\)This requires that the expectation values of pairs of operators factorize, i.e. \( \langle \sigma_{\alpha}^\dagger \sigma_{\beta} \rangle = \langle \sigma_{\alpha}^\dagger \rangle \langle \sigma_{\beta} \rangle \). This is indeed the case in the absence of nonlinearity and dephasing.

66
in-plane modes are degenerate with an energy shift that we will denote by $\Delta_{xy}$, while their linewidth is given by $\Gamma_{xy} = \frac{3\pi\chi_0}{(\omega_0/c)^2a^2}$. The intensity reflection coefficient is independent of the polarization of the incident light and can be written as

$$R = \frac{(\Gamma_{xy}/2)^2}{(\omega_d - \omega_0 - \Delta_{xy})^2 + (\Gamma_{xy}/2)^2}.$$  

(5.25)

These expression is plotted in Figure 5.4 as a function of the lattice constant. Perfect reflection occurs when $\omega_d = \omega_0 + \Delta_{xy}$, which we now understand as the consequence of a collective resonance, although it may be still seem somewhat peculiar given the diluteness and vanishing thickness of the array. At oblique incidence, we still observe resonances but the analysis is complicated by coupling between the $s$ and $p$ polarizations mediated by the array [2].

![Figure 5.4: Reflection coefficient at normal incidence as a function of frequency and lattice constant. The dashed line indicates $\omega_d = \omega_0 + \Delta_{xy}$, where perfect reflection occurs.](image)

67
5.3 Deterministic interaction with a single atom

The linear response of the atom array is a classical phenomenon, which could equally be observed with classical dipoles. At sufficiently strong driving, the quantum nonlinearity of the atoms will start to play a role, resulting in saturation. The number of photons required to see saturation can be estimated by the number of atoms within the spot size of the incident light. The diffraction limit sets a lower bound of order $\lambda_0^2$ on the spot size. Since the lattice constant has to be less than a wavelength to observe perfect reflection, the number of photons at which the quantum nonlinear effects become pronounced is necessarily greater than one.

For many applications in quantum optics, a quantum nonlinearity at the single photon level is desirable. In the present context, this can be accomplished by creating a deterministic interaction of photons with a single atom. We will show how to achieve this goal by placing an additional impurity atom in between the lattice sites as shown in Figure 5.5. For simplicity, we assume that each atom has only a single transition. The atoms making up the array all have the same resonance frequency $\omega_0$, transition dipole $d_0$, and corresponding free-space decay rate $\gamma_0$. The analogous quantities for the impurity are denoted by $\omega_s$, $d_s$, and $\gamma_s$. We assume that $\omega_0$ and $\omega_s$ are sufficiently close for the Markov approximation to apply, allowing us to evaluate the Green's function at a fixed frequency (we pick $\omega_0$).

Following the same steps as in Section 5.1, we derive the equations of motion for the atoms in the array. In momentum space, in the absence of an
Figure 5.5: An impurity atom (red) is placed at the center of a plaquette of the square lattice. The black and white colors indicate the two sublattices of the square lattice that are offset relative to each other by a potential.

As above, the quantities
\[ \Delta(k) = -\frac{3\pi\gamma_0}{(\omega_0/c)} \hat{d}_0^i \sum_{R} \text{Re}[G(R,0;\omega_0)]e^{-ikR}\hat{d}_0 \] (5.27)
\[ \Gamma(k) = \frac{6\pi\gamma_0}{(\omega_0/c)} \hat{d}_0^i \sum_{R} \text{Im}[G(R,0;\omega_0)]e^{-ikR}\hat{d}_0, \] (5.28)
capture the interactions between atoms in the array, where the sums run over all lattice vectors. Since we are now working with a single transition, \( \Delta(k) \) and \( \Gamma(k) \) are scalars. We plot \( \Delta(k) \) in Figure 5.6a for a circularly polarized transition, \( \hat{d}_0^i = (1,i,0)/\sqrt{2} \), and lattice constant \( a = 0.2\lambda_0 \). The dispersive and dissipative interactions between the atoms in the array and the impurity, which is associated with the annihilation operator \( s \), are given by

\[ D(k) = -\frac{1}{\sqrt{N}} \frac{3\pi\sqrt{\gamma_0\gamma_s}}{(\omega_0/c)} \hat{d}_0^i \sum_{n} \text{Re}[G(r_n,r_s;\omega_0)]e^{-ikr_n}\hat{d}_s \] (5.29)
\[ G(k) = \frac{1}{\sqrt{N}} \frac{6\pi\sqrt{\gamma_0\gamma_s}}{(\omega_0/c)} \hat{d}_0^i \sum_{n} \text{Im}[G(r_n,r_s;\omega_0)]e^{-ikr_n}\hat{d}_s. \] (5.30)
Here, \( r_n \) are the positions of the atoms in the array and \( r_s \) denotes the location of the impurity.

The equation of motion for the impurity can be derived by similar means, yielding

\[
\frac{d}{dt} \langle s \rangle = -i \left( \omega_s - \frac{i}{2} \gamma_s \right) \langle s \rangle - i \sum_k \left[ D(k)^* - \frac{i}{2} G(k)^* \right] \langle \sigma_k \rangle,
\]

(5.31)

where \( \Omega_s = \mathbf{d}_s^\dagger \mathbf{E}_s^\dagger (r_s) \). The equations are readily solved by performing a Laplace transform, \( S(q) = \int_0^\infty dt \, s(t) e^{-qt} \) and similarly for \( \sigma_k \). Assuming that \( \langle \sigma_k \rangle = 0 \) at \( t = 0 \), we can eliminate the array atoms to obtain

\[
\langle S(q) \rangle = \langle s(0) \rangle + i \left[ iq - \omega_s + \frac{i}{2} \gamma_s - \Sigma(iq) \right] \langle S(q) \rangle
\]

(5.32)

where

\[
\Sigma(\omega) = \sum_k \frac{[D(k) - iG(k)/2][D(k)^* - iG(k)^*/2]}{\omega - \omega_0 - \Delta(k) + i\Gamma(k)/2}
\]

(5.33)

is the so-called self-energy. It describes the modification of the internal properties of the impurity, its resonance frequency and decay rate, due to the presence of the array. We can remove the frequency dependence of the self-energy by means of yet another Markov approximation. Since the evolution of the impurity atom is expected to be peaked around the frequency \( \omega_s \), we replace \( \Sigma(\omega) \) by the constant value \( \Sigma(\omega_s) \). We can see from Equation (5.32) that \( \langle s(t) \rangle \) then oscillates with frequency \( \omega_s + \text{Re} \Sigma(\omega_s) \) with an envelope that decays at a rate

\[
\Gamma_s = \gamma_s - 2 \text{Im} \Sigma(\omega_s).
\]

(5.34)

Clearly, the Markov approximation is only justified if \( \Sigma(\omega) \) varies little over the
frequency range between $\omega_s \pm |\Sigma(\omega_s)|$. This condition can always be satisfied by making $\gamma_s/\gamma_0$ sufficiently small because the magnitude of $\Sigma$ is proportional to $\gamma_s$ while its frequency dependence scales with $\gamma_0$.

In Figure 5.6b, we plot $\Gamma_s$ as a function of the detuning between the array atoms and the impurity. The array is the same as in Figure 5.6a, $a = \lambda_0$ and $\mathbf{d}_0^a = (1, i, 0)/\sqrt{2}$. The transition dipole of the impurity is chosen to be orthogonal to that of the array atoms, $\mathbf{d}_s^i = (1, -i, 0)/\sqrt{2}$. The reason for this choice is that it maximizes the coupling of the impurity to the band edge, which is located at the corner of the Brillouin zone (the high symmetry point $M$) and has energy $\Delta \approx 1.1\gamma_0$.

![Figure 5.6](image)

Figure 5.6: (a) Band structure of a square lattice of atoms with a single, circularly polarized optical transition. (b) Decay rate of an impurity placed inside the array as shown in Figure 5.5. The transition of the impurity has opposite circular polarization relative to the atoms making up the array. The lattice constant is $a = 0.2\lambda_0$ in both cases.

We can see from Figure 5.6b that the emission rate of the impurity is greatly enhanced when it comes into resonance with the band edge. The enhancement is caused by emission of the impurity into the modes of the array, which themselves do not radiate as they are located outside the light cone. An excitation that is initially located on the impurity atom can thus become
delocalized over the entire array. In practice, the excitation will radiate into the far field when it reaches the edge of the array, giving rise to a complicated radiation pattern. However, it is possible to modify the emission properties of the array by applying a weak staggered potential that detunes the two sublattices shown in Figure 5.5 relative to each other. Such a potential provides momentum kicks to couple the mode at the corner of the Brillouin zone (\(M\)) to the one at the center (\(\Gamma\)). Since the mode at the \(\Gamma\) point emits radiation perpendicular to the array, we expect that the excitation on the impurity can be mapped onto a collimated beam.

To verify this idea, we performed a numerical simulation of an array of 30x30 atoms. Figure 5.7a shows the local field intensity in steady state when the impurity is weakly driven. Within the Markov approximation, this steady state picture is equivalent to the emission pattern of a single excitation. It can be seen that the radiation pattern is indeed much more collimated than the dipole pattern that one would obtain in the absence of array. The radially indicated power plotted in Figure 5.7 shows that most of the power is emitted into a cone with half apex angle less than 30 degrees.

The array effectively acts as an antenna in this example. The diffraction limit, which prevents a single dipole from emitting a collimated beam, is circumvented by delocalizing the excitation over a large area. This result makes it possible, in principle, to deterministically couple a single photon to a single atom using only far-field optics. By simply matching the emission pattern in Figure 5.7a, the evolution can be time reversed to focus light directly onto the impurity. The large degree of tunability and dynamic reconfigurability of the array render it a promising platform for applications in quantum optics.
Figure 5.7: (a) Field intensity as a function of position for an array of $30 \times 30$ atoms with lattice constant $a/\lambda_0 = 0.2$. The impurity is weakly driven at frequency $\omega_d = \omega_0 + 1.1\gamma_0$, corresponding to the band edge. The two sublattices of the array are detuned relative to each other by $0.2\gamma_0$. (b) Radiated power integrated up to the polar angle $\theta$. The total power is normalized to 1.
Chapter 6

Two-dimensional semiconductors

6.1 Introduction

Two-dimensional materials have emerged as an exciting playground for exploring new physics as well as promising systems for a variety of technological applications [126, 127]. The reduced dimensionality not only allows us to study phenomena such as the quantum Hall effect, but it also offers unprecedented control as gate electrodes and probes can be brought into close proximity. In addition, different two-dimensional materials can be stacked into so-called heterostructures, enabling the design of entirely novel materials. The building blocks to choose from include insulators (e.g. hexagonal BN), semiconductors (transition metal dichalcogenides), semimetals (graphene), magnetic materials (CrI$_3$), superconductors (NbSe$_2$), and topologically nontrivial materials (WTe$_2$). Here, we explore the optical properties of two-dimensional, direct band gap semiconductors with a particular focus on transition metal dichalco-
genides (TMDs).

6.2 Excitons

We start by reviewing the properties of excitons. This is a vast subject with applications ranging from photovoltaics to quantum dots. We will keep the discussion at a relatively high level, focusing on models that describe the optical response of Wannier excitons. Readers interested in a more microscopic description can find more details in Chapter 8 or in the extensive literature on this topic such as the textbook by Haug and Koch [128].

In many situations, a semiconductor can be thought of as an (almost) incompressible electron fluid. If an electron is removed from this fluid, it leaves behind a hole that behaves in many ways similar to a free positive charge. The electron can be placed in one of the empty bands, the conduction bands, where it has properties that closely resemble a free negative charge. We can create an electron-hole pair by promoting an electron from a valence band into a conduction band. The band gap sets the minimum energy required for this process, suggesting that the contribution from creating electron-hole pairs to the polarizability vanishes at low frequency where photons carry insufficient energy. However, this simple picture neglects an important ingredient: the Coulomb attraction between electrons and holes. Electrons and holes can form bound states not dissimilar from the hydrogen atom. Due to the binding energy, the energy to create an exciton can be smaller than the band gap. This results in discrete resonance in the polarizability of the semiconductor, located in energy below the continuum at which it becomes possible to create
unbound electron-hole pairs.

We pursue a rather phenomenological approach to describe these effects, though all results can be derived using more rigorous methods [128]. We associate with each excitonic bound state an annihilation operator $x_{k \alpha}$, where $\alpha$ is a discrete index that labels the bound state and $k$ is the center-of-mass momentum of the exciton. As we are only interested in two-dimensional semiconductors, we will assume that $k$ is confined to the $xy$ plane. In the limit that the typical separation between excitons is much greater than the Bohr radius, that is the typical separation between the electron and the hole making up the exciton, we can treat $x_{k \alpha}$ as a bosonic operator [129].

An exciton can be created from the semiconductor in its ground state by absorbing a photon with in-plane momentum $k$. We denote the corresponding transition dipole moment and the transition frequency by $d_\alpha(k)$ and $\omega_\alpha(k)$, respectively. If we assume translational invariance of the entire system, including the dielectric environment, in the $xy$ plane, the light–matter interaction is described by the Hamiltonian

$$H = \sum_{\alpha, k} \omega_\alpha(k) x_{k \alpha}^\dagger x_{k \alpha} - \sum_{\alpha, k} \left[ d_\alpha^\dagger(k) E^+(k, 0) x_{k \alpha}^\dagger + \text{h.c.} \right] + H_{ph}, \quad (6.1)$$

where $H_{ph}$ is the Hamiltonian of the electromagnetic field. Here, we placed the two-dimensional semiconductor at $z = 0$ and introduced the in-plane Fourier

---

1Strictly speaking, a semiconductor is only invariant under discrete translations determined by its crystal structure. Therefore, the momentum of the excitons is a quasi-momentum that is defined modulo reciprocal lattice vectors. However, the wavelength of light considered here (several hundreds of nm) is much larger than typical lattice constants (a fraction of a nm) such that the relevant photon momenta occupy a small region of the first Brillouin zone. We may therefore neglect these complications and treat the semiconductor in its continuum limit.
transform of the electric field,

\[ E^+(k, z) = \int d^2r \, E^+(r, z)e^{-ik\cdot r}. \quad (6.2) \]

Within the Markov approximation, the total electric field can be written as a sum of the input field and the field produced by the excitons as

\[ E^+(k, z) = E^+_0(k, z) + \frac{1}{\varepsilon_0} \frac{\omega_0^2}{c^2} \sum_{\alpha} G(k; z, 0; \omega_0) d_{\alpha}(k)x_{k\alpha}. \quad (6.3) \]

The Fourier transformed Green’s function was defined in Equation (5.8). We assumed that all frequencies \( \omega_{\alpha}(k) \) are sufficiently similar to replace them by a single frequency scale \( \omega_0 \). One can now follow the same steps as in Chapter 4 to trace out the photonic degrees of freedom. The resulting non-Hermitian Hamiltonian is given by

\[
H = \sum_{\alpha, k} x_{k\alpha}^\dagger \left[ \omega_{\alpha}(k)\delta_{\alpha\beta} + \Delta_{\alpha\beta}(k) - \frac{i}{2} \Gamma_{\alpha\beta}(k) \right] x_{k\beta} \\
\quad - \sum_{\alpha, k} \left[ E^+_0(k, 0) \cdot d_{\alpha}(k)x_{k\alpha} + \text{h.c.} \right], \quad (6.4)
\]

where

\[
\Delta_{\alpha\beta}(k) - \frac{i}{2} \Gamma_{\alpha\beta}(k) = -\frac{\omega_0^2}{\varepsilon_0 hc^2} d_{\alpha}^\dagger(k)G(k; 0, 0; \omega_0)d_{\beta}(k). \quad (6.5)
\]

To proceed, we have to specify \( d_{\alpha}(k) \). We consider Wannier excitons, for which the center-of-mass coordinates can be separated from the relative coordinates. The relative motion is described by the wavefunction \( \phi_{\alpha}(r_e - r_h) \), where \( r_e \) and \( r_h \) are the positions of the electron and hole, respectively.\(^2\) The

\^In Chapter 8, we will encounter an example in which the relative and center-of-mass motion cannot be separated such that \( \phi_{\alpha} \) also depends on \( k \).
The dipole moment is then given by \[128\]

\[
d_{\alpha}(k) = -e r_{\alpha}(k) \phi_{\alpha}(0),
\]

where \(e\) is the electron charge and \(r_{\alpha}(k)\) the matrix elements of the position operator between the conduction and valence bands occupied by the exciton in question. It is usually justified to neglect the dependence on \(k\) since the photon momentum is small compared to typical momentum scales in semiconductors. We note that unlike the transition dipole of a point dipole, \(d_{\alpha}\) has units of charge. This is a direct consequence of the fact that the exciton operators \(x_{k\alpha}\) describe a polarization wave that is delocalized over the entire plane of the two-dimensional semiconductor.

At high symmetry points, the orientation of \(r_{\alpha}\) can be inferred from group theory consideration (see Section 6.3.2 for an example). Its magnitude can be extracted from ab initio calculations or using \(k \cdot p\) theory \[130\]. Typical values are on the order of the lattice constant. The dimensionless number

\[
\varphi_{\alpha} = |\phi_{\alpha}(0) r_{\alpha}|
\]

characterizes the strength of the transition. Since \(|\phi_{\alpha}(0)|\) is inversely proportional to the Bohr radius, we generally expect \(\varphi_{\alpha}\) to be comparable to the ratio of the lattice constant to the Bohr radius and thus less than unity.

To conclude this section, we consider a material that supports two degenerate exciton modes with orthogonal in-plane polarizations and equal transition strength \(\varphi\). This situation will be particularly relevant for the transition metal dichalcogenides discussed in Section 6.3. Using Equation (5.12), we find that
the eigenvalues of $\Gamma_{\alpha\beta}(k)$ are given by

$$\Gamma_(k) = \gamma_0 \cos \theta \Theta \left( \frac{\omega_0}{c} - k \right), \quad \Gamma_-(k) = \frac{\gamma_0}{\cos \theta} \Theta \left( \frac{\omega_0}{c} - k \right), \quad (6.8)$$

where

$$\gamma_0 = \frac{e^2 \varphi^2 \omega_0}{\varepsilon_0 \hbar c}. \quad (6.9)$$

As in Section 5.1, $\cos \theta = \sqrt{1 - (ck/\omega)^2}$ and the labels $\|$ and $\perp$ refer to polarizations perpendicular and parallel to $k$. It is not surprising that these expressions are formally equivalent to Equation (5.14) and Equation (5.15) since excitons in two dimensions can be thought of as the continuum limit of a lattice of point dipoles.

In contrast to the array of atoms, we are able to provide analytic expressions for the eigenvalues of $\Delta(k)$ as there are no sums over reciprocal lattice vectors. $\Delta(k)$ vanishes inside the light cone, $k < \omega_0/c$. Outside the light cone, the eigenvectors are also either parallel or perpendicular to $k$ and are given by

$$\Delta_(k) = \frac{1}{2} \gamma_0 \sqrt{(ck/\omega_0)^2 - 1} \Theta \left( k - \frac{\omega_0}{c} \right), \quad (6.10)$$

$$\Delta_-(k) = -\frac{\gamma_0}{2 \sqrt{(ck/\omega_0)^2 - 1}} \Theta \left( k - \frac{\omega_0}{c} \right), \quad (6.11)$$

These functions are plotted in Figure 6.1a. They describe the dispersion relation of polarization waves propagating along the surface not unlike surface plasmon polaritons. The divergence of $\Delta_\perp$ at the edge of the light cone is an artifact of the Markov approximation. More accurately, the vertical lines representing the light cone should be replaced by the photon dispersion
\[ \omega = ck. \] Hence, we can understand the dispersion of the transverse polarized mode close to the light cone as an electromagnetic wave that only weakly interacts with the excitons. The longitudinal mode does not exhibit this behavior as free space does not support longitudinally polarized plane waves. The energy of the two modes in the limit of large \( k \) can be understood from the interaction between dipoles as illustrated in Figure 6.1b. Dipoles that are aligned head to tail, as in the case of the longitudinal polarization, interact repulsively, which explains the linear increase of \( \Delta_{\parallel} \) when \( k \gg \omega_0/c \).

![Figure 6.1: (a) Schematic drawing of the dipole waves for the \( p \) polarization (upper band) and \( s \) polarization (lower band) for \( k \) along the \( x \) axis. (b) The energy shifts \( \Delta_{\parallel}(k) \) (solid blue) and \( \Delta_{\perp}(k) \) (solid red). The dashed lines show the result from the Coulomb exchange interaction, which excludes retardation.](image)

We note that this result has been discussed in the literature on transition metal dichalcogenides, although often using an entirely different approach [131–134].\(^3\) The energy shift between longitudinal and transverse polarizations can be derived from the long-range Coulomb exchange contribution to the interaction between electrons and holes. The result is shown by the dashed lines in Figure 6.1a. It agrees with our result in the limit of large mo-

\(^3\)A notable exception is reference [135], whose treatment closely resembles our approach.
mentum but fails to reproduce the correct behavior near the light cone. This is expected as the exchange interaction neglects the effects of retardation, which is equivalent to increasing the speed of light to infinity or shrinking the light cone to zero. It is nevertheless intriguing that a seemingly quantum phenomenon like the exchange interaction can be equivalently described within the framework of classical electromagnetism.\footnote{Even though the discussion of this chapter employed a quantum formalism, we could have derived the same results classically using the same methods as in Chapter 4.}

6.3 Transition metal dichalcogenide monolayers

6.3.1 Basic properties

Monolayers of transition metal dichalcogenides (TMDs) have emerged as a class of two-dimensional semiconductors with unique optical properties [136, 137]. The lattice structure of a single layer of the materials considered here is shown in Figure 6.2a. Metal and chalcogen atoms are arranged in a hexagonal lattice. The chalcogen atoms are displaced from the metal atoms out of the plane. In a bulk material, these layers are stacked with strong covalent bonding within each layer but only weak van der Waals attraction between the layers. The hexagonal first Brillouin zone of the monolayer is shown in Figure 6.2b.

The four most commonly studied TMDs are MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$. They share many of their properties, including a direct band gap at the $K$ point, the corner of the Brillouin zone. The band structure for MoSe$_2$ is plotted in Figure 6.3. We point that the six corners of the Brillouin zone correspond to two distinct quasi-momenta. Every other corner is connected
Figure 6.2: (a) Lattice structure of monolayer TMDs. The left is a top view, while the right shows the individual layers of chalcogens and metal atoms as viewed from the side. (b) Brillouin zone associated with the lattice in (a). $\Gamma$, $M$, $K$, and $K'$ denote high symmetry points.

by a reciprocal lattice vector such that three corners making up an equilateral triangle are indistinguishable. The remaining two sets of three points are commonly labeled by $K$ and $K'$. They are related by time reversal, which implies that the energies at $K$ and $K'$ are degenerate in the absence of a magnetic field.

TMDs host tightly bound excitons with a Bohr radius on the order of $1\text{ nm}$ and a binding energy of several $100\text{ meV}$. The binding energy is two orders of magnitude larger compared to conventional direct band gap semiconductors such as GaAs, which leads to an unusually strong optical response. The strong binding is a consequence of reduced dielectric screening in two-dimensional materials and the large effective masses [139].

### 6.3.2 Selection rules

For the remainder of our discussion of TMDs, we will only consider the lowest energy excitons. These are excitons where both the hole and the electron occupy the $K$ or $K'$ valley. We further restrict ourselves to direct excitons, that is excitons for which the electron and hole reside in the same valley. While
Figure 6.3: Band structure of monolayer MoSe$_2$. The band structure was computed using the tight-binding model in reference [138]. The valence band maximum defines the energy zero, while the conduction band minimum is located at approximately 1.5 eV. The model underestimates the band gap as the parameters were extracted from density function theory calculations without $GW$ corrections.

Indirect excitons between the $K$ and $K'$ valley have a comparable energy, they are not optically active (often called dark excitons for this reason) because photons do not carry sufficient momentum to induce transitions between different valleys.

The selection rules at the $K$ point can be derived from simple symmetry considerations. The full point group of the lattice in Figure 6.2 is $D_{3h}$, which is the symmetry group associated with an equilateral, triangular prism. We remark that TMD monolayers lack inversion symmetry, which allows for a band gap to exist at the $K$ point in the first place. In materials such as graphene that have both a hexagonal lattice and inversion symmetry, the conduction and valence bands are degenerate at the $K$ point, forming a so-called Dirac point [140]. The symmetry at the $K$ point is further reduced.
from $D_{3h}$ to $C_{3h}$ as the $K$ point is not invariant under certain reflections in $D_{3h}$. The group $C_{3h}$ consists of only a three-fold rotation as well as a mirror plane in the plane of the TMD. Hence, the wavefunctions at the $K$ point can be classified using two quantum numbers, one for each symmetry. There is an angular momentum quantum number $m$, which determines the phase $e^{-2\pi im/3}$ accumulated by the wavefunction when rotated by $120^\circ$. In systems with continuous rotational symmetry, $m$ can be any integer, while here it is only defined modulo 3. The mirror plane defines the quantum number $\sigma_h = \pm 1$, which is the parity of the wavefunction under reflection.

For the angular momentum quantum number to be well defined, it is necessary to specify the center of rotation. Choosing it to pass through one of the metal atoms, ab initio calculations show that $m = 0$ in the conduction band [138] at both $K$ and $K'$. This result has the simple interpretation that the wavefunction is dominated by $d_0$ orbitals. Similarly, the ab initio results indicate that the valence band inherits its character from $d_{+2}$ orbitals at $K$ and $d_{-2}$ orbitals at $K'$. We hence infer the quantum number $m = -1$ (equivalent to $m = 2$ modulo 3) at $K$ and $m = +1$ at $K'$. The opposite sign is required by time reversal symmetry. All wavefunctions have even parity with respect to the mirror plane, $\sigma_h = +1$.

It is now straightforward to deduce the selection rules. A photon with in-plane, right-handed, circular polarization, denoted by $\sigma_+$, preserves the parity $\sigma_h$ but changes the angular momentum by $+1$. Similarly, left-handed, circularly polarized light, referred to as $\sigma_-$, decreases $m$ by 1. Hence, to excite an electron from the valence band into the conduction band at $K$ requires a $\sigma_+$ photon. At $K'$, the required polarization is $\sigma_-$, where the opposite sign is
again a consequence of time reversal symmetry. The quantum numbers and selection rules are summarized in Figure 6.4.

![Figure 6.4: Quantum numbers of the highest valence band and lowest conduction band at $K$ and $K'$ as well as the resulting selection rules.](image)

So far, we ignored the role of spin. It turns out that spin plays an important role in TMDs due to the strong spin–orbit coupling originating from the heavy metal atoms. The two spin components, pointing approximately up and down along the axis perpendicular to the plane of the TMD, are split by several hundred meV in the valence band, as schematically sketched in Figure 6.5. The spin splitting in the conduction band is much smaller, on the order of 10s of meV, because the diagonal term of the spin–orbit interaction vanishes for $m = 0$ orbitals and spin–orbit coupling therefore only enters in second order perturbation theory [141].

Spin–orbit coupling also affects the selection rules. To zeroth order, the spin is perfectly aligned with the $z$ axis. A spin that points up or down adds or removes a half unit of angular momentum, respectively. Hence, the selection rules for spin conserving transitions are unaffected since the difference between angular momentum quantum numbers remains unchanged and the electric field does not couple directly to spin. Spin–orbit coupling mixes different spin
orientations via a term proportional to $S_+L_- + S_-L_+$, where $S_\pm$ and $L_\pm$
are raising and lowering operators for spin and orbital angular momentum. Similarly, this term mixes different orbital angular momentum states with opposite parity $\sigma_h$. Since only energetically separated bands are coupled, these effects are perturbative and we can nevertheless assign an approximate spin orientation and orbital angular momentum to each band. A detailed group theoretical analysis carried out in Appendix D.1 indeed confirms that the selection rules for transitions that conserve the approximate orientation of the spin are the same as for the spinless case. In addition, spin–orbit coupling allows for transitions that flip the orientation. As this necessarily requires a change in parity, these transitions have an out-of-plane ($z$) polarization. We demonstrate in the Appendix D.1 that only the upper of the spin-split valence bands supports such a transition. These results are illustrated in Figure 6.5.

Excitons that can decay via a circularly polarized transition are often re-
ferred to as bright, while all other excitons are called dark, even the ones with a dipole allowed, $z$-polarized transition. The origin of this terminology is that the $z$-polarized transition is much weaker than the circularly polarized ones as it is only introduced perturbatively by spin–orbit coupling. Nevertheless, the $z$-polarized transition has been directly observed in photoluminescence measurements and its emission can be enhanced by suitably engineering the electromagnetic environment \([3]\). Figure 6.5 further highlights a significant distinction between WSe$_2$ and MoSe$_2$: The (approximate) spin orientation of the lowest conduction band is different for the two materials, which affects their optical properties. The lowest energy exciton is bright in MoSe$_2$ but not in WSe$_2$ such that we expect MoSe$_2$ to photoluminesce more brightly at low temperature. This effect has indeed been experimentally observed \([142–144]\).

### 6.4 Reflection spectrum

We saw in Section 6.2 that optical resonances in two-dimensional semiconductors can in many ways be thought of as the continuum limit of the arrays of atoms discussed in Chapter 5. We will strengthen this notion by showing that excitons also result in high reflection when excited on resonance. The discussion differs from the atom array in two aspects. First we generalize our treatment to include an arbitrary number of dielectric or metallic layers. This consideration is of great practical relevance since two-dimensional semiconductors such as TMDs are hardly ever suspended in free space but are rather placed on a substrate. In addition, they are often stacked with other two-dimensional materials such as hexagonal to provide a passivating encap-
sulation, graphene as a gate electrode, or even more complex materials such as the magnetic material CrI₃ [145]. Secondly, we allow for nonradiative decay and pure dephasing of the excitons, which may occur in a semiconductor due to phonons. Dephasing in particular requires a slight extension of our previous calculations because its inherent nonlinearity implies that expectation values of the form \( \langle x_{k\alpha}^\dagger x_{k\beta} \rangle \) no longer factorize.

To reduce clutter, we only consider normally incident light (\( k = 0 \)) and drop all momentum labels. We include one bright exciton from each the \( K \) and \( K' \) valleys, labeled by \( x_{\pm} \), with opposite transition dipoles \( d_{\pm} = d(1, \pm i, 0)^\dagger/\sqrt{2} \). The additional dephasing with rate \( \gamma_d \) is described by the dissipator

\[
D_d[Q] = 2\gamma_d \sum_{\alpha = \pm} \left( x_{\alpha}^\dagger x_{\alpha} Q x_{\alpha}^\dagger x_{\alpha} - \frac{1}{2} \{ x_{\alpha}^\dagger x_{\alpha} x_{\alpha}^\dagger x_{\alpha}, Q \} \right). \tag{6.12}
\]

We note that dephasing establishes a preferred basis. The choice of dephasing between the valleys is physically motivated as it arises due to phonon scattering within each valley.

The equations of motion for the two excitons are given by

\[
\frac{d}{dt} \langle x_{\alpha} \rangle = -i \sum_{\beta} \left[ \left( \omega_{\alpha} - \omega + i \frac{\gamma_m}{2} \right) \delta_{\alpha\beta} + \Delta_{\alpha\beta} - i \frac{1}{2} \Gamma_{\alpha\beta} \right] \langle x_{\beta} \rangle
+ i d_{\alpha} \langle E_{0}^+ \rangle, \tag{6.13}
\]

where \( \gamma_m \) is the nonradiative decay rate. In the absence of a magnetic field, the excitons are degenerate such that \( \omega_+ = \omega_- = \omega_0 \). Rotational symmetry of the system about the \( z \) axis further implies that \( \Delta_{\alpha\beta} = \Delta \delta_{\alpha\beta} \) and \( \Gamma_{\alpha\beta} = \gamma_r \delta_{\alpha\beta} \).
Defining the detuning \( \delta = \omega - \omega_0 - \Delta \), the equation is readily solved in steady state to give

\[
\langle x_\alpha \rangle = -\frac{d_\alpha^+ E_0^+ (0)}{\delta + i(\gamma_r + \gamma_{nr} + 2\gamma_d)/2}.
\]

(6.14)

Because dephasing is nonlinear, we have to derive separate equations of motion for \( \langle x^\dagger_\alpha x_\beta \rangle \). We find that

\[
\frac{d}{dt} \left( \langle x^\dagger_\alpha x_\beta \rangle + \langle x^\dagger_\alpha \rangle \langle x_\beta \rangle \right) = -\left( \gamma_r + \gamma_{nr} + 2\gamma_d \right) \left( \langle x^\dagger_\alpha x_\beta \rangle + \langle x^\dagger_\alpha \rangle \langle x_\beta \rangle \right)
\]

\[
+ 2\gamma_d \delta_{\alpha\beta} \langle x^\dagger_\alpha x_\beta \rangle,
\]

(6.15)

which has the steady state solution

\[
\langle x^\dagger_\alpha x_\beta \rangle = \frac{\gamma_r + \gamma_{nr} + 2\gamma_d}{\gamma_r + \gamma_{nr} + (1 - 2\delta_{\alpha\beta})\gamma_d} \langle x^\dagger_\alpha \rangle \langle x_\beta \rangle.
\]

(6.16)

To find the reflection coefficient, we need to compute the total electric field, which is given by

\[
E^+(z) = E_0^+(z) + \frac{1}{\varepsilon_0} \frac{\omega_0^2}{c^2} G(z, 0; \omega_0) \sum_\alpha d_\alpha x_\alpha.
\]

(6.17)

In addition to the incident field, the free field \( E_0^+(z) \) now also includes a component that is reflected by the substrate. At some position \( z_0 \) high above the sample, the reflected field can be written as

\[
E_0^+(z_0) = r_0 E_i^+(z_0) + \frac{1}{\varepsilon_0} \frac{\omega_0^2}{c^2} G(z_0, 0; \omega_0) \sum_\alpha d_\alpha x_\alpha,
\]

(6.18)

where \( r_0 \) is the reflection coefficient of the substrate in the absence of the excitonic resonance and \( E_i^+ \) is the amplitude of the incident field. The reflection
coefficient can be expressed as

$$ R = \frac{\langle E_i^+(z_0)^\dagger E_i^+(z_0) \rangle}{\langle E_i^+ | E_i^+ \rangle} $$

$$ = |r_0|^2 + \frac{2}{\varepsilon_0} \frac{\omega_0^2}{c^2} \text{Re} \left[ \frac{r_0^* (E_i^+)^\dagger G(z_0, 0; \omega_0) \sum_\alpha d_\alpha \langle x_\alpha \rangle}{\langle E_i^+ \rangle^2} \right] $$

$$ + \frac{1}{\varepsilon_0^2} \frac{\omega_0^4}{c^4} \sum_{\alpha, \beta} d_\alpha^\dagger G(z_0, 0; \omega_0)^\dagger G(z_0, 0; \omega_0) d_\beta \frac{\langle x_\alpha^\dagger x_\beta \rangle}{\langle E_i^+ \rangle^2}. \quad (6.19) $$

We made use of the fact that the incident field, which is assumed to be in a coherent state, factorizes with the atomic operators.

The orientations of the fields and dipole moments are all confined to the $xy$ plane. Due to rotational symmetry, the Green’s function projected onto this plane must be proportional to the identity. Introducing the shorthand

$$ g = -2i \frac{\omega_0}{c} G(z_0, 0; \omega_0) $$

for a scalar $g$, we obtain

$$ R = |r_0|^2 + \text{Im} \left[ \frac{r_0^* g \gamma_0}{\delta + i(\gamma_r + \gamma_m + 2\gamma_d) / 2} \frac{\langle E_i^+ \rangle^\dagger \langle E_0^+ \rangle}{\langle E_i^+ \rangle^2} \right] + $$

$$ \frac{\gamma_r + \gamma_m + 2\gamma_d}{\gamma_r + \gamma_m} \frac{|g|^2 \gamma_0 / 4}{\delta^2 + (\gamma_r + \gamma_m + 2\gamma_d)^2 / 4} \frac{\langle E_0^+ \rangle^2}{\langle E_i^+ \rangle^2}, \quad (6.21) $$

where we recall that $\gamma_0 = |d_\alpha|^2 \omega_0 / \varepsilon_0 c$ is the decay rate of zero momentum excitons in free space. Finally, we would like to relate $E_0^+(0)$ to $E_i^+$. It turns out that

$$ \langle E_0^+(0) \rangle = g \langle E_i^+ \rangle. \quad (6.22) $$

To see this, we note that the field $E_0^+(0)$ could in principle be produced by
placing a dipole source at position \( z_0 \) far above the TMD. Therefore, for some constant \( e \), we have \( \mathbf{E}^+_0(z) = \mathcal{G}(z, z_0; \omega_0)e \). Next, we make use of the fact that \( \mathcal{G}(z_0, z; \omega_0) = \mathcal{G}(z, z_0; \omega_0)^T \) \cite{120}. However, symmetry again allows us to treat the Green’s function as a scalar and implies that in fact \( \mathcal{G}(z_0, z; \omega_0) = \mathcal{G}(z, z_0; \omega_0) \). The constant \( e \) is fixed such that the downward traveling component of \( \mathbf{E}^+_0(z) \) equals \( \mathbf{E}^+_i \) when \( z \) approaches \( z_0 \) from below.

Since \( z_0 \) is assumed to be far away from the TMD and in vacuum, the downward component of the Green’s function is simply given by the free space Green’s function Equation (5.12), whereby \( e = -2i(\omega_0/c)\mathbf{E}^+_i \).

Combining these results yields the final answer

\[
R = |r_0|^2 + A \frac{\left( \gamma_r + \gamma_{nr} + 2\gamma_d \right)/2}{\delta^2 + \left( \gamma_r + \gamma_{nr} + 2\gamma_d \right)^2/4} + B \frac{\delta}{\delta^2 + \left( \gamma_r + \gamma_{nr} + 2\gamma_d \right)^2/4} \quad (6.23)
\]

where we defined

\[
A = \frac{\gamma_0^2}{2(\gamma_r + \gamma_{nr})} |g|^4 - \gamma_0 \text{Re} \left( r_0^* g^2 \right), \quad B = \gamma_0 \text{Im} \left( r_0^* g^2 \right). \quad (6.24)
\]

For completeness, we also recall the expression for the radiative decay rate,

\[
\gamma_r = -2i \frac{\omega_0}{c} \gamma_0 \text{Im} \mathcal{G}(0, 0; \omega_0). \quad (6.25)
\]

In order to observe strong reflection from a TMD monolayer, it is necessary that radiative decay dominates over both nonradiative decay and dephasing processes. This can be achieved in high-quality samples as shown in Figure 6.6. The measured reflectance from a monolayer of MoSe\(_2\) close to the bright exciton resonance is plotted in Figure 6.6a. The reflection spectra are
Figure 6.6: (a) Measured reflectance from a monolayer of MoSe$_2$ encapsulated in hexagonal boron nitride and placed on a SiO$_2$/Si substrate. The different colors correspond to temperatures between 4 K and 300 K as indicated by the legend. (b) Fitted parameters as a function of temperature. The solid curves are fits of the function $a + bT + c/[\exp(\Omega/kT) - 1]$, which phenomenologically captures the expected temperature dependence due to coupling to acoustic and longitudinal optical phonons [146].

highly asymmetric owing to interference between light reflected by the substrate and the TMD. Formally, this asymmetry is captured by a nonzero value of $B$ in Equation (6.23). To compare the measured spectra with our model, we first compute the Green’s function evaluated at the points $G(z_0, 0; \omega_0)$ and $G(0, 0; \omega_0)$ using the transfer matrix formalism outlined in Appendix D.2 and the known thicknesses and dielectric constants of the various layers in the sample. The remaining parameters $\gamma_0$, $\gamma_{nr}$, and $\gamma_d$, which are intrinsic properties of the TMD, can then be determined by fitting the model to the data. The extracted rates, plotted in Figure 6.6b, indicate that dephasing and nonradiative decay depend on temperature whereas the vacuum radiative rate $\gamma_0$ is temperature independent. This observation agrees well with our expectation that $\gamma_{nr}$ and $\gamma_d$ are mediated by phonons, while $\gamma_0$ is a purely photonic
The dependence of the radiative decay rate $\gamma_r$ on the electromagnetic environment offers a unique avenue to control the radiative properties of excitons. For example, the radiative decay rate $\gamma_r$ can be tuned by varying the distance between the TMD and a mirror. This effect was experimentally observed by suspending a monolayer of MoSe$_2$ above a thick layer of gold. The distance between the TMD and the gold mirror could be varied by applying a voltage between them, resulting in an attractive capacitative force. The measured reflection spectra are shown in Figure 6.7. By fitting the spectra at different voltages, it is possible to determine the distance between the TMD and the mirror as well as the linewidths. A detailed description of the fitting procedure was published in reference [6].

The strong dependence of the linewidth on the position of the TMD opens up many exciting avenues in optomechanics and quantum optics. We will discuss a particular application in detail in Chapter 7, where we show that a mirror can greatly prolong the exciton lifetime, which in turn enhances quantum nonlinearities.
Figure 6.7: (a) Measured reflectance from a monolayer of MoSe$_2$ above a thick layer of gold. The monolayer is encapsulated in hexagonal boron nitride and gated with few-layer graphene. The voltage $V_B$ is applied between the gold layer and the graphene bottom gate. (b) Line cuts of (a) at different voltages. The solid curves show the fit of the theoretical model. (c) Total linewidth $\gamma = \gamma_r + \gamma_{nr} + 2\gamma_d$ as a function of the applied voltage. The inset shows the fitted distance $z$ between the TMD and the gold mirror. The red curve was obtained from a finite element simulation of the electromechanical response. (d) Fitted decay rates as a function of the voltage. The value of $\gamma_{fit}$ is computed from $\gamma_0$, $\gamma_{nr}$, and the distance $z$, while the total linewidth $\gamma$ was obtained by directly fitting the spectra.
Chapter 7

Quantum nonlinear optics in atomically thin materials

7.1 Introduction

The realization of strong nonlinear interactions between individual quanta of light (photons) has been a long-standing goal in optical science and engineering that is both of fundamental and technological significance [147]. While in conventional optical materials the nonlinearity at light powers corresponding to single photons is negligibly weak, remarkable advances have been recently made towards realizing this goal. One promising approach to quantum nonlinear optics is based on quantum emitters confined to cavities or nanophotonic structures that greatly enhance light–matter interactions. Proof-of-principle experiments have been carried out with neutral atoms [148–150], quantum dots [151], quantum wells [152, 153], and color centers in diamond [154, 155]. At the same time, experiments with cold gases [156], ensembles of solid state quantum emitters [157], and excitons in transition metal dichalcogenides
(TMDs) [4, 158] have demonstrated strong light–matter coupling without the need for nanophotonic structures. This is achieved via spatially delocalized optical excitation, which, however, reduces the nonlinearity, thereby rendering the system effectively linear at the level of individual photons. A number of solutions to this challenge have been proposed, for example, exploiting Rydberg blockade to induce strong, nonlocal interactions between ultracold atoms that result in strong photon–photon interactions [159]. This approach has been applied to realize photon blockade [160–162], two- and three-photon bound states [163] and symmetry protected collisions between strongly interacting photons [164]. Extending such techniques to the domain of integrated solid-state systems is an outstanding challenge.

This chapter describes a novel approach to quantum nonlinear optics, which makes use of resonant, atomically thin materials. One example of such a material is a two-dimensional semiconductor such as a TMD monolayer, which supports tightly bound, optically active excitons [165]. In free space, excitons with zero in-plane momentum decay with a radiative rate \( \gamma \), emitting a plane wave to either side of the TMD. Interactions between excitons render the system nonlinear, giving rise to a shift of the two-exciton state relative to the noninteracting case. However, in practice this nonlinearity is very weak, requiring a large number of excitons to create a resolvable shift. To enhance the nonlinear optical response, in our approach, the TMD is placed in front of a partially reflecting broadband mirror as shown in Figure 7.1a. When the separation between the TMD and the mirror is close to a half-integer multiple of the exciton resonance wavelength, the light emitted by the TMD towards the left (Figure 7.1a) and the light reflected by the mirror
Figure 7.1: (a) An atomically thin (2D) emitter is positioned at a distance $d$ in front of a partially reflecting mirror with reflection and transmission coefficients $r_0$ and $t_0$, respectively. The free-space radiative decay rate is given by $\gamma$, while $\gamma'$ denotes the loss rate. The setup is formally equivalent to (b), where the two-dimensional emitter is replaced by an atom and a one-dimensional waveguide takes the role of the free-space plane-wave mode. (c) Transmission spectrum in the limit $\gamma \ll \nu_{\text{FSR}}$ for $\gamma' = 0$ and $T_0 = 0.1$ at various distances $d$. (d) Maximum transmission as a function of $d$. The dashed lines indicate the distances for which the full spectra are shown in (c). The maximum transmission is periodic in $d$ with period $\lambda_0/2$. (e) Transmission at the Fabry–Pérot resonance ($d = d_{\text{FP}}$, $\delta = \delta_{\text{FP}}$) as a function of the loss rate. Transmission is high provided $\gamma' \ll \gamma_{\text{FP}} = T_0 \gamma$. 

97
destructively interfere, which leads to significant suppression of the radiative linewidth, enhancement of the exciton lifetime and an associated enhancement of the optical nonlinearity. This effect can be understood in terms of the formation of long-lived exciton-polaritons, with a substantial excitonic component, which become very sensitive to nonlinear frequency shifts arising from exciton-exciton interactions.

Before proceeding, we note an important connection with the single-atom system shown in Figure 7.1b, where a point-like emitter is coupled to a one-dimensional waveguide. Both systems can be thought of as a single-channel scattering problem with an emission rate $\gamma$ into the channel of interest and a loss rate $\gamma'$. In the case of a single atom, $\gamma'$ is typically dominated by emission into unconfined free-space modes. By contrast, conservation of in-plane momentum prevents scattering into undesired channels for a TMD, and loss only emerges due to nonradiative decay and material imperfections such as disorder. The relevant condition of low loss, $\gamma' \ll \gamma$, has already been demonstrated in high quality samples [4, 158]. Similar considerations apply to other two-dimensional systems such as ordered arrays of trapped atoms with subwavelength spacing [2, 166].

### 7.2 Linear response

The key idea of this work can be understood by first considering the linear response of a TMD in free space. The amplitude reflection coefficient close to an excitonic resonance is given by the complex Lorentzian $r_{\text{TMD}}(\delta) = -i(\gamma/2)/[\delta + i(\gamma + \gamma')/2]$, where $\delta$ denotes the detuning from resonance [167].
Strikingly, the TMD acts as a perfect reflector at zero detuning in the absence of losses despite being much less than a wavelength thick. The vanishing transmission is the result of resonant scattering into a single channel, where the incident field destructively interferes with the scattered field. The effect has been discussed in a variety of other contexts including a single atom coupled to a one-dimensional waveguide \[168\], classical plasmonic resonators \[169\], and ordered arrays of atoms \[2, 166\].

A nearby mirror significantly modifies the optical response. The intensity transmission coefficient \( T \) can be computed by summing over all multiple reflections between the TMD and the mirror, see Appendix E.1. As shown in Figure 7.1c and d, the transmission spectrum strongly depends on the distance \( d \). In particular, perfect transmission is only attainable at specific distances close to half-integer multiples of the exciton transition wavelength \( \lambda_0 \). This distinction from a conventional Fabry–Pérot resonator originates from the frequency dependence of the TMD. Perfect transmission through a Fabry–Pérot resonator occurs when two conditions are met: The round trip phase is an integer multiple of \( 2\pi \) and the reflection coefficients of the two mirrors are equal. Applied to our system, the latter condition may be stated as \( |r_{\text{TMD}}(\delta)|^2 = |r_0|^2 \), which sets the detuning at which the Fabry–Pérot resonance occurs, \( \delta_{\text{FP}} = \pm(\gamma/2)\sqrt{T_0/R_0} \). The former condition then determines the allowed distances \( d_{\text{FP}} \) according to the relation \( r_0e^{2ik_{\text{FP}}d_{\text{FP}}} = -R_0 \pm i\sqrt{R_0T_0} \), where \( k_{\text{FP}} \) is the wavenumber corresponding to the resonance frequency. Here, \( r_0 \) (assumed to be real and negative) and \( t_0 \) denote the amplitude reflection and transmission coefficient of the mirror, while \( R_0 = |r_0|^2 \) and \( T_0 = |t_0|^2 \) refer to the respective intensity coefficients. We may
estimate the width $\gamma_{\text{FP}}$ of the high-transmission resonance by considering
the phase accumulated by a photon during $N \approx 1/T_0$ round trips before
it is transmitted through the mirror. If the photon is detuned by $\Delta$ from
the resonance, it accumulates an additional propagation phase $\varphi_{\text{prop}}(\Delta) = 2Nd\Delta/c$, where $c$ is the speed of light. Furthermore, the reflection phase
impacted by the TMD is modified by $\varphi_{\text{TMD}}(\Delta) \approx 2N\Delta/\gamma$. The width of the
resonance follows from $\varphi_{\text{prop}}(\gamma_{\text{FP}}) + \varphi_{\text{TMD}}(\gamma_{\text{FP}}) \approx 1$. In the limit $\varphi_{\text{prop}} \gg \varphi_{\text{TMD}}$, the phase from the TMD can be neglected and the system resembles a
conventional Fabry–Pérot resonator. We are interested in the opposite limit,
$\varphi_{\text{prop}} \ll \varphi_{\text{TMD}}$, requiring that $\gamma$ be much smaller than the free spectral range $\nu_{\text{FSR}} = c/(2d)$, which yields $\gamma_{\text{FP}} \approx T_0\gamma$. For a highly reflecting mirror, $\gamma_{\text{FP}}$ is much smaller than the free-space linewidth $\gamma$. The narrow linewidth can
be physically understood in terms of a long-lived polariton formed by an
exciton and a photon localized between the TMD and the mirror. Spontaneous
emission from the polariton is suppressed because the photonic component
destructively interferes with the field emitted by the exciton [170].

Since the polaritons are predominantly composed of excitonic degrees of
freedom, the interaction between them is comparable to the interaction be-
tween excitons in the absence of a mirror. Yet, polaritons may interact over
a much longer duration owing to their extended lifetime. If we denote the
interaction energy between two excitons by $\chi$, we expect that a strong quan-
tum nonlinearity can be observed if $\chi > T_0\gamma$, corresponding to an effective
enhancement of the nonlinearity by a factor $1/T_0$ compared to free space.
The quantum nonlinearity results in photon antibunching as the presence of
a single polariton blocks transmission by shifting the Fabry–Pérot resonance
by more than its width. In what follows, we confirm this simplified analysis and show that this effect is robust to loss, provided the loss rate $\gamma'$ is smaller than $\gamma_{\text{FP}}$, as is required to maintain near unity transmission (see Figure 7.1e).

7.3 Quantum nonlinear response

The above classical approach fully accounts for the linear response of the system but it is insufficient to capture quantum nonlinear effects. To this end, we quantize both the excitonic degrees of freedom and those of the electromagnetic field. The spatial mode of the excitons that couples to the light field is described by the bosonic annihilation and creation operators $a$ and $a^\dagger$. The internal dynamics of the excitons are governed by the Hamiltonian $H_0 = \omega_0 a^\dagger a + (\chi_1 / 2) a^\dagger a^\dagger a a$, where $\omega_0$ is the resonant frequency of the excitons and $\chi_1$ is the dispersive nonlinearity due to exciton–exciton interactions. A level diagram of the the three lowest energy states is shown in Figure 7.2a.

As detailed in Appendix E.2, we employ an input–output formalism to eliminate the photonic degrees of freedom, upon which the equation of motion for a system operator $Q$ can be expressed in terms of the Heisenberg–Langevin equation [171]

$$
\dot{Q} = -i \left[ Q, H_0 + \frac{\gamma}{2} \text{Im} \left( r_0 e^{2ik_0/d} \right) a^\dagger a + \Omega a^\dagger + \Omega^* a \right] + D[Q] + F[Q],
$$

(7.1)

where $k_0 = \omega_0/c$ and

$$
\Omega = \sqrt{\frac{\gamma}{2}} \left( 1 + r_0 e^{2ik_0/d} \right) \langle b_{\text{n,R}} \rangle + \sqrt{\frac{\gamma}{2}} t_0 e^{ik_0/d} \langle b_{\text{n,L}} \rangle
$$

(7.2)
is the Rabi frequency. It is composed of a superposition of the input fields $b_{\text{in,R}}$ and $b_{\text{in,L}}$, illustrated in Figure 7.1a, which evolve as freely propagating photonic modes (as if the TMD and mirror were absent). The dissipative dynamics are described by

$$\mathcal{D}[Q] = \left[ \gamma + \gamma \text{Re} \left( r_0 e^{2i\kappa d} \right) + \gamma' \right] \left( a^\dagger Q a - \frac{1}{2} \left\{ Q, a^\dagger a \right\} \right) + \frac{\chi_2}{2} \left( a^\dagger a^\dagger Q a a - \frac{1}{2} \left\{ Q, a^\dagger a^\dagger a a \right\} \right).$$ \hspace{1cm} (7.3)

In addition to the radiative decay rate $\gamma$ and the loss rate $\gamma'$, we include a nonlinear decay rate $\chi_2$. This rate accounts for the dissipative nonlinearity that may arise from nonradiative decay involving a pair of excitons, or from excitons scattering off each other into a spatial mode outside the mode of interest. Excitons may further be subject to pure dephasing, though the effect has been excluded here for the sake of clarity. We show in Appendix E.5 that a pure dephasing rate $\gamma_d$ affects the system in a qualitatively and quantitatively similar fashion to the loss rate $\gamma'$. Finally, the term $\mathcal{F}[Q]$ in Equation (7.1) is a Langevin noise operator, an expression for which is given in Appendix E.2.

Equation (7.1) is valid under three assumptions: (i) The Markov approximation applies, requiring that $\gamma \ll \omega_0$. This is typically justified for optical transitions and indeed holds for excitons in TMDs. (ii) The photons initially occupy a coherent state that is uncorrelated with the excitons. (iii) Retardation can be neglected during a round trip of a photon traveling between the TMD and the mirror. We show in Appendix E.2 that this gives rise to the conditions $\gamma \ll \nu_{\text{FSR}}$, $\gamma \ll \nu_{\text{FSR}} \left[ 1 + \text{Re} \left( r_0 e^{2i\kappa d} \right) \right] / \text{Im} \left( r_0 e^{2i\kappa d} \right)$, and $\chi_{1,2} \ll \nu_{\text{FSR}} \left[ 1 + \text{Re} \left( r_0 e^{2i\kappa d} \right) \right]$, the first one being equivalent to the earlier
condition that the Fabry–Pérot resonance be dominated by the linewidth of the TMD. As shown in Appendix E.2, all three inequalities are easily met for $d$ on the order of an optical wavelength.

When these conditions are satisfied, the mirror affects the exciton dynamics in a rather simple fashion. It shifts the resonance frequency by $(\gamma/2) \text{Im} \left( r_0 e^{2i k_0 d} \right)$ and renormalizes the radiative decay rate to $\tilde{\gamma} = \gamma + \gamma \text{Re} \left( r_0 e^{2i k_0 d} \right)$. As alluded to previously, we may view the changes in energy and decay rate as a result of the formation of an exciton-polariton, where the excitonic degrees of freedom hybridize with a photonic mode that occupies the region between the TMD and mirror. At particular distances, the lifetime of the polariton can be significantly enhanced compared to an exciton in free space due to destructive interference between the radiation emitted by the exciton and the localized photonic mode.

After solving for the exciton dynamics governed by Equation (7.1), we can obtain the scattered field from the input–output relations [171]

$$b_{\text{out},L} = t_0 e^{i k_0 d} b_{\text{in},L} + r_0 e^{2i k_0 d} b_{\text{in},R} + \frac{\sqrt{\gamma}}{2} \left(1 + r_0 e^{2i k_0 d}\right) a,$$

$$b_{\text{out},R} = t_0 e^{i k_0 d} b_{\text{in},R} - \frac{t_0}{t_0^*} r_0^* b_{\text{in},L} + \sqrt{\frac{\gamma}{2}} t_0 e^{i k_0 d} a.$$ (7.4)

These expressions, which are derived in Appendix E.2, have the simple interpretation that the output field arises from a superposition of the input fields with the field emitted by the TMD. Supposing that light is incident from the left, the reflection and transmission coefficients can be computed according to $R = \langle b_{\text{out},L}^\dagger b_{\text{out},L} \rangle / \langle b_{\text{in},R}^\dagger b_{\text{in},R} \rangle$ and $T = \langle b_{\text{out},R}^\dagger b_{\text{out},R} \rangle / \langle b_{\text{in},R}^\dagger b_{\text{in},R} \rangle$. For a weak input field, the coefficients computed in this manner agree with the classical
result under the same conditions for which the Heisenberg–Langevin equation holds. The input–output relations also give us access to higher-order photon correlation functions such as the normalized two-time correlation function of the transmitted field,

\[ g^{(2)}_T(\tau) = \frac{\langle b^\dagger_{\text{out},R}(0)b^\dagger_{\text{out},R}(\tau) b_{\text{out},R}(\tau) b_{\text{out},R}(0) \rangle}{\langle b^\dagger_{\text{out},R}(0)b_{\text{out},R}(0) \rangle \langle b^\dagger_{\text{out},R}(\tau)b_{\text{out},R}(\tau) \rangle}. \]  

(7.5)

Such correlation functions can be computed by expressing them in terms of two-time correlation functions of the excitonic operators, which can be related to one-time expectation values using the quantum regression theorem [123]. Finally, we numerically evaluate the one-time expectation values from Equation (7.1) in a truncated Fock space. More details on the numerical methods are provided in Appendix E.4.

### 7.4 Antibunching

For the remainder of the discussion, we focus on the special case \( d = d_{\text{FP}} \), where the sharp Fabry–Pérot resonance occurs. It is possible to neglect the difference between \( k_{\text{FP}} \) and \( k_0 \) under the same conditions that allowed us to ignore retardation. Hence, the resonance condition reads \( r_0 e^{-2ik_0d_{\text{FP}}} = -R_0 \pm i\sqrt{R_0T_0} \) and the radiative decay rate of the exciton-polariton is given by \( \tilde{\gamma} = T_0 \gamma = \gamma_{\text{FP}} \), consistent with the width of the transmission peak. To quantify the effect of line narrowing on the nonlinear dynamics, we plot \( g^{(2)}_T(\tau) \) for different values of the dispersive nonlinearity \( \chi_1 \) in Figure 7.2b. Both the loss rate \( \gamma' \) and the dissipative nonlinearity \( \chi_2 \) are taken to be zero, and we assume that a weak, monochromatic, coherent state resonant with the transmission
peak ($\delta = \delta_{\text{FP}}$) is incident on the TMD from the left. The figure clearly shows that $g_T^{(2)}(0)$ drops significantly below unity for $\chi_1 > \gamma_{\text{FP}}$, confirming the presence a nonclassical state of light with strong photon antibunching [123]. The effect may be understood by observing that the transmission peak of the single and two-exciton transitions are shifted relative to each other by $\chi_1$. If this shift exceeds the peak width $\gamma_{\text{FP}}$, the second photon is reflected with high probability. The mechanism is closely related to polariton blockade in quantum well cavities, where the presence of a single polariton blocks subsequent photons from entering the cavity [172]. In the limit $\chi_1 \to \infty$, the transmission probability of the second photon is given by $T_0$, which explains the small but nonvanishing value of $g_T^{(2)}(0)$. By setting $\chi_1 = \delta_{\text{FP}}$, it is possible to achieve $g_T^{(2)}(0) = 0$ because the transmission peak of the single exciton transition then perfectly matches a zero in transmission of the two-exciton transition (cf. Figure 7.1c at zero detuning). We note that the line narrowing also affects the time scale over which antibunching is observed, the relevant time scale now being $1/\gamma_{\text{FP}}$ rather than the free-space lifetime $1/\gamma$.

A dissipative nonlinearity can also give rise to photon antibunching. Figure 7.2c shows $g_T^{(2)}(0)$ as a function of either $\chi_1$ or $\chi_2$, where the other parameter is set to zero. The two nonlinearities have a qualitatively similar effect on photon antibunching with the main difference being that the perfect antibunching dip at $\chi_1 = \delta_{\text{FP}}$ is absent for the dissipative nonlinearity. While in both cases antibunching is caused by reduced transmission at the two-exciton transition, the dissipative nonlinearity accomplishes this by reducing the peak height rather than by shifting its position.

In order to observe antibunching in the presence of loss, it is necessary
Figure 7.2: (a) Three lowest energy levels of the anharmonic oscillator used to model quantum nonlinear effects. Dispersive and dissipative nonlinearities are denoted by $\chi_1$ and $\chi_2$, respectively. (b) Second order correlation function $g^{(2)}(\tau)$ of the transmitted light at the Fabry–Pérot resonance ($d = d_{FP}$, $\delta = \delta_{FP}$) for different values of $\chi_1$ while $\chi_2 = \gamma' = 0$. Pronounced photon antibunching is observed when $\chi_1 > \gamma_{FP}$. (c) Dependence of $g_T^{(2)}(0)$ on the strength of the nonlinearity. Only $\chi_1$ (blue) or $\chi_2$ (red) is varied, while the other parameter is set to zero. (d) $g_T^{(2)}(0)$ as a function of $\gamma'$ and $T_0$. The experimentally relevant regime to observe strong antibunching is located below the horizontal dashed line ($\chi_1 > \gamma_{FP}$) and above the red line ($\gamma_{FP} > \gamma'$).
that the nonlinearity is large compared to not only $\gamma_{FP}$ but also $\gamma'$. This is illustrated in Figure 7.2d, where we plot $g_{T}^{(2)}(0)$ as a function of both $\gamma'$ and $T_{0}$ for a fixed values of $\chi_{1}$ and $\chi_{2}$. In addition, we still require that $\gamma' < \gamma_{FP}$ to ensure high transmission. These conditions may be summarized as

$$\chi > T_{0}\gamma > \gamma', \quad (7.6)$$

where $\chi$ stands for $\chi_{1}$ or $\chi_{2}$. In Figure 7.2d, these inequalities correspond to the region below the dashed horizontal line, to the left of the dashed vertical line, and above the diagonal red line. We point out that strong antibunching can be observed in the region $\gamma_{FP} < \gamma' < \sqrt{T_{0}\gamma}$ below the red line. However, this region is of little practical relevance as it would be challenging to observe antibunching given the weak transmitted signal.

### 7.5 Experimental parameters

We next discuss the feasibility of our scheme with TMDs. Theoretical calculations [173] have estimated the interaction energy between two excitons delocalized over an area $A$ in WS$_{2}$ (we expect it to be comparable in other TMDs) as $g \approx 4 \text{meV} \mu\text{m}^{2}/A$. The parameter $\chi_{1}$ is obtained by computing the interaction energy of two excitons whose in-plane wavefunction is proportional to the electric field profile of the incident laser. For a Gaussian beam with waist $w_{0}$, we obtain $\chi_{1} = g/(\pi w_{0}^{2})$, where we assumed that the interaction

---

$^1$We note that this value differs from existing estimates based on prior experimental measurements [4]. Our current understanding is that the discrepancy is due to dielectric screening by the substrate used in reference [4], which can be reduced, for instance, by suspending the samples. However, further work is required for a complete quantitative understanding of exciton–exciton interactions in TMDs.
is short ranged. The exciton transition in WS$_2$ occurs at $\lambda_0 \approx 600$ nm [139], which yields $\chi_1 \approx 13 \mu$eV for a diffraction limited spot ($w_0 = \lambda_0/2$). With the intrinsic linewidth given by $\gamma \approx 3$ meV [174], the transmission coefficient of the mirror must therefore satisfy $T_0 \lesssim 1/230$, which is experimentally feasible. In order to prevent the photonic mode from diverging over the course of $\sim 230$ roundtrips, the mirror must be curved with a radius of curvature that matches the incident beam. In practice, the enhancement will be limited by the loss rate $\gamma'$, which depends on the quality of the material. Values of $\gamma' < 0.1\gamma$ have recently been achieved [4]. While the current limiting factors are not fully understood, improved exciton properties have been observed in suspended devices [6], and further advances in material quality will likely result in an additional decrease of $\gamma'$. We note that exciton dispersion places a lower bound on the loss rate. The bound is determined by the time scale $t_d = mw_0^2/(2\hbar)$, $m$ being the exciton mass, after which the exciton wavefunction starts to significantly spread out, leading to a reduced overlap with the photonic mode, and thereby spoiling the Fabry–Pérot resonance. For our purpose, the effect is expected to negligible since the associated rate $\hbar/t_d$ contributing to $\gamma'$ is found to be less than 1 $\mu$eV.

### 7.6 Outlook

The above considerations indicate that TMDs are a promising platform for exploring quantum nonlinear optical phenomena. In addition, our approach is compatible with methods that seek to increase the interaction strength between excitons in order to alleviate the requirements on the loss rate. It
has been proposed that this may be accomplished using excited states of the exciton [173] or by exploiting scattering resonances between excitons [175]. Interlayer excitons in TMD heterostructures offer an alternative route as their permanent dipole moment gives rise to much stronger interactions [176]. Finally, applying a periodic potential to the TMD can enhance the interaction strength by increasing the local exciton density at the potential minima. The potential may be implemented with a modulation of the dielectric environment [177] or via the energy landscape arising from a moiré pattern in a heterostructure [178].

In summary, we have demonstrated that a partially reflecting mirror can be used to dramatically enhance the lifetime of polaritons associated with a resonant two-dimensional material, which in turn enhances the sensitivity to weak nonlinearities. In contrast to other approaches of generating non-classical states of light with weak nonlinearities, such as the unconventional photon blockade [179–182], our scheme does not require fine tuning between the nonlinearity and the loss rate. While we focused on TMDs, the approach is applicable to other emitters coupled to a single scattering channel such as two-dimensional arrays of trapped ultracold atoms [2, 166]. In addition, the approach may be useful as a spectroscopic tool by narrowing emission lines, which does not require reaching the quantum nonlinear regime. The scheme can be naturally extended to multiple emitters such as several closely spaced layers of TMDs, which could replace the conventional mirror entirely [183]. Furthermore, future work could explore the crossover into the non-Markovian regime by moving the emitter sufficiently far away from the mirror such that retardation is no longer negligible [184, 185].
Chapter 8

Rotons in optical excitation spectra of monolayer semiconductors

8.1 Introduction

Rotons are quasiparticles whose dispersion exhibits a minimum at finite momentum. The concept was first proposed by Landau as an explanation for the properties of superfluid $^4$He [186, 187]. More recently, rotons have been predicted and observed in ultracold Bose gases with long-range interactions [188, 189], engineered spin–orbit coupling [190, 191], and shaken optical lattices [192]. However, the study of rotons and other many-body effects in ultracold gases is impeded by the weak interactions between neutral atoms. It is therefore desirable to explore platforms with strong interparticle interactions that simultaneously retain a greater degree of tunability than conventional condensed matter systems such as $^4$He. Over the past few years, monolayers of semiconducting transition metal dichalcogenides (TMDs) have emerged as promising
candidates in this respect [136]. TMDs support tightly bound neutral excitons with binding energies of several hundred meV, which facilitates the optical investigation of many-body effects. The charge carrier density of TMDs can be readily tuned with electrostatic gates. It is further possible to modify the properties of TMDs by stacking them with other van der Waals materials into heterostructures [126] or by changing the dielectric environment [177].

In this work, we investigate the many-body states formed by excitons in doped TMD monolayers. For concreteness, we focus on MoSe$_2$, although we expect our results to qualitatively apply to other TMDs. We first consider a single exciton in a Fermi sea of electrons, where all electrons, including the one that makes up the exciton, are spin and valley polarized. This regime can be accessed experimentally with moderate magnetic fields [193, 194] or by bringing the TMD in contact with a ferromagnetic material such as CrI$_3$ [145]. The exciton dispersion is significantly altered by the Fermi sea since the constituent electron is restricted to states above the Fermi energy $E_F$. We will show that as the Fermi energy is increased from zero, the binding energy of the exciton decreases while its mass increases. At a critical Fermi energy, the exciton mass diverges and the energy minimum is shifted to a finite momentum $p_{\text{rot}}$, which we refer to as a roton minimum. Our results imply that it is in general not justified to assume a constant exciton mass, independent of Fermi energy.

In contrast to ultracold gases and $^4$He, this roton minimum is a consequence of Pauli blocking rather than interparticle interactions. As illustrated in Figure 8.1(b), the exciton reduces the kinetic energy of the hole by adopting a nonzero center-of-mass momentum. A closely related effect has been pre-
dicted for the molecular state of an impurity in an ultracold Fermi gas, where the roton minimum is associated with the formation of Fulde–Ferrell–Larkin–Ovchinnikov states [195]. These states have, however, yet to be observed as they are expected to be unstable over a wide range of parameters [196]. Similar states have been predicted for the indirect exciton states in electron-hole bilayers in GaAs heterostructures [197–199]. In these systems, as well as in TMDs considered here, the roton states are more robust owing to the long-ranged nature of the Coulomb interaction compared to short-range interatomic interactions in ultracold gases.

The treatment of the fully polarized regime serves as a starting point for the experimentally more relevant case where both valleys are populated. The exciton, taken to occupy the $K$ valley, now additionally interacts with the Fermi sea electrons in the opposite $K'$ valley. As a result, the exciton is dressed by electron-hole excitations in the $K'$ conduction band, which leads to the formation of new quasiparticles known as attractive and repulsive polarons [200, 201]. We will demonstrate that the attractive polaron inherits the roton-like dispersion from the exciton. This offers a possible explanation for the difference between absorption and photoluminescence (PL) spectra of MoSe$_2$ at finite doping [193, 200, 202].

8.2 Exciton dispersion

We now proceed to a quantitative discussion, starting with the fully polarized case. We are interested in the bound state between an electron in the conduction band and a hole in the valence band. The Hamiltonian of the
electron-hole system $H_{\text{exc}} = H_K + H_I$ can be decomposed into a kinetic energy part $H_K$ and an interaction part $H_I$. The kinetic energy is simply $H_K = \sum_k \varepsilon_e(k)e_k^\dagger e_k + \sum_k \varepsilon_h(k)h_k^\dagger h_k$, where $e_k^\dagger (h_k^\dagger)$ creates an electron in the conduction band (hole in the valence band) with the respective dispersion $\varepsilon_{e,h}(k) = |k|^2/(2m_{e,h})$. The interaction Hamiltonian is given by the (attractive) Coulomb interaction between electrons and holes, $H_I = -\sum_{kk'q} V(q)e_{k+q}^\dagger h_{k'-q}^\dagger e_k$, where $V(q) = 1/|2\epsilon_0\epsilon(q)||q|$ takes into account nonlocal dielectric screening specific to monolayers with $\epsilon(q) = 1 + r_0|q|$ and $r_0 \approx 5$ nm in MoSe$_2$ [203]. We neglect electron-electron as well as electron-hole exchange terms, as they only affect the dispersion of the lowest exciton branch via a small mass renormalization [131–135, 204].

We calculate the exciton energy variationally. Defining the exciton creation operator $x_p^\dagger = \sum_k \varphi_p(k)e_k^\dagger$ for a given total momentum $p$, we minimize $W_{\text{exc}}(p) = \langle \text{FS}|x_p|H_{\text{exc}} - E_{\text{exc}}(p)|x_p|\text{FS}\rangle$, where $|\text{FS}\rangle$ denotes the electron Fermi sea. The electron making up the exciton is thus confined to states above the Fermi sea ($|k| > k_F$). The exciton energy $E_{\text{exc}}(p)$ (measured with respect to the semiconductor band gap at $E_F = 0$) acts as a Lagrange multiplier to ensure the exciton state is suitably normalized. We solve the eigenvalue problem corresponding to $\delta W_{\text{exc}}(p)/\delta \varphi_p(k) = 0$ numerically using angular momentum eigenstates on a nonuniform radial grid (see Appendix F.1 for details).

The dispersion thus obtained is shown in Figure 8.1(a) for Fermi energies between $E_F = 0$ meV and $E_F = 50$ meV. At large doping, the dispersion minimum shifts to finite momentum. The schematic illustration in Figure 8.1(b) provides a qualitative explanation for the emergence of such a roton state.
With the electron constrained to states above the Fermi sea, an electron-hole pair with zero total momentum carries a larger kinetic energy than an electron-hole pair in which the hole occupies a state closer to the valence band maximum. At small Fermi energies, the Coulomb attraction more than compensates for the cost in kinetic energy, allowing the lowest energy exciton to remain at zero momentum. The energy cost increases with increasing Fermi energy such that the excitonic ground state eventually shifts to finite momentum. While the roton minimum originates from Pauli blocking, the exact form of the electron-hole interaction plays a crucial role in determining the Fermi energy at which the roton minimum appears. In our case, using the dielectrically screened Coulomb potential, the roton minimum develops at $E_F \approx 20 \text{ meV} \approx E_0/25$, where $E_0$ denotes the exciton binding energy at zero Fermi energy. By contrast, a much greater Fermi energy of $E_F = E_0/2$ would be required if the electron and hole interacted via contact interaction (assuming equal carrier masses) [196]. The Pauli blocking effect is more pronounced for long-range interactions because scattering with large momenta to accessible states across the Fermi sea is suppressed. It is especially efficient in monolayer materials due to the short-range dielectric screening which further suppresses momenta on the order of $1/r_0$.

The properties of the dispersion are explored more quantitatively in Figures 8.1(c)–(e). Figure 8.1(c) shows the energy separation between the exciton at zero momentum and the lowest energy state, indicating that the ground state is no longer at zero momentum when the Fermi energy exceeds $E_F \approx 20 \text{ meV}$. In Figure 8.1(d), we plot the momentum at which the dispersion minimum occurs. As expected from the qualitative argument given in
the context of Figure 8.1(b), the momentum of the roton is on the order of the Fermi momentum (dashed line). Finally, the effective mass both at zero momentum and at the roton minimum $p_{\text{rot}}$ is plotted in Figure 8.1(e). The effective mass at the roton minimum corresponds to the curvature of the dispersion along the radial direction, while the mass in the tangential direction diverges as a consequence of rotational symmetry.

Figure 8.1: (a) Lower panel: Exciton dispersion at different Fermi energies, $E_F$. Upper panels: Electron wavefunction $|\varphi_p(k)|^2$ as a function of $(k_x, k_y)$ at three different center of mass momenta $p$ indicated by the red crosses. The blocked out circle is the Fermi sea. The axis limits are $\pm 0.25 \text{ Å}^{-1}$. (b) Schematic drawing illustrating the origin of the roton-like dispersion. As a function of Fermi energy: (c) Energy difference $\Delta E = E_{\text{exc}}(0) - \min E_{\text{exc}}(p)$ between the zero momentum exciton and the lowest energy state. (d) Momentum of the lowest energy exciton state (solid) and Fermi momentum (dashed). (e) Exciton mass at zero momentum (blue) and at the roton minimum (red).
The above treatment ignores screening by the Fermi sea. A common approach to include screening for the exciton problem is based on the $GW$ approximation and the corresponding screened ladder approximation [205, 206]. However, since the plasma frequency $\omega_{pl}(q) = \sqrt{n_e |q|^2 V(|q|)/m_e} \approx 90\,\text{meV}$ at $|q| = k_F$ for a Fermi energy of $E_F = 20\,\text{meV}$ is much smaller than the exciton binding energy, the electron gas is unable to respond on the time scales characteristic for the electron-hole interaction. More specifically, the time scale for the bound electron–hole pair to scatter off each other via the Coulomb interaction is set by $1/E_{exc} \ll 1/\omega_{pl}$, implying that many scattering events may occur during the lifetime of a virtual plasmon. This is in stark contrast to the physical picture of the noncrossing, screened ladder approximation, in which virtual excitations of the Fermi sea are created and annihilated sequentially before the bound electron-hole pair scatters again. Therefore, the aforementioned treatment of screening is likely be valid only in the limit $1/E_{exc} \gg 1/\omega_{pl}$, while in the opposite limit, the electrons might prefer to screen the exciton as a whole [200]. The above discussion highlights that an accurate treatment of screening is challenging and offers an explanation for the observed stability of excitons at high carrier densities [207], which is unexpected from the screened ladder calculations [206].

In our approach, screening can be taken into account by extending our ansatz to allow for electron–hole pair excitations in the Fermi sea. Such an ansatz not only enables a treatment of screening beyond the screened ladder approximation but it has moreover been shown to increase the robustness of the roton-like dispersion in ultracold Fermi gases [196, 208]. Translated to our system, the improvement of the variational ansatz is a consequence of
the fact that in the original electronic wavefunction, the roton state carries a large electron momentum of order $p_{\text{rot}}$ despite its zero group velocity [see Figure 8.1(a)]. A wavepacket formed by states near the roton minimum would therefore disperse very quickly, which implies that our ansatz is far from an energy eigenstate. This argument was used by Feynman to motivate the introduction of backflow corrections in superfluid helium [209], which significantly lower the variational energy of the roton. A quantitative treatment of these effects is however beyond the scope of the present work.

8.3 Polaron formation

We next discuss the situation in which the electrons are unpolarized. Since there exists a trion bound state between the excitons in the $K$ valley and electrons in the $K'$, dressing of the exciton by the electrons in the opposite valley must be considered. We treat this problem within the rigid exciton approximation [200, 201], in which the Hamiltonian is given by

$$
H_{\text{pol}} = \sum_{\mathbf{k}} E_{\text{exc}}(\mathbf{k}) x_{\mathbf{k}}^\dagger x_{\mathbf{k}} + \sum_{\mathbf{k}} \varepsilon_{\mathbf{e}}(\mathbf{k}) e_{\mathbf{k}}^\dagger e_{\mathbf{k}}' + \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} U_{\mathbf{q}} x_{\mathbf{k}+\mathbf{q}}^\dagger e_{\mathbf{k}'}^\dagger e_{\mathbf{k}'} x_{\mathbf{k}}, \quad (8.1)
$$

where $x_{\mathbf{k}}^\dagger$ creates an exciton at momentum $\mathbf{k}$ in the $K$ valley, and $e_{\mathbf{k}}^\dagger$ creates an electron at $\mathbf{K'} + \mathbf{k}$. We emphasize that due to the important role of Pauli blocking, we do not take the exciton mass to be independent of the Fermi energy as in previous works [200, 201] but we instead use the detailed exciton dispersion $E_{\text{exc}}(\mathbf{k})$ computed above. We further assume a contact interaction potential between electrons and excitons, $U_{\mathbf{q}} = U$, where the strength $U$ of the interaction can be related to the experimentally accessible trion binding
energy $E_T$, i.e. the binding energy of one exciton and one electron. The use of contact interaction is justified in the limit of low-energy scattering and has been shown to accurately reproduce experimental observations [200]. It is possible to show from Equation (8.1) that $1/U = -\sum_{|k|<\Lambda} [E_T + E_{\text{exc}}(k) + \varepsilon_e(k)]^{-1}$, at $E_F = 0$, where $\Lambda$ is a high-momentum cutoff that regularizes the interaction [196]. For the remaining numerical calculations, we use $E_T = 30 \text{meV}$ [210] and employ a finite cutoff, $\Lambda = 1 \text{nm}^{-1}$. The choice of cutoff is physically motivated by the exciton Bohr radius $a \approx 1 \text{nm}$, which introduces a length scale at which the Hamiltonian in Equation (8.1) becomes invalid as the exciton may no longer be treated as a rigid, point-like object.

The interaction with electrons gives rise to an exciton self-energy $\Sigma(E, \mathbf{p})$ and the dressed exciton (or Fermi polaron) energy $E_{\text{pol}}(\mathbf{p})$ can be obtained by solving the equation $E_{\text{pol}}(\mathbf{p}) = E_{\text{exc}}(\mathbf{p}) + \Re \Sigma(E_{\text{pol}}(\mathbf{p}), \mathbf{p})$. We calculate the self-energy using the non-self-consistent ladder approximation of the $T$-matrix [201, 211]. This approach is equivalent to a variational treatment known as the Chevy ansatz [212], where a polaron with momentum $\mathbf{p}$ is associated with a creation operator of the form $b_\mathbf{p}^\dagger = \alpha_\mathbf{p} x_\mathbf{p}^\dagger + \sum_{k,q} \beta_{\mathbf{p},k,q} x_{\mathbf{p}+\mathbf{k}}^\dagger e_{\mathbf{k}+\mathbf{q}}^\dagger e_{\mathbf{q}}^\dagger$. The polaron dispersion can then alternatively be computed by minimizing the quantity $W_{\text{pol}}(\mathbf{p}) = \langle \text{FS} | b_\mathbf{p}^\dagger [H_{\text{pol}} - E_{\text{pol}}(\mathbf{p})] b_\mathbf{p}^\dagger | \text{FS} \rangle$. The result is shown in Figure 8.2(a) at three different Fermi energies, where we plot the exciton spectral function $S(E, \mathbf{p}) = -2 \Im [E - E_{\text{exc}}(\mathbf{p}) - \Sigma(E, \mathbf{p}) + i\gamma/2]^{-1}$ as a function of energy $E$ and momentum $\mathbf{p}$, having introduced a momentum-independent broadening $\gamma$. The polaron states appear as peaks in the exciton spectral function, with the lower and higher energy peak corresponding to the attractive and repulsive polaron, respectively. The attractive polaron is bound to
Figure 8.2: (a) Spectral function $S(E, p)$ for three different Fermi energies, $E_F$. The dashed line indicates the exciton dispersion $E_{\text{exc}}(p)$. As a function of Fermi energy: (b) Momentum of the lowest energy attractive polaron state (solid) and Fermi momentum (dashed). (c) Mass of the attractive polaron at zero momentum (blue) and at the roton minimum (red). (d) Optical conductivity $\sigma(E)$ according to Equation (8.2). The lowest energy of the attractive polaron is shown by the dashed line. A linewidth of $\gamma = 3$ meV was used.

a dressing cloud of electrons, which lowers the energy below that of the bare exciton (dashed line). It also inherits the roton minimum from the exciton as shown in Figures 8.2(b) and (c). We emphasize that the roton minimum in the exciton spectral function is distinct from the minimum in the trion spectral function, which occurs even if the exciton mass is assumed to be independent of Fermi energy [201, 211]. While the range of validity of the approximations employed here might not extend to the highest electron densities considered, we expect the roton minimum to be a robust feature of the polaron dispersion.
8.4 Optical spectra

The reflection, transmission, and absorption by the monolayer is determined in linear response by the optical conductivity [201]

$$\sigma(E) \propto \left| \sum_{k} \varphi_{0}(k) \right|^{2} S(E, 0). \quad (8.2)$$

The in-plane momentum is zero since the momentum transferred by a photon is negligible for all incident angles. The optical conductivity is therefore insensitive to the presence or absence of the roton state. This is illustrated in Figure 8.2(d), where we plot the optical conductivity as a function of Fermi energy. At high doping, the spectral weight is transferred from the repulsive polaron to the attractive polaron at zero momentum rather than the lowest energy state corresponding to the roton minimum (dashed line).

In contrast to the optical conductivity, the roton state drastically modifies the photoluminescence properties of MoSe$_2$. To compute the emission spectrum and radiative decay rates, we apply Fermi’s golden rule to the fully quantized light-matter interaction Hamiltonian using the polaronic wavefunction obtained from the Chevy ansatz as the initial state. This yields the spectral emission rate $\Gamma_{\text{tot}}(\nu)$ of a photon with frequency $\nu$, which may be split into four separate terms, $\Gamma_{\text{tot}}(\nu) = \sum_{i=1}^{4} \Gamma_{i}(\nu)$, according to four different physical processes (see Appendix F.2). The first rate, $\Gamma_{1}$, corresponds to decay of the pure excitonic component of the polaron (amplitude $\alpha_{\mathbf{p}}$ in $b_{\mathbf{p}}^\dagger$). For a zero momentum state, it is sharply peaked at $\nu = E_{\text{pol}}(0)$ with a magnitude comparable to the decay rate $\Gamma_0$ of an exciton at zero momentum in undoped MoSe$_2$. The rate vanishes if $|\mathbf{p}| > \nu/c$ and the decay is instead deter-
mined by the remaining three rates, whose underlying process is represented schematically in Figure 8.3(a). The process associated with $\Gamma_2$ is similar to $\Gamma_1$ as it involves the recombination of the correlated electron-hole pair forming the exciton, but it does so while leaving behind an electron-hole pair in the opposite Fermi sea. The rates $\Gamma_3$ and $\Gamma_4$ result from radiative recombination of the valence band hole with an electron from the Fermi sea.

Figure 8.3: (a) Illustration of different polaron decay channels. (b) Emission spectra computed for the polaronic roton state at different Fermi energies. The dashed line indicates the energy of the roton state, where zero energy is defined by the attractive polaron at zero momentum. (c) Radiative recombination rates $\Gamma_i$ of the polaronic roton state as a function of Fermi energy. Here, $\Gamma_0$ is the decay rate of an exciton at zero momentum and zero Fermi energy.

In Figure 8.3(b), we plot the emission spectrum $\Gamma_{\text{tot}}(\nu)$ of the roton-like polaronic ground state at different Fermi energies. The zero of the frequency axis is chosen to coincide with the energy of the attractive polaron at zero
momentum, where maximum absorption is expected. The emission is clearly redshifted relative to absorption. In fact, the emission peak occurs with an energy of roughly $E_F$ below the roton state (dashed line) as a result of the electron-hole pair excitations left behind in the Fermi sea. The spectrally integrated decay rates, defined by $\Gamma_i = \int d\nu \Gamma_i(\nu)$, are shown in Figure 8.3(c).

Phonons may significantly contribute to the decay rate since they offer an additional pathway for the roton-like state to deposit its excess momentum. However, we expect that phonon-assisted decay gives rise to a qualitatively similar redshift and broadening as the decay channels discussed above. A complete calculation of the photoluminescence (PL) spectrum must further take into account the distribution of occupied states, which depends on pumping and relaxation mechanisms [213]. A detailed understanding of the relevant processes in TMDs is currently missing.

8.5 Outlook

Our results offer a potential explanation for experimental observations in absorption and PL spectra [202]. In particular, at high electron densities, the emission spectrum begins to redshift relative to the absorption peak and concurrently broadens and decreases in intensity. Both the energy shift and the broadening scale linearly with the Fermi energy $E_F$, with a proportionality constant of order unity. This doping dependent splitting between absorption and PL with an onset at a finite electron density is consistent with our model, where absorption probes zero momentum states, while PL can originate from states close to the lowest energy polaron. Additional experiments may provide
further verification of the proposed mechanism. A measurement of the sign change of the polaron mass at zero momentum would provide direct evidence for the emergence of a roton state. Due to the small photon momentum, such measurements are challenging although near-field techniques [214] or acoustic waves [215] could allow one to couple to polaron states with momenta exceeding \( \nu/c \). PL lifetime measurements offer a simpler but more indirect probe of the polaron dispersion. Our above treatment suggests that the PL lifetime is drastically increased when the roton minimum is fully developed.

In summary, we proposed a mechanism for the formation of roton states of optical excitations in TMD monolayers. Besides playing an important role in determining optical properties, the roton states open up exciting avenues for creating exotic phases of optical excitations such as supersolids [216] or chiral spin liquids [217]. In particular, if the optical excitations condense into the roton-like minimum, the exact form of interactions between excitations determines whether it is energetically favorable for the condensate to occupy a single momentum state or to fragment [216]. The latter scenario gives rise to a superfluid state with periodic density modulation, corresponding to a supersolid. Future work may extend the quantitative validity of our approach beyond low electron densities by including backflow corrections, adding a treatment of dynamical screening, and relaxing the rigid exciton approximation.
Appendix A

Supporting material for Chapter 2

A.1 Derivation of the effective Hamiltonian

In this section, we derive the effective interaction Hamiltonian in Equation (2.2) from a microscopic model of the system–environment interaction. The Hamiltonian of the closed system was described in Section 2.3.1

\[ H(s) = E_0(1 - s)(I - |\psi_0\rangle\langle\psi_0|) + E_0s(I - |m\rangle\langle m|), \quad (A.1) \]

where \(|m\rangle\) is the marked state and \(|\psi_0\rangle = \frac{1}{\sqrt{N}} \sum_{x=1}^{N} |x\rangle\). We assume that this Hamiltonian is implemented using \(L\) qubits, such that the states \(|x\rangle\) in the search space are represented by the \(N = 2^L\) eigenstates of the Pauli operators \(\{\sigma_j^z\}\), with \(j = 1,\ldots,L\), acting on the individual qubits. We consider the situation where each qubit is coupled to an independent, bosonic...
bath, described by the generic interaction Hamiltonian

$$V = \sum_{j=1}^{L} \sum_{\mu=x,y,z} \sigma^\mu_j \otimes \sum_k g^\mu_{jk} \left( b^\mu_{jk} + b^{\dagger \mu}_{jk} \right). \quad (A.2)$$

Here $b^\mu_{jk}$ are independent bosonic annihilation operators and $g^\mu_{jk}$ is the coupling strength to a particular mode. We further assume that the baths are identical such that the bath Hamiltonian is given by

$$H_B = \sum_k \omega_k \sum_{j=1}^{L} \sum_{\mu=x,y,z} b^{\dagger \mu}_{jk} b^\mu_{jk}. \quad (A.3)$$

We note that many of the present assumptions can be relaxed without affecting our results qualitatively. For instance, our calculation readily carries over to the situation where all qubits couple to the same environment provided the interaction remains local.

In a closed system, the excited states at energy $E_0$ are completely decoupled from the non-trivial subspace $\mathcal{S} = \text{span}\{ |m\rangle, |m\perp\rangle \}$. Although this is not the case in an open system, we can describe the dynamics of the subspace $\mathcal{S}$ near the avoided crossing by an effective Hamiltonian provided the steady-state population in the excited levels is negligible. In thermal equilibrium with a bath at temperature $T$, this gives rise to the condition $T \ll E_0/L$ near the avoided level crossing. Since $E_0$, the overall energy scale of the system, is an extensive quantity, this condition can be satisfied by a small but intensive temperature. In this limit, the effective Hamiltonian for the system and environment can be derived using the general formalism in reference [218],
yielding

\[ H_{\text{eff}} = PH(s)P + H_B + PV P \]
\[ + \frac{1}{2} \sum_{a,b,e} \left( \frac{1}{E_a - E_e} + \frac{1}{E_b - E_e} \right) |a\rangle \langle a| |V|e\rangle \langle e|V|b\rangle \langle b|, \quad (A.4) \]

where \( P \) is the projection operator onto \( S \). In the sum, the indices \( a, b \) run over the eigenstates of \( H(s) \) in \( S \) (low-energy states), while \( e \) refers to the states in the orthogonal subspace (excited states). There are two contributions to the interaction of the environment with the low-energy states: a direct interaction and one that is mediated by the excited states through virtual processes. We have neglected higher order terms, which include couplings between different excited states. Such processes cannot be described in terms of the parameters of the avoided crossing alone and are therefore beyond the scope of our discussion. Furthermore, these processes do not affect our results qualitatively as discussed in more detail in Appendix A.2.2.

The quantum speedup in the closed system is enabled by tunneling near the avoided level crossing. We will therefore restrict ourselves to that region, which allows us to replace the energy differences in the denominator of the last term in Equation (A.4) by \(-E_0/2\), neglecting terms of order \( \sqrt{\varepsilon^2 + \Delta^2}/E_0 \). This drastically simplifies the expression to

\[ H_{\text{eff}} \approx H_S + H_B + PV P - \frac{1}{2E_0} PV (I - P) VP, \quad (A.5) \]

where

\[ H_S(s) = PH(s)P = \frac{E_0}{2} - \frac{1}{2} \left[ \varepsilon(s) \tau^z + \Delta(s) \tau^x \right]. \quad (A.6) \]
Here $\tau^\mu$ are the Pauli matrices acting on $S$. In the $\{|m\}, |m_\perp\rangle$ basis, the projections of the Pauli operators acting on the physical qubits are given by (see the appendix of reference [219] for details)

$$P\sigma_j^x P = \frac{1}{N-1} \begin{pmatrix} 0 & \sqrt{N-1} \\ \sqrt{N-1} & N-2 \end{pmatrix}, \quad (A.7)$$

$$P\sigma_j^y P = \frac{s_j}{\sqrt{N-1}} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad (A.8)$$

$$P\sigma_j^z P = \frac{s_j}{N-1} \begin{pmatrix} N-1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (A.9)$$

where $s_j = \langle m | \sigma_j^{(z)} | m \rangle = \pm 1$. We observe that the off-diagonal terms in these matrices are of order $O(N^{-1/2})$ so that coupling between $|m\rangle$ and $|m_\perp\rangle$ is suppressed in the limit of large $N$. This fact has the simple physical interpretation that $|m\rangle$ and $|m_\perp\rangle$ are macroscopically distinct, while the environment acts only locally. In the following, we neglect all terms of order $O(N^{-1/2})$ and below.

The direct interaction of the environment with the low-energy subspace is hence given by

$$V_1 = PV P \approx \frac{1}{2} \sum_{j=1}^L \sum_k \left[ g_{jk}^x (I - \tau^z) \otimes (b_{jk}^x + b_{jk}^{x\dagger}) + g_{jk}^z s_j (I + \tau^z) \otimes (b_{jk}^z + b_{jk}^{z\dagger}) \right], \quad (A.10)$$
while the excited states mediate a two-boson interaction of the form

\[ V_2 = -\frac{1}{2E_0} PV(I - P)V \]

\[ \approx -\sum_{j=1}^{L} \sum_{k,l} \left[ \frac{g_{jk}^x g_{ji}^x}{4E_0} (I + \tau^z) \otimes \left( b_{jk}^x + b_{jk}^{x\dagger} \right) \left( b_{ji}^x + b_{ji}^{x\dagger} \right) \right] \]

\[ + \frac{g_{jk}^y g_{ji}^y}{2E_0} I \otimes \left( b_{jk}^y + b_{jk}^{y\dagger} \right) \left( b_{ji}^y + b_{ji}^{y\dagger} \right) \]

\[ + \frac{g_{jk}^z g_{ji}^z}{4E_0} (I - \tau^z) \otimes \left( b_{jk}^z + b_{jk}^{z\dagger} \right) \left( b_{ji}^z + b_{ji}^{z\dagger} \right) \].

This follows from the observation that \( P\sigma_i^+ \sigma_j^+ P \approx P\sigma_j^+ P\sigma_j^+ P \) when \( i \neq j \). We note that the field \( b_i^y \) only couples to the identity and therefore does not affect the dynamics of the system. In order to further simplify the expressions, let us focus on a single \( x \) mode and simplify the notation by only retaining a single subscript for the mode label. The bath plus effective interaction Hamiltonian involving this mode takes the form

\[ H_x = I \otimes \left[ \sum_k \omega_k b_k^\dagger b_k + \sum_k \frac{g_k}{2} \left( b_k + b_k^\dagger \right) - \sum_{k,l} \frac{g_k g_l}{4E_0} \left( b_k + b_k^\dagger \right) \left( b_l + b_l^\dagger \right) \right] - \]

\[ -\tau^z \otimes \left[ \sum_k \frac{g_k}{2} \left( b_k + b_k^\dagger \right) + \sum_{k,l} \frac{g_k g_l}{4E_0} \left( b_k + b_k^\dagger \right) \left( b_l + b_l^\dagger \right) \right]. \]

The terms coupling to the identity can be understood as the back action of the system on the environment. We account for this effect by diagonalizing these terms, resulting in a set of renormalized bosonic operators. It is straightforward to check that the single-boson term can be accounted for by introducing the shifted operators

\[ c_k = b_k + \frac{1}{1 - a} \frac{g_k}{2\omega_k}, \]

\[ (A.13) \]
where

\[ a = \frac{1}{E_0} \sum_k \frac{g_k^2}{\omega_k} = \frac{1}{E_0} \int_0^\infty d\omega J(\omega) \frac{1}{\omega}. \]  \hspace{1cm} (A.14)

The existence of the integral requires that \( J(\omega) \) decays sufficiently fast as \( \omega \to \infty \). Furthermore, the power-law dependence \( J(\omega) \propto \omega^{\eta} \) must satisfy \( \eta > 0 \). The Hamiltonian \( H_x \) can hence be written as

\[ H_x = I \otimes \left[ \sum_k \omega_k c_k^\dagger c_k - \sum_{k,l} \frac{g_{kl} \bar{g}_l}{4E_0} \left( c_k + c_k^\dagger \right) \left( c_l + c_l^\dagger \right) \right] - \tau^z \otimes \left[ \frac{\bar{\varepsilon}}{2} + \frac{1 - 2a}{1 - a} \sum_k g_k \left( c_k + c_k^\dagger \right) + \sum_{k,l} \frac{g_{kl} \bar{g}_l}{4E_0} \left( c_k + c_k^\dagger \right) \left( c_l + c_l^\dagger \right) \right], \]  \hspace{1cm} (A.15)

where we introduced the environment-induced bias

\[ \bar{\varepsilon} = \frac{E_0 a(3a - 2)}{4(1 - a)^2}. \]  \hspace{1cm} (A.16)

This induced bias results in a shift of the avoided level crossing. Since the location of the avoided level crossing bears no significance, as long as it is known, we will drop the environment-induced bias in what follows.

The quadratic term coupling to the identity can be diagonalized perturbatively using the techniques outlined in Appendix A.4. The result is that

\[ H_x = I \otimes \sum_k \bar{\bar{\omega}}_k d_k^\dagger d_k \]

\[ - \tau^z \otimes \left[ \sum_k \bar{g}_k \left( d_k + d_k^\dagger \right) + \sum_{k,l} \frac{\bar{g}_k \bar{g}_l}{E} \left( d_k + d_k^\dagger \right) \left( d_l + d_l^\dagger \right) \right], \]  \hspace{1cm} (A.17)
where

\[ \tilde{\omega}_k = \omega_k - \frac{g_k^2}{2E_0}, \quad (A.18) \]

\[ \tilde{g}_k = \frac{1 - 2a}{1 - a} \left( 1 - \frac{g_k}{2E_0} \sum_{l \neq k} \frac{g_l}{\omega_k - \omega_l} + \frac{g_k}{2E_0} \sum_l \frac{g_l}{\omega_k + \omega_l} \right) \frac{g_k}{2}, \quad (A.19) \]

\[ \tilde{E} = \left( \frac{1 - a}{1 - 2a} \right)^2 E_0, \quad (A.20) \]

and \( d_k \) are new bosonic operators. They can be related to \( c_k \) by

\[ d_k \approx c_k + \frac{g_k}{2E_0} \sum_{l \neq k} \frac{g_l}{\omega_k - \omega_l} c_l - \frac{g_k}{2E_0} \sum_l \frac{g_l}{\omega_k + \omega_l} c_l \dagger. \quad (A.21) \]

Before proceeding, it is worth verifying the validity of perturbation theory employed here. The correction of the energy eigenvalues is certainly small since \( g_k^2 \) is inversely proportional to the volume of the bath. It vanishes entirely in the thermodynamic limit and we will therefore neglect it below. In addition, we require that the correction to the bosonic operators be small, i.e.,

\[ \frac{g_k^2}{4E_0^2} \left[ \sum_{l \neq k} \frac{g_l^2}{(\omega_k - \omega_l)^2} + \sum_l \frac{g_l^2}{(\omega_k + \omega_l)^2} \right] \ll 1. \quad (A.22) \]

Let us consider the first sum by re-writing it in terms of the noise spectral density \( J(\omega) \). We introduce the mode spacing \( \Delta \omega \) at frequency \( \omega_k \) such that

\[ \frac{g_k^2}{4E_0^2} \sum_{l \neq k} \frac{g_l^2}{(\omega_k - \omega_l)^2} = \frac{1}{4E_0^2} \int_{\omega_k - \Delta \omega}^{\omega_k + \Delta \omega} d\omega J(\omega) \left[ \int_{0}^{\omega_k - \Delta \omega} \frac{d\omega'}{(\omega - \omega')^2} - \int_{\omega_k - \Delta \omega}^{\infty} d\omega' \frac{J(\omega')}{(\omega - \omega')^2} \right]. \quad (A.23) \]
We are interested in the continuum limit $\Delta \omega \to 0$, which yields

$$
\frac{g_k^2}{4E_0^2} \sum_{l \neq k} \frac{g_l^2}{(\omega_k - \omega_l)^2} = \frac{J(\omega_k)}{2E_0^2} \lim_{\Delta \omega \to 0} \Delta \omega \left[ \int_0^{\omega_k - \Delta \omega} \frac{J(\omega')}{(\omega_k - \omega')^2} d\omega' + \int_{\omega_k + \Delta \omega}^{\infty} \frac{J(\omega')}{(\omega_k - \omega')^2} d\omega' \right] = \frac{J(\omega_k)^2}{E_0^2},
$$

where we employed L’Hôpital’s rule to evaluate the limit. This shows that the first sum in Equation (A.22) is small as long as the weak coupling limit $J(\omega) \ll E_0$ is satisfied. The second sum can be bounded from above by

$$
\frac{g_k^2}{4E_0^2} \sum_l \frac{g_l^2}{(\omega_k + \omega_l)^2} \leq \frac{g_k^2}{4E_0^2} \sum_{l \neq k} \frac{g_l^2}{(\omega_k - \omega_l)^2} + \frac{g_k^4}{16E_0^2\omega_k^2} \leq \frac{J(\omega_k)^2}{E_0^2} + \lim_{\Delta \omega \to 0} \Delta \omega^2 \frac{J(\omega_k)^2}{16E_0^2\omega_k^2}.
$$

The last term is again small in the weak coupling regime since we can always take $\omega_k \geq \Delta \omega$ without modifying the spectrum of the bath significantly. Hence, perturbation theory is valid in the weak coupling regime.

The Hamiltonian in Equation (A.17) indeed has the form of the effective Hamiltonian in Equation (2.2). There will be a similar contribution for each qubit and polarization of the bath modes. Since these contributions all commute, we expect the dynamics to be well described by a single contribution, with the only modification being that $J(\omega)$ should multiplied by the number of channels that couple to the environment.
We argued throughout Chapter 2 that it is possible to treat the fast oscillators of the environment by introducing a renormalized tunneling rate between the two well states. More specifically, we consider the system and bath Hamiltonian

\[
H = -\frac{1}{2} (\varepsilon \tau^z + \Delta \tau^x) + \sum_k \omega_k b_k^\dagger b_k
\]

\[
+ \tau^z \otimes \left[ \sum_k g_k \left( b_k + b_k^\dagger \right) + \sum_{k,l} \frac{g_k g_l}{E} \left( b_k + b_k^\dagger \right) \left( b_l + b_l^\dagger \right) \right]
\] (A.26)

in the absence of tunneling, \( \Delta = 0 \). The eigenstates in this case can be written as

\[
|\tau, n\rangle = e^{-i\tau^z S}|\tau\rangle \otimes \prod_k \frac{1}{\sqrt{n_k!}} (b_k^\dagger)^{n_k} |0\rangle = e^{-i\tau^z S}|\tau\rangle \otimes |n\rangle
\] (A.27)

where \( \tau = m, m_\perp \) labels the two eigenstates of \( \tau^z \). The unitary \( S \) diagonalizes the system bath interaction,

\[
e^{i\tau^z S} \left\{ \sum_k \omega_k b_k^\dagger b_k + \tau^z \otimes \left[ \sum_k g_k \left( b_k + b_k^\dagger \right) 
\right.
\]

\[
\left. + \sum_{k,l} \frac{g_k g_l}{E} \left( b_k + b_k^\dagger \right) \left( b_l + b_l^\dagger \right) \right] \right\} e^{-i\tau^z S} = \sum_k \omega_k b_k^\dagger b_k,
\] (A.28)

where we dropped all terms acting only on the system on the right-hand side of the equation. We have also neglected corrections to the spectrum of the environment by the system–environment interaction since they are inversely proportional to the volume of the bath, as already observed in the derivation of the effective Hamiltonian in Appendix A.1. The Hamiltonian to be diag-
onalized here is in fact very similar to that in Appendix A.1 and the same
methods can be applied. We obtain

\[ e^{-i\tau^z S} = e^{-i\tau^z S_1} e^{-i\tau^z S_2} \]  \hspace{1cm} (A.29)

where

\[ S_1 = i \sum_k \delta_k \left( b_k - b_k^\dagger \right), \quad \delta_k = \frac{1}{1 - a^2 \omega_k}, \quad a = \frac{4}{E} \int d\omega \frac{J(\omega)}{\omega} \]  \hspace{1cm} (A.30)

effects a displacement to remove the single-boson terms, while

\[ S_2 = \sum_{k,l} \left[ A_{kl} b_k^\dagger b_l + \frac{i}{2} B_{kl} \left( b_k b_l - b_k^\dagger b_l^\dagger \right) \right], \]  \hspace{1cm} (A.31)

\[ A_{kl} = -\frac{2i}{\omega_k - \omega_l} \frac{g_k g_l}{E} (1 - \delta_{kl}), \quad B_{kl} = -\frac{2}{\omega_k + \omega_l} \frac{g_k g_l}{E} \]  \hspace{1cm} (A.32)
diagonalizes the two-boson terms in the weak coupling limit, \( J(\omega) \ll E \). We
point out that we omitted a term proportional to \( \tau^z \) in the expression for
the displacement \( \delta_k \). Such a term merely gives rise to a state-independent
displacement in Equation (A.29), which does not affect the renormalized tunneling rate as will be apparent shortly. In addition, we will drop the pre-factor
involving \( a \) since we are only interested in the asymptotic scaling with the size
of the search space.

For a given set of occupation number \( \mathbf{n} \), the renormalized tunneling rate
can now be expressed as

\[ \tilde{\Delta}_\mathbf{n} = \Delta\langle m, \mathbf{n} | \tau^x | m, \mathbf{n} \rangle' = \Delta\langle \mathbf{n} | e^{-iS_2} e^{-2iS_1} e^{-iS_2} | \mathbf{n} \rangle'. \]  \hspace{1cm} (A.33)
Here the prime reminds us that we should only consider processes that are fast compared to the dynamics of the system. At zero bias, the only time scale of the system is set by the renormalized tunneling rate. Hence, the renormalized tunneling rate may be determined self-consistently by evaluating the expectation value in Equation (A.33) with a low-frequency cutoff \( \Omega = p\tilde{\Delta}_n \), where \( p \) is an unimportant numerical factor as long as \( p \gg 1 \). We point out this argument readily generalizes to the case of finite bias, where the cutoff should be taken to be \( \Omega = p\sqrt{\varepsilon^2 + \tilde{\Delta}_n^2} \). We do not discuss this more complicated case here since the transition between the coherent and incoherent regime first occurs at the smallest gap of the system, that is, at zero bias. Any potential quantum speedup is lost when the system is rendered incoherent during any part of the evolution. Thus, the coherence properties at zero bias fully determine the performance of the algorithm.

The renormalized tunneling rate in Equation (A.33) clearly depends on the occupation numbers \( \mathbf{n} \) and it is therefore not unique at finite temperature. Nevertheless, we can obtain a typical value \( \tilde{\Delta} \) by taking a thermal expectation value

\[
\tilde{\Delta} = \Delta \text{tr} \left\{ e^{-iS_2} e^{-2iS_1} e^{-iS_2} \right\},
\]

(A.34)

where \( \rho = e^{-\sum \omega_k b_k^\dagger b_k/T}/\mathcal{Z} \) is the thermal state at temperature \( T \).

### A.2.1 Single-boson processes

Before we consider Equation (A.34) fully, it is instructive to compute the renormalized tunneling rate in the absence of two-boson processes, i.e., setting \( S_2 = 0 \). The trace in Equation (A.34) is most readily evaluated by observing
that
\[ \tilde{\Delta} = \Delta(e^{-2iS_1}) = \Delta e^{-2(S_1^2)}, \quad (A.35) \]
since \( S_1 \) is linear in the bosonic operators and the expectation value is with respect to a Gaussian state. Hence
\[
\tilde{\Delta} = \Delta \exp \left[ -2 \sum_k' \delta_k^2 (1 + 2N(\omega_k)) \right] \\
= \Delta \exp \left[ -2 \int_{p\Delta}^{\infty} d\omega \frac{J(\omega)}{\omega^2} \coth \frac{\omega}{2T} \right], \quad (A.36)
\]
where we cut off the integral at \( p\Delta \) in accordance with the prescription of adiabatic renormalization. At zero temperature, the integral is convergent for \( \eta > 1 \) and we can safely extend the lower limit to 0:
\[
\tilde{\Delta} = \Delta \exp \left[ -2 \int_{0}^{\infty} d\omega \frac{J(\omega)}{\omega^2} \right] \quad \text{if} \quad \eta > 1. \quad (A.37)
\]
When \( \eta < 1 \), the integral diverges with small \( \tilde{\Delta} \) as \( \tilde{\Delta}^{\eta-1} \). Thus,
\[
\tilde{\Delta} \approx \Delta \exp \left[ -\frac{2\alpha}{1-\eta} \left( p\Delta \right)^{\eta-1} + \log c \right], \quad (A.38)
\]
where the constant \( c \) depends on the high frequency behavior of the noise spectrum \( J(\omega) \). We re-arrange the expression to
\[
\varepsilon \left( \frac{\tilde{\Delta}}{c\Delta} \right)^{1-\eta} \log \left( \frac{\tilde{\Delta}}{c\Delta} \right) = -\frac{2\alpha}{1-\eta} \left( \frac{1}{p\varepsilon\Delta} \right)^{1-\eta}. \quad (A.39)
\]
135
The expression on the left has a global minimum of $-1/e(1 - \eta)$ such that a non-zero solution for $\tilde{\Delta}$ only exists if

$$2\alpha \left( \frac{1}{p_c \Delta} \right)^{1-\eta} < \frac{1}{e}, \quad (A.40)$$

or

$$\alpha < \frac{1}{2e} (p_c \Delta)^{1-\eta}. \quad (A.41)$$

This shows that there exists a critical coupling strength

$$\alpha^* \propto \Delta^{1-\eta} = O(N^{(\eta-1)/2}) \quad (A.42)$$

above which $\tilde{\Delta} = 0$. Our simple argument does not predict the precise value of $\alpha^*$ due to the dependence on $p$. Nevertheless, more detailed studies have confirmed that the form of Equation (A.42) is qualitatively correct [220, 221]. This result implies that for a fixed $\alpha$, the dynamics are incoherent even at zero temperature for sub-ohmic environments in the limit of large $N$.

At $\eta = 1$, the exponent in Equation (A.36) diverges logarithmically with $\tilde{\Delta}$ such that

$$\tilde{\Delta} \propto \Delta^{1/(1-2\alpha)} = O(N^{-1/2(1-2\alpha)}). \quad (A.43)$$

This expression is only valid if $\tilde{\Delta} < \Delta$, which implies that $\alpha < 1/2$. If $\alpha > 1/2$, the renormalized tunneling rate vanishes. The critical coupling strength is therefore independent of $N$ at $\eta = 1$, as expected from Equation (A.42).

The above arguments can be readily generalized to the case of finite temperature. Assuming that $T \gg \tilde{\Delta}$, as will be naturally the case for large systems, we can approximate $\coth \omega/2T \approx 2T/\omega$ near the lower limit of
the integral. The integral is convergent for \( \eta > 2 \) and we obtain to a good approximation

\[
\tilde{\Delta} = \Delta \exp \left[-2 \int_0^\infty d\omega \frac{f(\omega)}{\omega^2} \coth \frac{\omega}{2T} \right] \quad \text{if } \eta > 2. \tag{A.44}
\]

For \( \eta > 2 \), adiabatic renormalization predicts that \( \tilde{\Delta} = 0 \) unless \( \alpha < \frac{1}{4eT} (pc\Delta)^{2-\eta} \). \tag{A.45}

For fixed temperature, there exists a critical coupling strength

\[
\alpha^* \propto \frac{\Delta^{2-\eta}}{T} = O(N^{(\eta-2)/2}) \tag{A.46}
\]

above which \( \tilde{\Delta} = 0 \). For fixed \( \alpha \), we can alternatively identify a critical coupling temperature with the same scaling as the critical coupling strength,

\[
T^* \propto \frac{\Delta^{2-\eta}}{\alpha} = O(N^{(\eta-2)/2}). \tag{A.47}
\]

The renormalized tunneling rate vanishes for any \( T > T^* \). At \( \eta = 2 \), the renormalized tunneling rate vanishes unless \( \alpha T < 1/4 \), showing that the critical coupling strength and temperature are again independent of the search space size.

We point out that Equation (A.47) is only valid if \( \eta > 1 \) since otherwise the assumption that \( T \gg \tilde{\Delta} \) cannot be satisfied in the limit of large \( N \). For \( \eta < 1 \), we found above that the incoherent tunneling rate vanishes even at zero temperature in the limit of large \( N \) and fixed \( \alpha \). This can be summarized
as

\[ T^* = \begin{cases} 
0, & \text{if } \eta < 1 \\
O(N^{(n-2)/2}), & \text{if } \eta > 1 
\end{cases} \quad (A.48) \]

At \( \eta = 1 \), a non-zero critical temperature, which scales as \( T^* = O(N^{-1/2}) \) only exists if \( \alpha < 1/2 \).

### A.2.2 Two-boson processes

We repeat the above analysis for two-boson processes, ignoring single boson processes for the moment. The expectation value in Equation (A.34) is harder to compute in this case since \( S_2 \) is a quadratic operator involving terms of the form \( b_k^\dagger b_l, b_k b_l, \) and \( b_k^\dagger b_l^\dagger \). We will only evaluate it perturbatively by expanding the exponential to the lowest non-trivial order. By ignoring terms that scale inversely with the volume of the bath, we hence obtain

\[
\tilde{\Delta} \approx \Delta \exp \left[ -2 \sum_{k,l} A_{kl} A_{lk} N(\omega_k) (1 + N(\omega_l)) 
- \sum_{k,l} B_{kl} B_{lk} [(1 + N(\omega_k)) (1 + N(\omega_l)) - N(\omega_k)N(\omega_l)] \right]
\approx \Delta \exp [-\phi - \chi], \quad (A.49)
\]

where

\[
\phi = 2 \int' d\omega d\omega' \frac{J(\omega)J(\omega')}{(\omega - \omega')^2} N(\omega) (1 + N(\omega')), \quad (A.50)
\]

\[
\chi = \int' d\omega d\omega' \frac{J(\omega)J(\omega')}{(\omega + \omega')^2} [(1 + N(\omega))(1 + N(\omega')) - N(\omega)N(\omega')]. \quad (A.51)
\]
In both cases, the integral is to be taken over processes that are fast compared to the low-frequency cutoff $p\tilde{\Delta}$. For $\phi$, which describes two-boson scattering processes, this corresponds to $|\omega - \omega'| > p\tilde{\Delta}$, stating that the beating frequency of the two modes is fast. The two-boson absorption and emission processes are captured by $\chi$, for which we therefore impose that $\omega + \omega' > p\tilde{\Delta}$. We point out that the above expansion is only justified if $A_{kl}$ and $B_{kl}$ as well as $N(\omega_k)N(\omega_l)A_{kl}$ and $N(\omega_k)N(\omega_l)B_{kl}$ are small matrices in the sense that each column forms a vector with magnitude much less than one. This is indeed the case for $A_{kl}$ and $B_{kl}$ in the weak coupling limit $J(\omega) \ll E$, as shown explicitly in Appendix A.1. A similar treatment can be applied to the other two matrices, giving rise to the condition

$$J(\omega)N(\omega) \ll E. \quad (A.52)$$

At high frequencies $\omega \gg T$, this is trivially satisfied in the weak coupling limit. At low frequencies $\omega \ll T$, however, this leads to the additional constraint

$$\frac{J(\omega)}{\omega} \ll \frac{E}{T}. \quad (A.53)$$

It is important to note that this inequality can only be satisfied as $\omega \to 0$ for ohmic and super-ohmic environments. Restricting ourselves to this particular parameter regime is not a significant limitation since single-boson processes alone will render the dynamics incoherent even at zero temperature for sub-ohmic environments. Therefore, two-boson processes are expected to modify the dynamics qualitatively only for ohmic and super-ohmic environments.

We now investigate the low-frequency divergences of $\phi$ and $\chi$ to identify
the critical coupling strength and temperature as in the case of single-boson processes. At zero temperature, \( \phi \) vanishes while \( \chi \) is always finite. Hence, two-boson processes only weakly modify the tunneling rate at zero temperature. At non-zero temperatures, \( \chi \) remains finite whereas \( \phi \) exhibits an infrared divergence for any \( \eta \). The functional form of the divergence with the low-frequency cutoff \( p \tilde{\Delta} \) can be found to be given by

\[
\phi \propto \frac{\alpha^2 T^{2\eta+1}}{E^2 \Delta}. \tag{A.54}
\]

Using similar arguments to the ones for the single-boson processes, this allows us to identify a critical coupling strength

\[
\alpha^* \propto E T^{-(\eta+1/2)} \tilde{\Delta}^{1/2} = O(N^{-1/4}) \tag{A.55}
\]

and a critical temperature

\[
T^* \propto \alpha^{-2/(2\eta+1)} E^{2/(2\eta+1)} \tilde{\Delta}^{1/(2\eta+1)} = O(N^{-1/(4\eta+2)}). \tag{A.56}
\]

The divergence of \( \phi \) as \( \tilde{\Delta} \to 0 \) originates from the denominator in Equation (A.50), the form of which is dictated by conservation of energy during the scattering process. It is for this reason that higher-order terms in the effective Hamiltonian Equation (A.4) are not expected to modify the scaling of the critical temperature or the critical coupling strength.
A.2.3 Combined effects

We will now show that the single-boson and two-boson processes approximately decouple in the regime of interest. We start by expressing Equation (A.34) in a coherent state basis

\[ \hat{\Delta} = \Delta \int D\alpha \, \beta \langle \alpha | e^{-iS_2 \rho e^{-iS_2} | \beta} \rangle \langle \beta | e^{-2iS_1} | \alpha \rangle, \] (A.57)

where we introduced the short-hand notation \( D\alpha = \prod_k d^2 \alpha_k / \pi \) and \( | \alpha \rangle = \prod_k | \alpha_k \rangle \). The state \( | \alpha_k \rangle \) is a coherent state of the mode \( b_k \) and the integral runs over the entire complex plane for each mode. We note that the matrix elements may be written as

\[ \langle \alpha | e^{-iS_2 \rho e^{-iS_2} | \beta} = e^{-f(\alpha^*, \beta)} \langle \alpha | \beta \rangle, \] (A.58)
\[ \langle \beta | e^{-2iS_1} | \alpha \rangle = e^{g(\beta^*, \alpha)} \langle \beta | \alpha \rangle, \] (A.59)

where \( g(\beta^*, \alpha) \) is a linear function, while \( f(\alpha^*, \beta) \) contains only quadratic terms [125]. Computing the function \( f \) is rather cumbersome due to the presence of the squeezing terms \( b_k b_l \) and \( b_k^* b_l^* \) in \( S_2 \). For our purposes, it suffices to exploit the general structure of a Gaussian integral over a real vector \( \mathbf{v} \),

\[ \int \left( \prod_n \frac{d\nu_n}{\sqrt{2\pi}} \right) \exp \left[ -\frac{1}{2} \mathbf{v}^T M \mathbf{v} + \mathbf{w}^T \mathbf{v} \right] = \frac{1}{\det M} \exp \left[ \mathbf{w}^T M^{-1} \mathbf{w} \right]. \] (A.60)
Applied to Equation (A.57), we can see that the matrix $M$ is determined by $S_2$, while the vector $w$ follows from $S_1$. We may thus write

$$\tilde{\Delta} = \Delta \left< e^{-2iS_2} \right> \left< e^{-2iS_1'} \right>, \quad (A.61)$$

where the operator $S_1'$ accounts for both single-boson processes and the coupling between single-boson and two-boson processes. Under the same conditions that we were able to expand $e^{-2iS_2}$ in the previous section, we can also expand $S_1'$ in powers of $A_{kl}$ and $B_{kl}$. To leading order, we clearly must have $S_1' \approx S_1$, which shows that the single-boson and two-boson processes decouple under the assumption that $J(\omega) \ll E$ and $J(\omega)N(\omega) \ll E$. The nature of the dynamics of the system may thus be deduced by considering the two processes separately.

### A.3 Thermalization rates

#### A.3.1 Incoherent regime

It is necessary to determine the scaling of the thermalization rate in order to exclude the possibility of a quantum speedup in the incoherent regime. In particular, a speedup over the classical algorithm is possible if the thermalization rate decays slower with the size of the search space than $N^{-1}$. In the incoherent regime, adiabatic renormalization predicts that the system is localized. However, adiabatic renormalization does not take into account incoherent tunneling. To estimate the rate of incoherent tunneling, we perform perturbation theory in the bare tunneling rate $\Delta$. It is convenient to switch
to the basis that diagonalizes the Hamiltonian in the absence of tunneling,
\[
e^{iS}He^{-iS} = -\frac{1}{2}(\varepsilon \tau^z + \Delta e^{iS}\tau^x e^{-iS}) + \sum_k \omega_k b_k^\dagger b_k,
\]
where \(S\) is given by Equation (A.29). We move to the interaction picture, where the time-evolution is fully governed by
\[
V(t) = -\frac{\Delta}{2} e^{-i\tau^z t} e^{iS(t)\tau^+_x} e^{-iS(t)} + \text{h.c.},
\]
with \(\tau^+ = (\tau^x + i\tau^y)/2\) and
\[
S(t) = e^{it \sum_k \omega_k b_k^\dagger b_k} S e^{-it \sum_k \omega_k b_k^\dagger b_k}.
\]
Starting with the initial state \(|\psi(0)\rangle = |m_\perp, n\rangle\), the probability that the system ends up in \(|m\rangle\) after time \(t\) is given to lowest order in perturbation theory by
\[
p(t) = \sum_{n'} \left| \langle m, n'| \int_0^t dt' V(t') |m_\perp, n\rangle \right|^2
= \int_0^t dt' \int_0^{t'} dt'' \langle m_\perp, n| V(t') |m \rangle \langle m| V(t'') |m_\perp, n\rangle.
\]
By expressing \(e^{iS}\) in terms of \(S_1\) and \(S_2\) and taking a thermal average over the initial state, we obtain
\[
p(t) = \left(\frac{\Delta}{2}\right)^2 \int_0^t dt' \int_0^t dt'' e^{iS_2(t'') - iS_2(t')} \langle e^{iS_2(t')} e^{2iS_1(t')} e^{iS_2(t')} \times e^{-iS_2(t'')} e^{-2iS_1(t'')} e^{-iS_2(t'')} \rangle
\]
143
We note that the expectation value in the integrand is a function of $t' - t''$ only, which allows us to write

$$p(t) = \int_0^t dt' \Gamma(t'),$$

(A.67)

where

$$\Gamma(t) = \left(\frac{\Delta}{2}\right)^2 \int_{-t}^t dt' e^{i \epsilon t'} \left\langle e^{i S_2(t')} e^{2i S_1(t')} e^{i S_2(t')} \times e^{-i S_2(0)} e^{-2i S_1(0)} e^{-i S_2(0)}\right\rangle$$

(A.68)

is the instantaneous decay rate at time $t$. Typically, we can extend the limits of this integral to infinity to obtain a single decay rate $\Gamma = \lim_{t \to \infty} \Gamma(t)$. This is a good approximation for almost all $t$ provided the width over which the integrand contributes significantly is small compared to $1/\Gamma$. Since the width of the integrand is independent of $N$, the decay rate scales as $O(N^{-1})$, and thus the condition for extending the limits of the integral is always fulfilled in the limit of large $N$. We will not evaluate the above expression any further as we are only interested in the scaling with the search space size.

### A.3.2 Coherent regime

For completeness we briefly discuss the thermalization rate in the coherent regime, i.e., $\eta > 1$ at zero temperature. The thermalization rate in this regime has no immediate implications for the scalability of the quantum algorithm since a quantum speedup is always available in the coherent regime. However, a thermalization rate that exceeds the classical scaling $O(N^{-1})$ enables a
quantum speedup by thermalization alone.

In the coherent regime, thermalization occurs via transitions between the eigenstates of the closed system rather than by incoherent tunneling. The thermalization rate is readily obtained by applying Fermi’s Golden rule after adiabatic renormalization. For the single-boson processes, this yields at zero bias

$$\Gamma_1 = 2\pi \sum_k g_k^2 \delta(\omega_k - \Delta) = 2\pi J(\Delta) = O(N^{-\eta/2}).$$  \hspace{1cm} (A.69)$$

Interestingly, the thermalization rate exceeds the classical limit for $1 < \eta < 2$. We further remark that the rate drops below the classical scaling for $\eta > 2$. In this regime, incoherent tunneling and processes coupling to $\tau^x$ and $\tau^y$, which we have neglected, will dominate the thermalization rate.

For the the two-boson processes, the Golden rule rate is given by

$$\Gamma_2 = \frac{2\pi}{E^2} \int_0^{\Delta} d\omega J(\omega) J(\Delta - \omega) = O(N^{-(\eta+1/2)}).$$  \hspace{1cm} (A.70)$$

This vanishes parametrically faster than the single-boson decay rate such that two-boson emission only contributes weakly to the thermalization rate.

**A.4 Diagonalization of quadratic Hamiltonians**

We briefly review the diagonalization of a general quadratic Hamiltonian of the form

$$H = \beta^\dagger M \beta,$$  \hspace{1cm} (A.71)$$

where $M$ is a Hermitian matrix and $\beta = (b_1, b_2, \ldots, b_1^\dagger, b_2^\dagger, \ldots)$ is a vector formed by creation and annihilation operators. We closely follow the notation
of reference [222], where the diagonalization of both fermionic and bosonic Hamiltonians is discussed in detail. For the sake of clarity, we focus on bosons below.

The goal is to introduce new bosonic operators \( \gamma = (c_1, c_2, ..., c_1^\dagger, c_2^\dagger, ...) \) such that the Hamiltonian can be written as

\[
H = \sum_i \lambda_i c_i^\dagger c_i
\]

up to a constant. The new operators \( \gamma \) are related to the original operators by a linear transformation

\[
\begin{pmatrix}
  c \\
  c^\dagger
\end{pmatrix} = T
\begin{pmatrix}
  b \\
  b^\dagger
\end{pmatrix}.
\]

(A.73)

The fact that \( b^\dagger \) is the adjoint of \( b \) implies that \( T \) must take the form

\[
T = \begin{pmatrix}
  A & B \\
  B^* & A^*
\end{pmatrix}.
\]

(A.74)

Furthermore, the conservation of canonical commutation relations leads to the additional constraint

\[
T^{-1} = \mu T^\dagger \mu, \quad \mu = \begin{pmatrix}
  I & 0 \\
  0 & -I
\end{pmatrix}.
\]

(A.75)

Equation (A.71) can hence be written as

\[
H = \gamma^\dagger \mu T \mu MT^{-1} \gamma.
\]

(A.76)
Assuming that $M$ is positive definite, it is shown in [222] that there exists a transformation $T$ satisfying Equation (A.74) and Equation (A.75) which diagonalizes $\mu M$ to give

$$T \mu M T^{-1} = \frac{1}{2} \begin{pmatrix} \lambda \delta_{ij} & 0 \\ 0 & -\lambda \delta_{ij} \end{pmatrix}.$$  \hspace{1cm} (A.77)

This immediately yields the desired result Equation (A.72) up to a constant.

It is often useful to express the transformation described by the matrix $T$ as a unitary transformation $S$ acting on the creation and annihilation operators, i.e.

$$c_i = S b_i S^\dagger, \quad S^\dagger S = S S^\dagger = I.$$ \hspace{1cm} (A.78)

The transformation takes the form $S = \exp(i \beta^\dagger K \beta/2)$, where $K$ is a Hermitian matrix. By direct substitution into Equation (A.78) and comparison to Equation (A.73) we obtain

$$T = e^{-i n K}.$$ \hspace{1cm} (A.79)

Finally, we note that the vacuum $|0_c\rangle$, where $c_i |0_c\rangle = 0$ for all $i$, is related to the vacuum $|0_b\rangle$, for which $b_i |0_b\rangle = 0$, by

$$|0_c\rangle = S |0_b\rangle.$$ \hspace{1cm} (A.80)

All other Fock states transform in the same manner.
Appendix B

Supporting material for Chapter 3

B.1 Upper bound on total variation distance

In this appendix, we relate the overlap of two quantum states to the total variation distance between the probability distributions encoded by them. The desired probability distribution is \( p(s) \), encoded in the state

\[
|\psi\rangle = \sum_s \sqrt{p(s)} e^{i\gamma(s)} |s\rangle. \tag{B.1}
\]

The prepared state is

\[
|\phi\rangle = \sum_s \sqrt{q(s)} e^{i\delta(s)} |s\rangle, \tag{B.2}
\]

where \( q(s) \) will be the observed probability distribution. In both cases we allow for arbitrary phases \( \gamma(s) \) and \( \delta(s) \).
The total variation distance may be defined as

\[ d = ||p - q|| = \frac{1}{2} \sum_s |p(s) - q(s)|. \]  \hspace{1cm} (B.3)

The fidelity between states \(|\psi\rangle\) and \(|\phi\rangle\) is given by

\[ F = |\langle \phi | \psi \rangle|^2 = \left| \sum_s e^{i\gamma(s) - i\delta(s)} \sqrt{p(s)q(s)} \right|^2. \]  \hspace{1cm} (B.4)

The triangle inequality allows us to remove the phases,

\[ 1 - F \geq 1 - \left| \sum_s \sqrt{p(s)q(s)} \right|^2, \]  \hspace{1cm} (B.5)

which can be rewritten as

\[ 1 - F \geq \frac{1}{4} \left[ \sum_s (\sqrt{p(s)} - \sqrt{q(s)})^2 \right] \left[ \sum_s (\sqrt{p(s)} + \sqrt{q(s)})^2 \right]. \]  \hspace{1cm} (B.6)

Finally, applying the Cauchy–Schwarz inequality yields

\[ 1 - F \geq \frac{1}{4} \left[ \sum_s \left| \sqrt{p(s)} - \sqrt{q(s)} \right| \left| \sqrt{p(s)} + \sqrt{q(s)} \right| \right]^2, \]  \hspace{1cm} (B.7)

which is equivalent to

\[ 1 - F \geq d^2. \]  \hspace{1cm} (B.8)
B.2 Ising chain

B.2.1 Parent Hamiltonian

Glauber dynamics [90] defines a Markov chain according to the following prescription. We pick a spin at random and draw its new orientation from the Gibbs distribution with all other spins fixed. Starting from configuration \( s \), the probability of flipping spin \( i \) in the Ising chain is thus given by

\[
p_i = \frac{1}{2n \cosh[\beta(s_{i-1} + s_{i+1})]} e^{-\beta s_i(s_{i-1} + s_{i+1})}.
\]  
(B.9)

By promoting the values of the spins \( s_i \) to operators \( \sigma_i^z \), we can concisely write the generator of the Markov chain as

\[
M = \sum_i p_i \sigma_i^z + \left( \mathbb{1} - \sum_i p_i \right).
\]  
(B.10)

Equation (3.2) immediately gives

\[
H_q = \frac{1}{2} \sum_i \frac{1}{\cosh[\beta(\sigma_{i-1}^z + \sigma_{i+1}^z)]} \left[ e^{-\beta \sigma_i^z(\sigma_{i-1}^z + \sigma_{i+1}^z)} - \sigma_i^z \right].
\]  
(B.11)

Straightforward algebra finally yields

\[
H_q = \frac{n}{2} \mathbb{1} - \frac{1}{4} \sum_i \left[ \left( 1 + \frac{1}{\cosh 2\beta} \right) \sigma_i^z + 2 \tanh(2\beta) \sigma_i^z \sigma_{i+1}^z - 
\left( 1 - \frac{1}{\cosh 2\beta} \right) \sigma_{i-1}^z \sigma_i^z \sigma_{i+1}^z \right].
\]  
(B.12)

In Equation (3.3), we dropped the unimportant constant.
B.2.2 Free fermion solution

Ground state

The Hamiltonian in Equation (3.3) can be mapped onto a free-fermion model using a Jordan–Wigner transformation. We define the fermion annihilation and creation operators $a_i, a_i^\dagger$ and relate them to the Pauli matrices according to

$$\sigma_i^x = 2a_i^\dagger a_i - 1, \quad (B.13)$$
$$\frac{1}{2}(\sigma_i^z + i\sigma_i^y) = e^{i\pi \sum_{j=1}^{i-1} a_j^\dagger a_j}, \quad (B.14)$$
$$\frac{1}{2}(\sigma_i^z - i\sigma_i^y) = e^{i\pi \sum_{j=1}^{i-1} a_j^\dagger a_j^\dagger}. \quad (B.15)$$

Equation (3.3) becomes

$$H_q = -\hbar \sum_{i=1}^{n} (2a_i^\dagger a_i - 1) - J_1 \sum_{i=1}^{n-1} (a_i^\dagger - a_i)(a_{i+1}^\dagger + a_{i+1})$$
$$- J_2 \sum_{i=1}^{n-2} (a_i^\dagger - a_i)(a_{i+2}^\dagger + a_{i+2})$$
$$+ e^{i\pi N} \left[ J_1 (a_n^\dagger - a_n)(a_1^\dagger + a_1) + J_2 (a_{n-1}^\dagger - a_{n-1})(a_1^\dagger + a_1) \right.$$
$$\quad \left. + J_2 (a_n^\dagger - a_n)(a_2^\dagger + a_2) \right], \quad (B.16)$$

where $N = \sum_{i=1}^{n} a_i^\dagger a_i$ is the total number of fermions. While the fermion number itself is not conserved, the parity $e^{i\pi N}$ is, allowing us to consider the even and odd subspaces independently.

151
We define the momentum space operators

\[ a_k = \frac{1}{\sqrt{n}} \sum_{j=1}^{n} e^{-ikj} a_j, \quad (B.17) \]

which satisfy fermionic commutation relations for suitably chosen \( k \). We let

\[ k = \frac{2\pi}{n} \times \begin{cases} (l + 1/2) & \text{if } N \text{ is even} \\ l & \text{if } N \text{ is odd} \end{cases} \quad (B.18) \]

for \( l = 0, 1, \ldots, n - 1 \) \(( \text{mod } n)\). With this definition, the inverse Fourier transformed operators have the formal property \( a_{i+n} = -e^{i\pi N} a_i \), which accounts for the boundary terms in Equation (B.16). The Hamiltonian simplifies to

\[ H_q = \sum_k \begin{pmatrix} a_k^\dagger & a_{-k} \end{pmatrix} h_k \begin{pmatrix} a_k \\ a_{-k}^\dagger \end{pmatrix}, \quad (B.19) \]

where

\[ h_k = \begin{pmatrix} -h - J_1 \cos k - J_2 \cos 2k & -iJ_1 \sin k - iJ_2 \sin 2k \\ iJ_1 \sin k + iJ_2 \sin 2k & h + J_1 \cos k + J_2 \cos 2k \end{pmatrix} \quad (B.20) \]

While the above Hamiltonian can be diagonalized by a standard Bogoliubov transformation, it will prove more convenient for our purposes to map
the Hamiltonian onto non-interacting spins. For $0 < k < \pi$, we define

\[
\tau_k^x = a_k^\dagger a_{-k} + a_{-k} a_k, \tag{B.21}
\]
\[
\tau_k^y = -i(a_k^\dagger a_{-k} - a_{-k} a_k), \tag{B.22}
\]
\[
\tau_k^z = a_k^\dagger a_k - a_{-k} a_{-k}. \tag{B.23}
\]

It is straightforward to check that these operators satisfy the same commutation relations as Pauli matrices. In addition, operators corresponding to different values of $k$ commute such that we can think of these operators as independent spin-$1/2$ systems, one for each value of $k$. We restrict the range of momenta to $0 < k < \pi$ due to the redundancy $\tau_{-k}^\alpha = -\tau_k^\alpha$. The cases $k = 0$ and $k = \pi$ require a special treatment as both $\tau_k^x$ and $\tau_k^y$ vanish.

For concreteness, we assume that the number of spins, $n$, is even. The special cases $k = 0$ and $k = \pi$ are then both part of the odd parity subspace ($e^{i\pi N} = -1$). The Hamiltonian of the even parity subspace is simply

\[
H_{q}\text{even} = 2 \sum_{0 < k < \pi} E_k \left( \cos \theta_k \tau_k^x + \sin \theta_k \tau_k^y \right), \tag{B.24}
\]

where

\[
E_k = \sqrt{(h + J_1 \cos k + J_2 \cos 2k)^2 + (J_1 \sin k + J_2 \sin 2k)^2} \tag{B.25}
\]

and the angle $\theta_k$ is defined by

\[
E_k \cos \theta_k = -h - J_1 \cos k - J_2 \cos 2k, \tag{B.26}
\]
\[
E_k \sin \theta_k = J_1 \sin k + J_2 \sin 2k. \tag{B.27}
\]
The ground state is given by

$$|\text{GS}_{\text{even}}\rangle = \prod_{0<k<\pi} e^{i\theta_k \tau_k^z/2}|0\rangle,$$

(B.28)

where \(|0\rangle\) is the vacuum with respect to the \(a_k\) operators. It is easy to see that \(|\text{GS}_{\text{even}}\rangle\) indeed has even parity. The ground state energy is

$$E_{\text{GS}}^{\text{even}} = -2 \sum_{0<k<\pi} E_k.$$

(B.29)

In the odd parity subspace, we have

$$H_q^{\text{odd}} = 2 \sum_{0<k<\pi} E_k \left( \cos \theta_k \tau_k^x + \sin \theta_k \tau_k^y \right)$$

$$- (h + J_1 + J_2)(2a_0^{\dagger}a_0 - 1) - (h - J_1 + J_2)(2a_\pi^{\dagger}a_\pi - 1).$$

(B.30)

The construction of the ground state is analogous to the even case with the additional requirement that either the \(a_0\) fermion or the \(a_\pi\) fermion, whichever has the lower energy, be occupied. The resulting energy is gapped above \(E_{\text{GS}}^{\text{even}}\) when \(h + J_1 + J_2\) and \(h - J_1 + J_2\) have the same sign. In the case of opposite signs, the even and odd sector ground states are degenerate in the thermodynamic limit, corresponding to the symmetry breaking ground states of the ferromagnetic phase.

In Section 3.3, we consider adiabatic evolution starting from the ground state at \(J_1 = J_2 = 0\). Following the above discussion, this state is part of the even subspace. Since the time evolution preserves parity, we may restrict our discussion to the even subspace, dropping all associated labels in what
Excitation spectrum and phase diagram

Excited states can be constructed by flipping any of the $\tau$ spins. The singly excited states are given by

$$|k\rangle = \tau_k^x |\text{GS}\rangle,$$

with an energy $4E_k$ above the ground state. We mention that any spin rotation commutes with the parity operator, which is in contrast to the Bogoliubov picture, where it is necessary to excite Bogoliubov fermions in pairs. This automatic accounting in the spin picture is also reflected by the fact that there are half as many $\tau$ spins as there are Bogoliubov operators or physical spins.

We identify the phase boundaries by looking for parameters for which the excitation gap vanishes, $E_k = 0$. In the thermodynamic limit, we can treat $k$ as a continuous variable to identify the minima of $E_k$. There are three distinct cases:

1. The gap vanishes at $k = 0$ when $h + J_1 + J_2 = 0$.

2. The gap vanishes at $k = \pi$ when $h - J_1 + J_2 = 0$.

3. The gap vanishes at $k = \pi - \cos^{-1} \frac{J_1}{2J_2}$ when $h - J_2 = 0$. A solution only exits for $|J_1| < 2|h|$.

Based on the identification in Section 3.3, cases 1 and 2 delineate the ferromagnetic phase from the paramagnetic and cluster-state-like phase. Case 3 separates the paramagnetic phase from the cluster-state-like phase.
The dispersion is linear in all three cases, except for the two special points simultanously satisfying $h = J_2$ and $h = \pm J_1$. These are tricritical points, where the dispersion minima from case 3 and either case 1 or 2 merge into a single minimum with quadratic dispersion. Hence, the dynamical critical exponent is $z = 1$ at all phase transitions except for the tricritical points, where $z = 2$. The gap closes as $\sim n^{-z}$, as can be easily seen by considering the value of $k$ closest to the dispersion minimum for a finite-sized system. We note that in case 3, the gap displays an oscillatory behavior as a function of system size for fixed $(h, J_1, J_2)$ and may even vanish exactly. Nevertheless, the envelope follows the expected $\sim n^{-1}$ scaling.

B.2.3 Numerical details

To compute the fidelity, we numerically integrate the Schrödinger equation for each spin $\tau_k$. We work in an the instantaneous eigenbasis $|\chi_k^\pm(t)\rangle$, which are eigenstates of $H_k = 2E_k (\cos \theta_k \tau_k^z + \sin \theta_k \tau_k^y)$ with energies $\pm 2E_k$ [see Equation (B.24)]. It is convenient to parametrize each adiabatic path by a dimensionless time $s$ running from 0 to 1. Writing the state at time $s$ as

$$|\psi_k(s)\rangle = c_k(s)|\chi_k^-(s)\rangle + d_k(s)|\chi_k^+(s)\rangle,$$

(B.32)

the coefficient $c_k$ and $d_k$ are determined by the Schrödinger equation

$$\frac{i}{ds} \begin{pmatrix} c_k \\ d_k \end{pmatrix} = \begin{pmatrix} -2E_k(s) \frac{dt}{ds} & \frac{i}{2} \frac{d\theta_k}{ds} \\ \frac{i}{2} \frac{d\theta_k}{ds} & 2E_k(s) \frac{dt}{ds} \end{pmatrix} \begin{pmatrix} c_k \\ d_k \end{pmatrix}$$

(B.33)
with the initial condition $c_k(0) = 1$, $d_k(0) = 0$. The final fidelity is obtained by solving this equation for each spin and multiplying the individual fidelities,

$$\mathcal{F} = \prod_{0 < k < \pi} |c_k(1)|^2. \quad (B.34)$$

We note that all terms in Equation (B.33) can be evaluated without having to solve for the physical evolution time $t(s)$. The terms $E_k(s)$ and $d\theta_k/ds$ are readily computed from Equations (B.25)–(B.27), while $dt/ds$ follows from Equation (3.4):

$$\frac{dt}{ds} = \frac{1}{\varepsilon} \sqrt{\sum_{\mu,\nu} g_{\mu\nu}(s) \frac{d\lambda_\mu}{ds} \frac{d\lambda_\nu}{ds}}. \quad (B.35)$$

Here, $\lambda_1 = J_1$, $\lambda_2 = J_2$, setting $\hbar = 1$ throughout. To vary the total evolution time $t_{\text{tot}}$, we simply adjust the value of $\varepsilon$. Indeed,

$$t_{\text{tot}} = \frac{1}{\varepsilon} \int \sqrt{\sum_{\mu,\nu} g_{\mu\nu} d\lambda_\mu \lambda_\nu}, \quad (B.36)$$

where the integral runs along the path of interest.

In practice, it can be challenging to find a suitably accurate discretization of the time steps for large systems because $ds/dt$ and $d\theta_k/ds$ are sharply peaked around the phase transitions. We obtained good convergence by evolving under constant $s = s_n$ for an interval $\Delta s_n \times \frac{1}{2} \left| \frac{d\theta_k}{ds} \right|_{s = s_n} = 10^{-3}$ before incrementing the time to $s_{n+1} = s_n + \Delta s_n$. The number of steps is independent of the total time, yet the final fidelity is well estimated since the probability of leaving the ground state is small in each step. The results for the four paths in Section 3.3, a parametrization of which is given in Table B.1, are shown in Figure B.1. We observe that the fidelity follows a universal dependence
on $\varepsilon$, $1 - F \propto \varepsilon^2$. This can be understood from the fact that the first-order diabatic correction to the wavefunction is inversely proportional to the total time [98]. For each path, we extract the value of $\varepsilon$ at which $1 - F$ crosses $10^{-3}$, indicated by the crosses in Figure B.1. The dependence of this value on the system size is weak such that the total adiabatic time scale is largely determined by the integral in Equation (B.36), which we will analyze in detail in the next section.
<table>
<thead>
<tr>
<th>path</th>
<th>$J_1/h$</th>
<th>$J_2/h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>$2s$</td>
<td>$s$</td>
</tr>
<tr>
<td>(ii)</td>
<td>$2s$</td>
<td>$s^2$</td>
</tr>
<tr>
<td>(iii)</td>
<td>$3(1-s)^2s + 7.5(1-s)s^2 + 2s^3$</td>
<td>$1.5(1-s)s^2 + s^3$</td>
</tr>
<tr>
<td>(iv)</td>
<td>$6(1-s)^2s + 9(1-s)s^2 + 2s^3$</td>
<td>$-3(1-s)^2s + 4.5(1-s)s^2 + s^3$</td>
</tr>
</tbody>
</table>

Table B.1: Paramaterization of the four paths discussed in Section 3.3. The parameter $s$ ranges from 0 to 1.

### B.2.4 Adiabatic path length

The above numerical observations suggest that the adiabatic state preparation time is proportional to the quantity

$$l = \int \sqrt{\sum_{\mu,\nu} g_{\mu\nu} d\lambda_\mu d\lambda_\nu}, \quad (B.37)$$

which we will refer to as the adiabatic path length. In the same spirit, we shall call $g_{\mu\nu}$ the adiabatic metric as it endows the parameter space with a distance measure relevant for adiabatic evolution. We plot the adiabatic path length as a function of $n$ for the four paths discussed in Section 3.3 in Figure B.2. As expected, the plot looks almost identical to Figure 3.2d up to an overall factor.

We may gain an analytic understanding of the adiabatic path length by considering the metric close to the tricritical point. From Equation (B.28) and Equation (B.31) it is straightforward to show that

$$\partial_\mu |\text{GS}\rangle = \frac{i}{2} \sum_{0<k<\pi} \partial_\mu \theta_k |k\rangle. \quad (B.38)$$
Figure B.2: Adiabatic path length as a function of $n$. The black lines show the scalings $l \propto n, n^2, n^3$.

It then follows immediately from the definition in Equation (3.5) that

$$g_{\mu\nu} = \sum_{0<k<\pi} \frac{1}{64E_k^2} (\partial_{\mu} \theta_k)(\partial_{\nu} \theta_k). \quad (B.39)$$

With $\lambda_1 = J_1$ and $\lambda_2 = J_2$, this result may be written in matrix form as

$$g = \sum_{0<k<\pi} \frac{\sin^2 k}{64E_k^2} \begin{pmatrix}
(h - J_2)^2 & (h - J_2)(2h \cos k + J_1) \\
(h - J_2)(2h \cos k + J_1) & (2h \cos k + J_1)^2
\end{pmatrix}. \quad (B.40)$$

In the thermodynamic limit, the momentum sum turns into an integral, which can be evaluated analytically. Setting $h = 1$ and parametrizing $J_1 = 2 + \eta \cos \alpha$, $J_2 = 1 + \eta \sin \alpha$, we expand the result close to the tricritical point
(small \( \eta \)) to obtain

\[
G = \sum_{\mu, \nu} g_{\mu \nu} \frac{d\lambda_\mu}{d\eta} \frac{d\lambda_\nu}{d\eta}
\]  
(B.41)

\[
\approx \frac{3n}{2048} \times \left\{ \frac{1}{32} \frac{\sin^2 \alpha}{(\cos \alpha - \sin \alpha)^{5/2}} \eta^{-5/2} + O(\eta^{-3/2}), \quad -\frac{3\pi}{4} < \alpha < \frac{\pi}{4} \right\}.
\]

(B.42)

The first case corresponds to the ferromagnetic phase, while the second case applies to the paramagnetic and cluster-state-like phases. In both cases, the adiabatic metric diverges as a power law, \( G \sim n^{\sigma} \), with \( \rho = \frac{5}{2} \) in the ferromagnetic phase and \( \rho = 5 \) otherwise.

For finite sized systems, one can show that exactly at the critical point \( G \sim n^{\sigma} \), where \( \sigma = 6 \), in any direction not parallel to the \( J_1 \) axis. Based on finite-sized scaling arguments, we expect that the metric follows the expression for the infinite system as we approach the tricritical point until it saturates to the final value \( G \sim n^{\sigma} \). We are thus led to define a critical region \( \eta < \eta_c \) determined by \( n\eta_c^{\rho} \sim n^{\sigma} \), where the metric is approximately constant. These arguments imply that the path length should scale according to

\[
l \sim n^{\sigma(2 - 2\sigma + \rho \sigma)/(2\rho)} \approx \begin{cases} 
n, & -\frac{3\pi}{4} < \alpha < \frac{\pi}{4} \\
n^2, & \frac{\pi}{4} < \alpha < \frac{5\pi}{4} \end{cases}.
\]

(B.43)

The above prediction agrees well with the numerical results for paths (ii)–(iv) in Figure B.2, however, it fails for path (i), for which a cubic scaling is observed. Figure B.3 shows that the scaling hypothesis breaks down in the latter case and oscillatory terms in \( G \) contribute significantly to the path.
length \( l \). The oscillatory terms can be attributed to the fact that the dispersion minimum is neither at \( k = 0 \) or \( k = \pi \) as the tricritical point is approached from the ferromagnetic phase, thereby giving rise to an incommensurate length scale that breaks scale invariance.

![Figure B.3: Adiabatic metric \( G \) as a function of the distance \( \eta \) from the tricritical point when approaching from the ferromagnetic phase (left panel) and the paramagnetic phase (right panel). The different colors correspond to the system sizes indicated in the legend in the right panel. The black curves show the analytic result for an infinite chain.](image)

A similar analysis can be performed at the phase transition between the paramagnet and the ferromagnet, away from the tricritical point. One finds that the adiabatic path length defined always scales linearly with the system size.

### B.3 Weighted independent set problem

#### B.3.1 Parent Hamiltonian

For the weighted independent set problem, we use the Metropolis–Hastings update rule [107] instead of Glauber dynamics. A move is accepted with
probability \( p_{\text{accept}} = \min(1, e^{-\beta \Delta E}) \), where \( \Delta E \) is the change in energy. With single site updates, the probability of changing the occupation of vertex \( i \) is given by

\[
p_i = P_i e^{-\beta w_i n_i},
\]

assuming that the weight is nonnegative. The projector \( P_i = \prod_{j \in \mathcal{N}_i} (1 - n_j) \) projects onto configurations where the nearest neighbors \( \mathcal{N}_i \) of vertex \( i \) are all unoccupied. It ensures that the Markov chain never leaves the independent set subspace. We do not consider the possibility in which the Markov chain is initialized in a state outside this subspace such that it suffices to consider transitions within. Following the same steps as in Section B.2.1, we derive the parent Hamiltonian

\[
H_q = \sum_i P_i \left[ e^{-\beta w_i n_i} - e^{-\beta w_i/2} \sigma_i^x \right].
\]

This can be brought into the form of Equation (3.6) by expanding \( e^{-\beta w_i n_i} = (1 - n_i) + e^{-\beta w_i n_i} \).

### B.3.2 Chain graph

The parent Hamiltonian for the (unweighted) maximum independent set problem on a chain has been previously discussed in a different context [110, 111]. For general parameters, the Hamiltonian is not exactly solvable and we instead use numerical diagonalization. The complexity of the problem is reduced as we only need to consider the subspace of independent sets. For a chain of \( n \) vertices with open boundary condition, the dimension of the Hilbert space is equal to \( F_{n+2} \), where \( F_n \) is the \( n \)th Fibonacci number. We consider periodic
boundary conditions, for which the dimension is $F_{n-1} + F_{n+1}$. We further restrict ourselves to states that are invariant under translation (zero momentum). Assuming that the initial state satisfies this condition, the evolution will be restricted to only these states since the Hamiltonian is translationally invariant. We find that for $n = 24$ vertices, the dimension of this subspace is $d = 4341$, which is amenable to exact diagonalization with modest computational effort. For $n = 30$, we have $d = 62075$, still allowing us to find the low-energy states in a short amount of time using a Lanczos type algorithm.

The gap as a function of $\beta$ along the one-parameter family $H_q(\beta)$ is shown in Figure B.4. At high temperature, the gap decays as $e^{-2\beta}$, in agreement with previous analytic results [111]. At low temperature, we observe that the gap depends on both temperature and system size as $e^{-\beta}/n^2$. The quadratic dependence on $n$ is a consequence of the diffusive propagation of domain walls, i.e. pairs of holes that break up the $\mathbb{Z}_2$ ordering. For the domain walls to propagate, it is necessary to de-excite an adjacent vertex. This results in an energy barrier, giving rise to the additional factor $e^{-\beta}$.

Due to exponentially vanishing gap it is not possible to adiabatically reach the zero temperature Gibbs state along path (i) discussed in Section 3.4.1. We therefore only prepare the Gibbs state at $\beta_c = 2 \log n$, whose overlap with the zero temperature Gibbs state is approximately 90%, almost independent of $n$. The constant overlap reflects the fact that the correlation length at $\beta_c$ is a fixed ratio of the system size. It is possible to increase the overlap by adding a constant to $\beta_c$ without changing the scaling behavior discussed here. To determine the state preparation fidelity, we numerically integrate the Schrödinger equation by exactly diagonalizing the Hamiltonian at discrete time steps $\Delta t$. 164
Figure B.4: Gap of the parent Hamiltonian for the maximum independent set problem on a chain graph along the one-parameter family $H_q(\beta)$. (a) Gap for four different system sizes as a function of $\beta$. The black lines show the functions $e^{-2\beta}$ and $e^{-\beta}$ up to a constant pre-factor. The dependence $e^{-2\beta}$ is theoretically expected at low temperature [111], although we find that in the zero-momentum subspace, it only holds for large systems at temperatures satisfying $\beta \gtrsim 2$. (b) Dependence of the gap on the number of vertices $n$ at $\beta = 8$. The black line indicates the power law $1/n^2$.

The steps are chosen such that $\Delta t |d|\text{GS}/dt| = 10^{-3}$, where $|\text{GS}\rangle$ denotes the instantaneous ground state. The expression is most conveniently evaluated using the identity $|d|\text{GS}/dt|^2 = \sum_n |\langle n| dH/\text{dt}|\text{GS}\rangle|^2/(E_n - E_{\text{GS}})^2$, where the sum runs over all excited states $|n\rangle$ with energy $E_n$. The time step is related to the change in the parameters along the path by Equation (3.4). The resulting fidelity as a function of the parameter $\varepsilon$ is shown in Figure B.5. As for the Ising chain, the fidelity satisfies approximately $1 - F \propto \varepsilon^2$, independent of the number of vertices $n$. The same is true along path (ii), for which it is in fact possible to adiabatically reach the zero-temperature Gibbs state in finite time.

The fact that the fidelity at a fixed value of $\varepsilon$ is approximately independent of $n$ again allows us to understand the adiabatic state preparation time $t_a$ in
Figure B.5: Infidelity $1 - \mathcal{F}$ of the adiabatic state preparation as a function of $\varepsilon$ for the two paths (see Table B.2 for an explicit parametrization). Path (i) terminates at $\beta_c = 2 \log n$, while path (ii) is continued to $\beta \to \infty$. The black crosses indicate where the infidelity first drops below $10^{-3}$.

Table B.2: The two paths for the independent set problem on the chain graph discussed in Section 3.4.1. The parameter $\beta$ ranges from 0 to $\infty$ and corresponds to the inverse temperature of the Markov chain in the case of path (i).

<table>
<thead>
<tr>
<th>path</th>
<th>$\Omega/V_g$</th>
<th>$V_c/V_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>$e^{-\beta/2}$</td>
<td>$e^{-\beta}$</td>
</tr>
<tr>
<td>(ii)</td>
<td>$e^{-\beta/2}$</td>
<td>$6e^{-\beta} - 5e^{-3\beta/2}$</td>
</tr>
</tbody>
</table>

terms of the adiabatic path length $l$ in Equation (B.37). The adiabatic path length from $\beta = 0$ to a point along paths (i) and (ii) is plotted in Figure B.6. For large $\beta$, the adiabatic path length diverges as $e^{\beta/2}L^3$ along path (i), which leads to the scaling $t_a \sim n^4$ when setting $\beta = \beta_c = 2 \log n$. By contrast, $l$ converges to a finite value as $\beta \to \infty$ along path (ii). The value grows linearly with $n$ such that $t_a \sim n$.

166
Figure B.6: Adiabatic path length, Equation (B.37), from 0 to $\beta$ along the paths (i) and (ii). The dashed lines in (i) show a fit to the function $A e^{\beta/2} n^3$, with constant $A$, to the value of $l$ at $\beta = 10$. Similarly, in (ii), $l$ at $\beta = 10$ was fitted to the linear function $B n + C$.

B.3.3 Star graph

Classical phase transition

The classical phase transition temperature for the model described in Section 3.4.2 can be computed exactly. The partition function is given by

$$Z = (1 + 2e^\beta)^b + e^{b\beta} (1 + e^\beta)^b.$$  \hfill (B.46)

The two terms correspond to the different configurations of the central vertex.

The probability that the central site is occupied is given by

$$p_1 = \frac{1}{Z} e^{b\beta} (1 + 2e^\beta)^b = \left[ 1 + \left( \frac{1 + 2e^\beta}{e^\beta + e^{2\beta}} \right)^b \right]^{-1}.$$  \hfill (B.47)

In the thermodynamic limit $b \to \infty$, this turns into the step function $p_1 = \Theta(\beta - \beta_c)$, where $\beta_c = \log \varphi$ with $\varphi = (\sqrt{5} + 1)/2$ being the golden ratio.

From the Helmholtz free energy $F = -\log Z / \beta$ and the total energy $U = \cdots$
\[ -\partial \log Z / \partial \beta, \text{ the entropy can be computed as } S = \beta(U - F). \]

**Two-state model**

The star graph described in Section 3.4.2 has three types of vertices: the vertex at the center and the inner and outer vertices on each branch. If we maintain the permutation symmetry between the branches, the parent Hamiltonian takes the general form

\[
H_q = V_{e,\text{cen}} n_{\text{cen}} + V_{g,\text{cen}} P_{\text{cen}} (1 - n_{\text{cen}}) - \Omega_{\text{cen}} P_{\text{cen}} \sigma_{\text{cen}}^x \\
+ V_{e,\text{in}} \sum_{i=1}^{b} n_{\text{in},i} + V_{g,\text{in}} \sum_{i=1}^{b} P_{\text{in},i}(1 - n_{\text{in},i}) - \Omega_{\text{in}} \sum_{i=1}^{b} P_{\text{in},i} \sigma_{\text{in},i}^x \\
+ V_{e,\text{out}} \sum_{i=1}^{b} n_{\text{out},i} + V_{g,\text{out}} \sum_{i=1}^{b} P_{\text{out},i}(1 - n_{\text{out},i}) - \Omega_{\text{out}} \sum_{i=1}^{b} P_{\text{out},i} \sigma_{\text{out},i}^x,
\]

where each row relates to a separate type of vertex and the sums run over all branches. With the weights specified in Section 3.4.2, we have \( V_{e,\text{cen}} = e^{-b \beta}, V_{e,\text{in}} = e^{-\beta}, V_{e,\text{out}} = e^{-\beta}, V_{g,\text{cen}} = V_{g,\text{in}} = V_{g,\text{out}} = 1, \Omega_{\text{cen}} = e^{-b \beta/2}, \Omega_{\text{in}} = \Omega_{\text{out}} = e^{-\beta/2} \) along the one-parameter family \( H_q(\beta) \).

We restrict our analysis to the subspace that is completely symmetric under permutations of the branches. We introduce the total occupation numbers \( n_{\text{in}} = \sum_{i=1}^{b} n_{\text{in},i} \) and \( n_{\text{out}} = \sum_{i=1}^{b} n_{\text{out},i} \) as well as the number of unoccupied branches \( n_0 \). The symmetric subspace is spanned by the states

\[
|n_{\text{cen}}, n_{\text{in}}, n_{\text{out}}, n_0\rangle,
\]

where \( n_{\text{cen}} \in \{0, 1\} \) while the other occupation numbers are nonnegative integers satisfying \( n_{\text{in}} + n_{\text{out}} + n_0 = b \). If \( n_{\text{cen}} = 1 \), the independent set constraint
further requires \( n_{\text{in}} = 0 \). Each of the states in Equation (B.49) is an equal superposition of \( b!/(n_{\text{in}}!n_{\text{out}}!n_0!) \) independent configurations. The dimension of the completely symmetric subspace is \((b + 1)(b + 4)/2\).

The permutation symmetry leads to a bosonic algebra. We define the bosonic annihilation operators \( b_{\text{in}} \), \( b_{\text{out}} \), and \( b_0 \), respectively associated with the occupation numbers \( n_{\text{in}} \), \( n_{\text{out}} \), and \( n_0 \), which may be viewed as a generalization of Schwinger bosons. We split up the Hamiltonian into blocks where the central spin is either 0 or 1 as well as an off-diagonal term coupling them. Explicitly,

\[
H_q = H^{(0)}_q \otimes (1 - n_{\text{cen}}) + H^{(1)}_q \otimes n_{\text{cen}} + H^{(\text{od})}_q \otimes \sigma^z_{\text{cen}},
\]

(B.50)

In terms of the bosonic operators

\[
H^{(0)}_q = \left( \begin{array}{c} b_{\text{in}}^\dagger \ b_{\text{out}}^\dagger \ b_0^\dagger \end{array} \right) \left( \begin{array}{ccc} V_{\text{e,in}} & 0 & -\Omega_{\text{in}} \\ 0 & V_{\text{e,out}} & -\Omega_{\text{out}} \\ -\Omega_{\text{in}} & -\Omega_{\text{out}} & V_{g,\text{in}} + V_{g,\text{out}} \end{array} \right) \left( \begin{array}{c} b_{\text{in}} \\ b_{\text{out}} \\ b_0 \end{array} \right) + V_{g,\text{cen}} P(n_{\text{in}} = 0),
\]

(B.51)

\[
H^{(1)}_q = \left( \begin{array}{c} b_{\text{out}}^\dagger \ b_0^\dagger \end{array} \right) \left( \begin{array}{cc} V_{\text{e,out}} & -\Omega_{\text{out}} \\ -\Omega_{\text{out}} & V_{g,\text{out}} \end{array} \right) \left( \begin{array}{c} b_{\text{out}} \\ b_0 \end{array} \right) + V_{e,\text{cen}},
\]

(B.52)

\[
H^{(\text{od})}_q = -\Omega_{\text{cen}} P(n_{\text{in}} = 0),
\]

(B.53)
where \( P(n_{\text{in}} = 0) \) projects onto states with no occupied inner vertices.

We diagonalize the Hamiltonian by treating the projectors perturbatively. We focus on the situation where all parameters follow the one-parameter family \( H_q(\beta) \) except for \( \Omega_{\text{cen}} \) and \( V_{e,\text{cen}} \), which may be adjusted freely. By diagonalizing the matrices in Equation (B.51) and Equation (B.52), we identify the lowest energy modes of the quadratic parts of \( H_q^{(0)} \) and \( H_q^{(1)} \) and associate with them the bosonic annihilation operators \( c_0 \) and \( c_1 \), respectively. Both modes have zero energy while the other modes are gapped at any finite value of \( \beta \). We may thus expect the ground state to be well approximated in the subspace spanned by

\[
|\psi_0\rangle = \frac{1}{\sqrt{b!}} c_0^{\dagger b} |0\rangle, \quad |\psi_1\rangle = \frac{1}{\sqrt{b!}} c_1^{\dagger b} |0\rangle, \quad \text{(B.54)}
\]

where \( |0\rangle \) denotes the bosonic vacuum. One can verify that along the one-parameter family \( H_q(\beta) \), these states correspond to the Gibbs state of the star with the central spin held fixed.

Next, we perform a Schrieffer–Wolff transformation [223] to project onto the subspace spanned by \( |\psi_0\rangle \) and \( |\psi_1\rangle \). We arrive at an effective Hamiltonian

\[
H_{\text{eff}} = \begin{pmatrix}
\epsilon_0 + \delta \epsilon_0 & -J - \delta J \\
-J - \delta J & V_{e,\text{cen}} + \delta \epsilon_1
\end{pmatrix}, \quad \text{(B.55)}
\]
where the terms

\[
\varepsilon_0 = \langle \psi_0 | P(n_{in} = 0) | \psi_0 \rangle = \left( \frac{1 + e^\beta}{1 + 2e^\beta} \right)^b,
\]

\[
J = \Omega_{cen} \langle \psi_1 | P(n_{in} = 0) | \psi_0 \rangle = \Omega_{cen} \left( \frac{1 + e^\beta}{1 + 2e^\beta} \right)^{b/2}
\]

are obtained from projecting the full Hamiltonian onto the low-energy subspace. The correction from coupling to excited states, as given by the Schrieffer–Wolff transformation to lowest nontrivial order, are

\[
\delta \varepsilon_0 = -\varepsilon_0 \sum_n \frac{1}{E_n} |\langle n | \sigma_{cen}^x | \psi_1 \rangle|^2
\]

\[
\delta \varepsilon_1 = -\Omega_{cen}^2 \sum_n \frac{1}{E_n} |\langle n | \sigma_{cen}^x | \psi_1 \rangle|^2
\]

\[
\delta J = -\Omega_{cen} \sqrt{\varepsilon_0} \sum_n \frac{1}{E_n} |\langle n | \sigma_{cen}^x | \psi_1 \rangle|^2
\]

where we used the relation \( P(n_{in} = 0) | \psi_0 \rangle = \sqrt{\varepsilon_0} \sigma_{cen}^x | \psi_1 \rangle \), which holds along the paths of interest. The sums run over all excited states \( |n \rangle \) of the unperturbed part of \( H_q^{(0)} \) with energy \( E_n \). We further neglected a term \( V_{e,cen} \) in the energy denominator, which is justified as long as \( V_{e,cen} \) is small compared to \( E_n \). The discussion remains valid even if this is not the case because the shifts from the Schrieffer–Wolff transformation can then be ignored as far as the ground state is concerned.

The effective Hamiltonian may be written as

\[
H_{eff} = \begin{pmatrix}
(1 - f)\varepsilon_0 & -(1 - f)J \\
-(1 - f)J & V_{e,cen} - f\Omega_{cen}^2
\end{pmatrix},
\]

171
where \( f = \sum_n |\langle n|\sigma^x_{cen}|\psi_1\rangle|^2/E_n \). We find numerically that \( f \) decays as an inverse power law in \( b \) such that our approximations are well justified in the thermodynamic limit. Along the one-parameter family \( H_q(\beta) \), we have \( V_{e,cen} = \Omega^2_{cen} \) such that \( H_{eff} \) depends on \( f \) only through an overall factor \((1 - f)\), which tends to 1 in the limit of large \( b \). The phase transition of the underlying classical model manifests itself as a first-order quantum phase transition from \( |\psi_0\rangle \) to \( |\psi_1\rangle \). The transition occurs when the two states are resonant, \( \varepsilon_0 = V_{e,cen} \), which can be solved to give \( \beta_c = \log(1 + \sqrt{5})/2 \) as expected. The tunneling rate at the phase transition point is given by \( J = \varphi^{-b} \), which bounds both the mixing time of the Markov chain and the time to adiabatically cross the phase transition along the one-parameter family \( H_q(\beta) \) by \( t_{m,a} \gtrsim \varphi^b \).

Following the discussion in Section 3.4.2, we expect an improvement of the adiabatic state preparation time by increasing the value of \( \Omega_{cen} \). We first observe that the Gibbs state at \( \beta = 0 \) can be efficiently prepared as it can be connected to the product state of all vertices unoccupied by a gapped path. For instance, one can start with \( V_{e,i} = 1 \) and \( V_{g,i} = \Omega_i = 0 \). Next, all \( \Omega_i \) are ramped up to 1 before doing the same for \( V_{g,i} \). One may then consider a path where \( \Omega_{cen} \) is held constant at 1 while all other parameters, including \( V_{e,cen} \), are varied according to \( H_q(\beta) \) from \( \beta = 0 \) to the desired final value of \( \beta \) (assumed to be below the phase transition). The time required to cross the phase transition is again \( t_a \sim 1/J \), where \( J \) is evaluated at the phase transition. The term \( f \Omega^2_{cen} \) in the effective Hamiltonian shifts the phase transition close to \( \beta = 0 \) such that \( t_a \sim (3/2)^{b/2} \). However, this does not yet result in a speedup for preparing the Gibbs state as one still has to decrease
\(\Omega_{\text{cen}}\) to its final value \(e^{-b\beta/2}\). It turns out that this step requires passing once again through a critical region, despite not crossing the phase transition a second time, which causes a slowdown that negates the speedup from the first segment of the path. In principle, it is possible to cross through this critical region within the sudden approximation. This will result in a final state infidelity on the order of \(1 - F \sim f\) since \(f\) quantifies the degree to which excited states are admixed.

A slight modification of the path achieves a final state infidelity that is not only polynomially but exponentially small in \(b\): First, \(V_{\text{cen}}\) is lowered from its initial value 1 to -1, which can be done in time \(t_a \sim (3/2)^{b/2}\) as before. Next, all other parameters are varied along \(H_q(\beta)\) for which only a time polynomial in \(b\) is required. Finally, \(V_{e,\text{cen}}\) is ramped to its final value \(e^{-b\beta}\). This last step may in fact be omitted as the overlap of the state at \(V_{e,\text{cen}} = -1\) with the state at \(V_{e,\text{cen}} = e^{-b\beta}\) is already exponentially close to unity.
Appendix C

Supporting material for Chapter 5

C.1 Regularization of the Green’s function

In this appendix, we discuss how to evaluate the expression for $\Delta(k)$ in Equation (5.10). Numerically, one can in principle evaluate Equation (5.7) directly, but the sum in momentum space often converges faster. In both cases, we have to subtract the divergent self-interaction term. More accurately, we should have defined

$$
\Delta(k) = -\frac{3\pi\gamma_0}{(\omega_0/c)} \left[ \frac{1}{A} \sum_B \text{Re} G(k + B; 0, 0; \omega_0) - \text{Re} G(0, 0; \omega_0) \right]. \quad (C.1)
$$

The first Green’s function has been Fourier transformed in the $x$ and $y$ coordinate, whereas the second Green’s function is taken to be fully in position

174
space. From Equation (5.11), we have

\[ G(k; 0, 0; !) = \frac{i}{2k_z} \begin{pmatrix} (\omega/c)^2 - k_x^2 & -k_xk_y & 0 \\ -k_xk_y & (\omega/c)^2 - k_y^2 & 0 \\ 0 & 0 & k_x^2 + k_y^2 \end{pmatrix} \]

\[ + \frac{1}{(\omega/c)^2} \delta(z = 0) \hat{z} \hat{z}. \quad (C.2) \]

The delta function corresponds to a self-interaction, which will drop out of Equation (C.1) and can therefore be safely ignored. We introduce a Gaussian regulator to define the function

\[ G_\Lambda(k; 0, 0; \omega) = \frac{i}{2k_z} e^{-k^2/\Lambda^2} \begin{pmatrix} (\omega/c)^2 - k_x^2 & -k_xk_y & 0 \\ -k_xk_y & (\omega/c)^2 - k_y^2 & 0 \\ 0 & 0 & k_x^2 + k_y^2 \end{pmatrix}, \quad (C.3) \]

where \( \Lambda \) is a momentum cutoff. Cutting of high momenta modifies the Green’s function on short length scales such that the regularized Green’s function evaluated at the source point,

\[ G_\Lambda(0, 0; \omega) = \int \frac{d^2k}{(2\pi)^2} G_\Lambda(k; 0, 0; \omega), \quad (C.4) \]
is now finite. A straightforward calculation yields

\[
\text{Re} \mathcal{G}_A(0, 0; \omega) = -\frac{\Lambda}{32\sqrt{\pi}(\omega/c)^2} e^{-(\omega/c)^2/\Lambda^2} (\mathbf{A} - 2(\omega/c)^2 \mathbf{1})
\]

\[
\times \begin{pmatrix}
\Lambda^2 - 2(\omega/c)^2 & 0 & 0 \\
0 & \Lambda^2 - 2(\omega/c)^2 & 0 \\
0 & 0 & -2\Lambda^2 - 4(\omega/c)^2
\end{pmatrix}.
\]

Equation (C.1) can now be evaluated as

\[
\Delta(k) = -\frac{3\pi \gamma_0}{(\omega_0/c)} \lim_{\Lambda \to \infty} \left[ \frac{1}{A} \sum_{\mathbf{B}} \text{Re} \mathcal{G}_A(k + \mathbf{B}; 0, 0; \omega_0) - \text{Re} \mathcal{G}_A(0, 0; \omega_0) \right].
\]

Numerically, fast convergence is observed by choosing a large but finite value of $\Lambda$. 
Appendix D

Supporting material for Chapter 6

D.1 Selection rules

Selection rules in a semiconductor are a consequence of the discrete symmetry of its crystal lattice [224]. The lattice of TMDs has the symmetry of the point group $D_{3h}$. Since we are interested in wavefunctions at the corners of the Brillouin zone, the relevant subgroup for the selection rules is $C_{3h}$, which is an Abelian group with six elements: the identity $E$, rotations $C_3$ and $C_3^2$ about an axis perpendicular to the plane of the TMD by an angle $2\pi/3$ and $4\pi/3$, respectively, a reflection $\sigma_h$ in the plane of the TMD, and the combined operations $S_3 = \sigma_h C_3$ and $S_3^5 = \sigma_h C_3^2$.

Since the group is Abelian, the Bloch wavefunctions at the $K$ and $K'$ points must be eigenfunctions under these symmetry operations. For each group operation $g$, we have $\psi(gr) = \chi_g \psi(r)$, where $\chi_g$ is the character of $g$ in the representation that the wavefunction belongs to. There are six distinct
representations of \( C_{3h} \) whose characters are given in Table D.1.

<table>
<thead>
<tr>
<th>( C_{3h} )</th>
<th>( E )</th>
<th>( C_3 )</th>
<th>( C_3^2 )</th>
<th>( \sigma_h )</th>
<th>( S_3 )</th>
<th>( S_3^5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A' )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( E'_+ )</td>
<td>1</td>
<td>( \varphi )</td>
<td>( \varphi^* )</td>
<td>1</td>
<td>( \varphi )</td>
<td>( \varphi^* )</td>
</tr>
<tr>
<td>( E'_- )</td>
<td>1</td>
<td>( \varphi^* )</td>
<td>( \varphi )</td>
<td>1</td>
<td>( \varphi^* )</td>
<td>( \varphi )</td>
</tr>
<tr>
<td>( A'' )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( E''_+ )</td>
<td>1</td>
<td>( \varphi )</td>
<td>( \varphi^* )</td>
<td>-1</td>
<td>-( \varphi )</td>
<td>-( \varphi^* )</td>
</tr>
<tr>
<td>( E''_- )</td>
<td>1</td>
<td>( \varphi^* )</td>
<td>( \varphi )</td>
<td>-1</td>
<td>-( \varphi^* )</td>
<td>-( \varphi )</td>
</tr>
</tbody>
</table>

Table D.1: Character table of \( C_{3h} \). The leftmost column shows the name of the six representations. Each number indicates the character associated with the group operation in the top row. (\( \varphi = e^{2\pi i/3} \))

A vector \( \mathbf{v} \) belongs to a reducible representation that can be decomposed into \( E'_+ \oplus E'_- \oplus A'' \). The first two representations are associated with the linear combinations of the components \( v_x \pm iv_y \), while the \( v_z \) component belongs to \( A'' \). In-plane, circularly polarized couples a wavefunction in representation \( R \) to only to wavefunctions in representation \( E'_+ \otimes R \). Similarly two wavefunctions may have a nonvanishing dipole matrix element along the \( z \) axis if their respective representations \( R \) and \( R' \) satisfy \( R' = A'' \otimes R \).

<table>
<thead>
<tr>
<th>( E'_+ )</th>
<th>( E'_- )</th>
<th>( A'' )</th>
<th>( E''_+ )</th>
<th>( E''_- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A' )</td>
<td>( A' )</td>
<td>( E'_+ )</td>
<td>( E'_- )</td>
<td>( A'' )</td>
</tr>
<tr>
<td>( E'_+ )</td>
<td>( E'_- )</td>
<td>( A' )</td>
<td>( E''_- )</td>
<td>( A'' )</td>
</tr>
<tr>
<td>( E'_- )</td>
<td>( E'_+ )</td>
<td>( E''_- )</td>
<td>( A'' )</td>
<td>( E''_+ )</td>
</tr>
<tr>
<td>( A'' )</td>
<td>( A' )</td>
<td>( E'_+ )</td>
<td>( E'_- )</td>
<td></td>
</tr>
<tr>
<td>( E''_- )</td>
<td>( E'_- )</td>
<td>( A' )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E''_+ )</td>
<td>( E'_+ )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table D.2: Multiplication table of \( C_{3h} \). Each entry shows the result of multiplying the representations indicated in the leftmost column and top row. The entries of the lower triangle are equal to the upper triangle as the multiplication of representations commutes.
The Bloch wavefunction of the valence band at $K$ is dominated by the $d_{\pm 2}$ orbitals of the transition metal atoms. Hence, it belongs to the representation $E'_-$.\footnote{A simple description of the symmetries of the bands can be found in reference [138].} Due to time reversal symmetry, the representation of the valence band wavefunction at $K'$ must be $E'_+$. In both valleys, the conduction band wavefunction is made up of $d_0$ orbitals of the metal atoms, which implies that it belongs to the representation $A'$. From Table D.2, we can see that $A' = E'_+ \otimes E'_-$. Hence, the valence and conduction band are connected by a circularly polarized dipole transition with opposite handedness for the $K$ and $K'$ valleys.

So far, we ignored the role of spin. To derive the selection rules in the presence of spin–orbit coupling, it is necessary to consider so-called double groups [224, 225]. Double groups allow for the possibility that a wavefunction picks up a negative sign upon rotation by $2\pi$ as is the case in systems with noninteger spin. For $C_{3h}$, whose double group is denoted by $C_{3h}^\ast$, this introduces six new group operations and six new representations, which are listed in Table D.3. The representations of a wavefunction with spin can be found by multiplying its spinless representation (orbital character) by the representations $\pm 1/2$. The relevant multiplication table is given in Table D.4.

For the valence band at the $K$ point, we find that representations of the spin-split bands are $+1/2 \otimes E'_- = +5/2$ and $-1/2 \otimes E'_- = +3/2$. The sign of the spin–orbit coupling is such that the $+5/2$ states are higher in energy as the spin is fully aligned with the orbital angular moment [138]. For the conduction band, we have $\pm 1/2 \otimes A' = \pm 1/2$. It is not possible to decide the ordering of the spin-split conduction bands because the first-order energy
correction from spin–orbit coupling vanishes due to the $d_0$ orbital character and higher order shifts may have either sign.

The resulting selection rules, which are readily obtained using Table D.4, are shown in Figure D.1. In addition to a pair of transitions with the same selection rule as in the spinless case, there is a $z$ polarized transition from the upper valence band. In the limit, where spin–orbit coupling can be treated perturbatively, the circularly polarized transitions are approximately spin conserving, while the $z$ polarized transition flips the spin. The spin flip is enabled by spin–orbit coupling, which mixes the $A'$ orbital, $-1/2$ spin state of the conduction band with $E''_0$ orbital, $+1/2$ spin states, which are then connected to the valence band via a $z$ polarized transition. The dipole element of the $z$ polarized transition is proportional to the spin–orbit coupling strength and therefore expected to be much weaker than the circularly polarized transitions. The $A'$ orbital, $+1/2$ spin state is coupled to $E''_{+1}$, $-1/2$ states, which cannot be connected to the valence band via a dipole transition.

Figure D.1: Representation of the highest valence band and lowest conduction band at the $K$ valley. The left panel shows the spinless case, while the right panel includes spin–orbit coupling (SOC). The arrows indicate dipole allowed transitions and their selection rules.
Table D.3: Character table of $C_{3h}^*$. The representations with noninteger spin are labeled by the lowest spin that transforms in the same way. ($\varphi = e^{2\pi i/3}, \chi = e^{i\pi/3}$)

<table>
<thead>
<tr>
<th>$C_{3h}^*$</th>
<th>$E$</th>
<th>$C_3$</th>
<th>$C_3^2$</th>
<th>$\sigma_h$</th>
<th>$S_3$</th>
<th>$S_3^5$</th>
<th>$E$</th>
<th>$C_3$</th>
<th>$C_3^2$</th>
<th>$\sigma_h$</th>
<th>$S_3$</th>
<th>$S_3^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A'$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$E'_+$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>1</td>
<td>$\varphi^*$</td>
</tr>
<tr>
<td>$E'$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>1</td>
<td>$\varphi^*$</td>
</tr>
<tr>
<td>$A''$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$E''_+$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>-1</td>
<td>-$\varphi^*$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>-1</td>
<td>-$\varphi^*$</td>
<td>1</td>
<td>-$\varphi^*$</td>
<td>1</td>
<td>-$\varphi^*$</td>
</tr>
<tr>
<td>$E''_-$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>-1</td>
<td>-$\varphi^*$</td>
<td>-$\varphi^*$</td>
<td>1</td>
<td>$\varphi^*$</td>
<td>-1</td>
<td>-$\varphi^*$</td>
<td>-$\varphi^*$</td>
<td>1</td>
<td>-$\varphi^*$</td>
</tr>
<tr>
<td>+1/2</td>
<td>1</td>
<td>$\chi$</td>
<td>$\chi^2$</td>
<td>$i$</td>
<td>$i\chi$</td>
<td>$i\chi^2$</td>
<td>-1</td>
<td>$-\chi$</td>
<td>$-\chi^2$</td>
<td>-$i\chi$</td>
<td>-$i\chi^2$</td>
<td></td>
</tr>
<tr>
<td>-1/2</td>
<td>1</td>
<td>$\chi^*$</td>
<td>$\chi^{*2}$</td>
<td>-$i\chi^*$</td>
<td>-$i\chi^{*2}$</td>
<td>-1</td>
<td>$-\chi^*$</td>
<td>$-\chi^{*2}$</td>
<td>$i\chi^*$</td>
<td>$i\chi^{*2}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+3/2</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-$i$</td>
<td>$-i$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-$i$</td>
<td>$-i$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>-3/2</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>$i$</td>
<td>-$i$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$i$</td>
<td>-$i$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>+5/2</td>
<td>1</td>
<td>$\chi^*$</td>
<td>$\chi^{*2}$</td>
<td>$i$</td>
<td>$i\chi^*$</td>
<td>$i\chi^{*2}$</td>
<td>-1</td>
<td>$-\chi^*$</td>
<td>$-\chi^{*2}$</td>
<td>-$i\chi^*$</td>
<td>-$i\chi^{*2}$</td>
<td></td>
</tr>
<tr>
<td>-5/2</td>
<td>1</td>
<td>$\chi$</td>
<td>$\chi^2$</td>
<td>-$i\chi$</td>
<td>-$i\chi^2$</td>
<td>-1</td>
<td>$-\chi$</td>
<td>$-\chi^2$</td>
<td>$i\chi$</td>
<td>$i\chi^2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(\varphi = e^{2\pi i/3}, \chi = e^{i\pi/3})
<table>
<thead>
<tr>
<th></th>
<th>$A'$</th>
<th>$E'_+$</th>
<th>$E'_-$</th>
<th>$A''$</th>
<th>$E''_+$</th>
<th>$E''_-$</th>
<th>$E''_+$</th>
<th>$E''_-$</th>
<th>$+1/2$</th>
<th>$-1/2$</th>
<th>$+3/2$</th>
<th>$-3/2$</th>
<th>$+5/2$</th>
<th>$-5/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A'$</td>
<td>$A'$</td>
<td>$E'_+$</td>
<td>$E'_-$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$E''_-$</td>
<td>$E''_+$</td>
<td>$E''_-$</td>
<td>$+1/2$</td>
<td>$-1/2$</td>
<td>$+3/2$</td>
<td>$-3/2$</td>
<td>$+5/2$</td>
<td>$-5/2$</td>
</tr>
<tr>
<td>$E'_+$</td>
<td>$E'_+$</td>
<td>$A'$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$-3/2$</td>
<td>$-5/2$</td>
<td>$-1/2$</td>
<td>$+5/2$</td>
<td>$+1/2$</td>
<td>$+3/2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E'_-$</td>
<td>$E'_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$-5/2$</td>
<td>$+3/2$</td>
<td>$-5/2$</td>
<td>$+1/2$</td>
<td>$-3/2$</td>
<td>$-1/2$</td>
<td>$+1/2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$E'_+$</td>
<td>$E'_-$</td>
<td>$-5/2$</td>
<td>$+5/2$</td>
<td>$-3/2$</td>
<td>$+3/2$</td>
<td>$-1/2$</td>
<td>$+1/2$</td>
<td>$-3/2$</td>
<td>$-5/2$</td>
<td>$-1/2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E''_+$</td>
<td>$E'$</td>
<td>$A'$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$+3/2$</td>
<td>$+1/2$</td>
<td>$+5/2$</td>
<td>$-1/2$</td>
<td>$-5/2$</td>
<td>$-3/2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E''_-$</td>
<td>$E'$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$-1/2$</td>
<td>$-3/2$</td>
<td>$+1/2$</td>
<td>$-5/2$</td>
<td>$+3/2$</td>
<td>$+5/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$+1/2$</td>
<td>$E''_+$</td>
<td>$A'$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-1/2$</td>
<td>$E''_+$</td>
<td>$A'$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$+3/2$</td>
<td>$E''_+$</td>
<td>$A'$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-3/2$</td>
<td>$E''_+$</td>
<td>$A'$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$+5/2$</td>
<td>$E''_+$</td>
<td>$A'$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$-5/2$</td>
<td>$E''_+$</td>
<td>$A'$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td>$E''_+$</td>
<td>$A''$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table D.4: Multiplication table of $C_{3h}^*$. 
D.2 Transfer matrix method

The Green’s function in a layered system with translational invariance in the $xy$ plane can be computed using a transform matrix method. At normal incidence, we may consider a single polarization of the electric field. The electric field can be decomposed into upward (+) and downward (−) propagating components as $E(z) = E_+(z) + E_-(z)$. The field at some point $z$ can be related to the field at $z' < z$ by the transfer matrix $T(z', z)$ according to

$$
\begin{pmatrix}
E_+(z') \\
E_-(z')
\end{pmatrix} = T(z', z) \begin{pmatrix} E_+(z) \\
E_-(z) \end{pmatrix}
$$

(D.1)

Any transfer matrix can be decomposed into propagation within layers with constant permittivity and transfer across interfaces. Propagation in a layer with permittivity $\varepsilon$ is described by the transfer matrix

$$T_{\text{prop}}(z', z) = \begin{pmatrix}
e^{i\sqrt{\varepsilon k_0}(z'-z)} & 0 \\
0 & e^{-i\sqrt{\varepsilon k_0}(z'-z)}
\end{pmatrix}
$$

(D.2)

where $k_0 = \omega / c$. For transfer across an interface from $\varepsilon$ above to $\varepsilon'$ below, we have

$$T_{\text{interface}}(\varepsilon', \varepsilon) = \frac{1}{2\sqrt{\varepsilon'}} \begin{pmatrix} \sqrt{\varepsilon} + \sqrt{\varepsilon'} & -\sqrt{\varepsilon} + \sqrt{\varepsilon'} \\
-\sqrt{\varepsilon} + \sqrt{\varepsilon'} & \sqrt{\varepsilon} + \sqrt{\varepsilon'} \end{pmatrix}.
$$

(D.3)

The reflection coefficient $r_0$ of a stack can be found from the relation

$$\begin{pmatrix} 0 \\
t_0 \end{pmatrix} = T(z_b, z_a) \begin{pmatrix} r_0 \\
1 \end{pmatrix},
$$

(D.4)
where $t_0$ is the transmission coefficient. The coordinate $z_a$ denotes a position above the top layer, while $z_b$ is located below the bottom layer.

Next, we consider a source at position $z$. At $z_a$ the field only propagates upwards such that

$$G(z, z) = (1, 1) T(z, z_a) \begin{pmatrix} G(z_a, z) \\ 0 \end{pmatrix}. \quad (D.5)$$

Here $G(z, z')$ is a shorthand for one of the diagonal, in-plane components of $\mathcal{G}(k = 0; z, z'; \omega)$. If we instead place a source at $z_a$, we obtain

$$G(z, z_a) = \frac{i}{2k_0} (1, 1) T(z, z_a) \begin{pmatrix} r_0 \\ 1 \end{pmatrix}. \quad (D.6)$$

The factor $i/2k_0$ originates from the value of the free space Green’s function $G_0(z, z)$. These equations can be solved for any pair of points by making use of the fact that $G(z, z') = G(z', z)$.

For completeness, we demonstrate explicitly that $G(z, z_a) = G(z_a, z)$. Solving for $r_0$ and plugging the result into Equation (D.6) yields

$$G(z, z_a) = -\frac{i}{2k_0 T_{11}(z_b, z_a)}$$

$$\times (1, 0) T(z_b, z_a) \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} T(z, z_a)^T \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} -1 \\ 1 \end{pmatrix}. \quad (D.7)$$
The transfer matrices have the symplectic properties

\[
\begin{pmatrix}
0 & 1 \\
-1 & 0
\end{pmatrix}
T_{\text{prop}}^{T}(z', z)
\begin{pmatrix}
0 & -1 \\
1 & 0
\end{pmatrix}
= T_{\text{prop}}^{-1}(z', z)
\]  \hspace{1cm} (D.8)

and

\[
\begin{pmatrix}
0 & 1 \\
-1 & 0
\end{pmatrix}
T_{\text{interface}}^{T}(\varepsilon', \varepsilon)
\begin{pmatrix}
0 & -1 \\
1 & 0
\end{pmatrix}
= \sqrt{\frac{\varepsilon}{\varepsilon'}} T_{\text{interface}}^{-1}(\varepsilon', \varepsilon),
\]  \hspace{1cm} (D.9)

from which it follows that

\[
\begin{pmatrix}
0 & 1 \\
-1 & 0
\end{pmatrix}
T(z, z_a)^T
\begin{pmatrix}
0 & -1 \\
1 & 0
\end{pmatrix}
= \frac{1}{\sqrt{\varepsilon_s}} T_a(z, z_a)^{-1},
\]  \hspace{1cm} (D.10)

where \(\varepsilon_s\) is the permittivity at the location \(z\). Hence,

\[
G(z, z_a) = -\frac{i}{2 \sqrt{\varepsilon_s k_0}} \frac{1}{T_{11}(z_b, z_a)}(1, 0) T(z_b, z)
\begin{pmatrix}
-1 \\
1
\end{pmatrix}.
\]  \hspace{1cm} (D.11)

By placing a source at \(z\), one can further show that

\[
\begin{pmatrix}
0 \\
G(z_b, z_a)
\end{pmatrix}
= T(z_b, z_a)
\begin{pmatrix}
G(z_a, z) \\
0
\end{pmatrix}
+ \frac{i}{2 \sqrt{\varepsilon_s k_0}} T(z_b, z)
\begin{pmatrix}
-1 \\
1
\end{pmatrix},
\]  \hspace{1cm} (D.12)

which together with Equation (D.11) establishes that \(G(z, z_a) = G(z_a, z)\).
Appendix E

Supporting material for
Chapter 7

E.1 Linear response

The reflection and transmission coefficients of a TMD (or any other two-dimensional, resonant emitter) are given by [167]

\[ r_{\text{TMD}}(\delta) = -\frac{i\gamma/2}{\delta + i(\gamma + \gamma')/2}, \quad t_{\text{TMD}}(\delta) = \frac{\delta + i\gamma'/2}{\delta + i(\gamma + \gamma')/2}. \]  

(E.1)

The transmission and reflection coefficients for the entire system, including the mirror, can be obtained by summing over all multiple reflection processes:

\[ r(\delta) = r_{\text{TMD}}(\delta) \]
\[ + t_{\text{TMD}}(\delta) r_0 e^{2ikd} \left[ 1 + r_{\text{TMD}}(\delta) r_0 e^{2ikd} + r_{\text{TMD}}(\delta)^2 r_0^2 e^{4ikd} + \cdots \right], \]
\[ t(\delta) = t_{\text{TMD}}(\delta) \left[ 1 + r_{\text{TMD}}(\delta) r_0 e^{2ikd} + r_{\text{TMD}}(\delta)^2 r_0^2 e^{4ikd} + \cdots \right] t_0 e^{ikd}. \]  

(E.3)
Here, \( k = k_0 + \delta / c \) is the wavenumber of the incident light. By evaluating the geometric sums, we obtain

\[
\begin{align*}
    r(\delta) &= r_0 e^{2i k d} - \frac{i \gamma / 2 (1 + r_0 e^{2i k d})^2}{\delta + i \gamma / 2 (1 + r_0 e^{2i k d}) + i \gamma'/2}, \\
    t(\delta) &= \frac{\delta + i \gamma'/2}{\delta + i \gamma / 2 (1 + r_0 e^{2i k d}) + i \gamma'/2} t_0 e^{i k d}.
\end{align*}
\]

(E.4)

(E.5)

It is easily verified that perfect transmission (zero reflection) occurs when \( \gamma' = 0, \delta = \pm (\gamma / 2) |t_0| / |r_0|, \) and \( r_0 e^{2i k d} = -|r_0|^2 \pm i |r_0| |t_0|. \)

### E.2 Heisenberg–Langevin equation

We derive a Heisenberg–Langevin equation for a two-dimensional emitter in front of a partially reflecting mirror [Equation (7.1)]. If the system is translationally invariant in the plane of the emitter, conservation of momentum allows us to consider each in-plane momentum component separately. The Hamiltonian for the zero-momentum components is given by

\[
H = H_0 + \sum_k \omega_k d_k^\dagger d_k + i \sum_k g_k (d_k^\dagger a - a^\dagger d_k),
\]

(E.6)

where \( a \) is the annihilation operator of a delocalized excitations (excitons in case of a TMD) and \( d_k \) is the photon annihilation operators for a plane-wave mode with momentum \( k \) normal to the mirror and the emitter. At this stage, the Hamiltonian only includes free-space photonic modes. The mirror will be introduced below by imposing suitable boundary conditions. We expect the form of the Hamiltonian to remain valid to a good approximation for a finite-sized system if the incident beam is chosen such that only a single transverse

187
mode needs to be taken into account at the location of the emitter. In this case, the operators $a$ and $d_k$ correspond to states whose transverse profile is determined by the incident light.

Following the input–output formalism in reference [171], we make the Markov approximation, $g_k \approx \sqrt{\gamma/2}$, within which the evolution of some system operator $Q$ may be written as

$$\dot{Q} = -i [Q, H_0] + \gamma \left( a^\dagger Q a - \frac{1}{2} \left\{ Q, a^\dagger a \right\} \right)$$

$$+ \sqrt{\frac{\gamma}{2}} \left( b^\dagger_{\text{in},R} [Q, a] - [Q, a^\dagger] b_{\text{in},R} \right) + \sqrt{\frac{\gamma}{2}} \left( c^\dagger_{\text{in}} [Q, a] - [Q, a^\dagger] c_{\text{in}} \right),$$

where the input fields are defined as

$$b_{\text{in},R}(t) = \sum_{k>0} d_k(t_0) e^{-i\omega_k(t-t_0)}, \quad c_{\text{in}}(t) = \sum_{k<0} d_k(t_0) e^{-i\omega_k(t-t_0)} \quad (E.8)$$

for an early time $t_0 \to -\infty$. In order to account for the mirror, we apply boundary conditions to the electric field. The electric field is computed within the Markov approximation assuming a linear dispersion relation $\omega_k = kc$. For the field propagating to the right, we obtain

$$E^+_{R}(z, t) \propto \sum_{k>0} g_k d_k(t) e^{ikz} \propto \begin{cases} b_{\text{in},R}(t - z/c) & \text{if } z < 0 \\ c_{\text{out}}(t - z/c) & \text{if } 0 < z < d \\ b_{\text{out},R}(t - (z-d)/c) & \text{if } d < z \end{cases}, \quad (E.9)$$
while for left-moving modes

\[ E_L^+(z, t) \propto \sum_{k<0} g_k d_k(t) e^{ikz} \propto \begin{cases} b_{\text{out}, L}(t + z/c) & \text{if } z < 0 \\ c_{\text{in}}(t + z/c) & \text{if } 0 < z < d \\ b_{\text{in}, L}(t + (z - d)/c) & \text{if } d < z \end{cases}. \quad (E.10) \]

Here we introduced

\[ c_{\text{out}}(t) = b_{\text{in}, R}(t) + \sqrt{\frac{\gamma}{2}} a(t), \quad b_{\text{out}, L}(t) = c_{\text{in}}(t) + \sqrt{\frac{\gamma}{2}} a(t). \quad (E.11) \]

The operators \( b_{\text{out}, R} \) and \( b_{\text{in}, L} \) correspond to the field to the right of the mirror. They are determined by the boundary conditions at the mirror,

\[ c_{\text{in}}(t) = r_0 c_{\text{out}}(t - 2d/c) + t_0 b_{\text{in}, L}(t - d/c), \quad (E.12) \]
\[ b_{\text{out}, R}(t) = t_0 c_{\text{out}}(t - d/c) - \frac{t_0}{t_0^*} r_0^* b_{\text{in}, L}(t), \quad (E.13) \]

where we used the fact that for a nonabsorbing mirror, the transmission coefficients from both sides are identical, while the reflection coefficient from the right is \(-t_0 r_0^*/t_0^*\), given the reflection coefficient \( r_0 \) from the left. Figure E.1 illustrates the physical interpretation of the various photon operators.

The dynamics of the system and the electric field are in principle fully determined by Equations (E.7), (E.11), (E.12), and (E.13) along with initial conditions for the input fields \( b_{\text{in}, R} \) and \( b_{\text{in}, L} \). However, the equations are nonlocal in time, which renders them difficult to solve. To turn them into local equations, we neglect retardation, \( a(t - 2d/c) \approx e^{2ikd} a(t) \), and we assume that the input field is sufficiently narrow band such that \( b_{\text{in}, R}(t - 2d/c) \approx e^{2ikd} b_{\text{in}, R}(t) \)
and \( b_{\text{in},L}(t - 2d/c) \approx e^{2 ik_0 d} b_{\text{in},L}(t) \). The validity of these approximations will be discussed below. Substituting back into Equation (E.7) yields the Heisenberg–Langevin equation

\[
\dot{Q} = -i \left[ Q, H_0 + \gamma \frac{1}{2} \text{Im} \left( r_0 e^{2ik_0 d} \right) a^\dagger a \right] \\
+ \gamma \left[ 1 + \text{Re} \left( r_0 e^{2ik_0 d} \right) \left( a^\dagger Q a - \frac{1}{2} \{ Q, a^\dagger a \} \right) \\
- \sqrt{\frac{\gamma}{2}} \left( \left[ Q, a^\dagger \right] \left( 1 + r_0 e^{2ik_0 d} \right) b_{\text{in},R} + \text{h.c.} \right) \\
- \sqrt{\frac{\gamma}{2}} \left( \left[ Q, a^\dagger \right] t_0 e^{ik_0 d} b_{\text{in},L} + \text{h.c.} \right),
\]

(E.14)

which is supplemented by the input–output relations

\[
b_{\text{out},R}(t) = t_0 e^{ik_0 d} b_{\text{in},R}(t) - \frac{t_0}{t_0} r_0 b_{\text{in},L}(t) + \sqrt{\frac{\gamma}{2}} t_0 e^{ik_0 d} a(t), \quad \text{(E.15)}
\]

\[
b_{\text{out},L}(t) = r_0 e^{2ik_0 d} b_{\text{in},R}(t) + t_0 e^{ik_0 d} b_{\text{in},L}(t) + \sqrt{\frac{\gamma}{2}} \left( 1 + r_0 e^{2ik_0 d} \right) a(t). \quad \text{(E.16)}
\]

For all remaining calculations, we assume that the input fields are prepared in a coherent states. It is then convenient to write the Heisenberg–Langevin
equation as

\[ \dot{Q} = -i \left[ Q, H_0 + \frac{\gamma}{2} \text{Im} \left( r_0 e^{2ik_0d} \right) a^\dagger a - i \left( \Omega a^\dagger - \Omega^* a \right) \right] \\
+ \gamma \left( 1 + \text{Re} \left( r_0 e^{2ik_0d} \right) \right) a^\dagger Qa - \frac{1}{2} \left[ Q, a^\dagger a \right] + \mathcal{F}_Q \]  

(E.17)

where we defined the Rabi frequency

\[ \Omega = \sqrt{\frac{\gamma}{2}} \left( 1 + r_0 e^{2ik_0d} \right) \langle b_{\text{in},R} \rangle + \sqrt{\frac{\gamma}{2}} t_0 e^{ik_0d} \langle b_{\text{in},L} \rangle \]  

(E.18)

and the Langevin noise term

\[ \mathcal{F}_Q = -\sqrt{\frac{\gamma}{2}} \left( \left[ Q, a^\dagger \right] \left( 1 + r_0 e^{2ik_0d} \right) \langle b_{\text{in},R} \rangle - \langle b_{\text{in},R} \rangle + \text{h.c.} \right) \\
- \sqrt{\frac{\gamma}{2}} \left( \left[ Q, a^\dagger \right] t_0 e^{ik_0d} \langle b_{\text{in},L} \rangle - \langle b_{\text{in},L} \rangle + \text{h.c.} \right). \]  

(E.19)

The Langevin noise term has the important property \( \langle \mathcal{F}_Q \rangle = 0 \) for any \( Q \). We have thus arrived at Equation (7.1) up to the additional dissipative terms \( \gamma' \) and \( \chi_2 \).

We next comment on the validity of the Heisenberg-Langevin equation. The Markov approximation \( g_k \approx \sqrt{\gamma/2} \) requires that \( g_k \) varies little over the range \( \omega_0 \pm \gamma \). In free space, this leads to the conditions \( \gamma \ll \omega_0 \), which is typically satisfied for optical transitions and for TMDs in particular. To understand the conditions under which it is justified to neglect retardation, we switch to a frame that rotates according to

\[ a(t) = \tilde{a}(t) e^{-i\omega_0 t}. \]  

(E.20)
We can then expand

\[ a(t - 2d/c) \approx \left[ \hat{a}(t) - \frac{2d}{c} \hat{a}(t) \right] e^{-i\omega_0(t - 2d/c)}. \quad (E.21) \]

The magnitude of \( \hat{a} \) compared to \( \tilde{a} \) is given by \( 1/\tau_S \), where \( \tau_S \) denotes the typical timescale over which the system evolves nontrivially. By following the derivation that led to the Heisenberg–Langevin equation, we obtain a relative correction of order \( \gamma d/c\tau_S \). The correction can be certainly neglected if it is smaller than the decay rate, which leads to the condition

\[ \frac{1}{\tau_S} \ll \left[ 1 + \text{Re} (r_0 e^{2i\delta}) \right] \nu_{FSR}. \quad (E.22) \]

There are four frequency scales that determine the time scale of the system: the detuning \( \delta \), the Lamb shift \( (\gamma/2) \text{Im} (r_0 e^{2i\delta}) \), the decay rate \( \gamma + \gamma \text{Re} (r_0 e^{2i\delta}) \), and the nonlinearity \( \chi_{1,2} \). By taking the detuning to be comparable to the Lamb shift, we obtain the three conditions

\[ \gamma \ll \frac{1 + \text{Re} (r_0 e^{2i\delta})}{\text{Im} (r_0 e^{2i\delta})} \nu_{FSR}, \quad (E.23) \]

\[ \gamma \ll \nu_{FSR}, \quad (E.24) \]

\[ \chi_{1,2} \ll \left[ 1 + \text{Re} (r_0 e^{2i\delta}) \right] \nu_{FSR}. \quad (E.25) \]

A similar argument can be applied to the input fields, showing that their time dependence can be approximated as \( \sim e^{-i\omega t} \) provided the bandwidth and, again, the detuning, are small compared to \( [1 + \text{Re} (r_0 e^{2i\delta})] \nu_{FSR} \).

At the Fabry–Pérot resonance, we have \( r_0 e^{2i\delta} = -R_0 \pm i\sqrt{R_0T_0} \), which
yields two sufficient conditions:

\[ \gamma \ll \sqrt{\frac{T_0}{R_0}\nu_{\text{FSR}}}, \quad \chi_{1,2} \ll T_0\nu_{\text{FSR}} \]  

(E.26)

With a wavelength scale separation between the TMD and the mirror (\(\nu_{\text{FSR}} \sim \omega_0\)), both conditions are readily met for the values of \(T_0\) required to achieve antibunching.

### E.3 Photon statistics

We may use the input–output relations to relate expectation values and correlation functions of the output field to functions of system operators. For simplicity, let us assume that there is no incident field from the right, while the field incident from the left is in a coherent state. It is convenient to introduce the scaled operators

\[
\begin{align*}
    a_L &= \frac{(1 + r_0 e^{2i\omega_0 t_0})^2}{r_0 e^{2i\omega_0 t_0}} \frac{a}{2\Omega/\gamma}, \\
    a_R &= (1 + r_0 e^{2i\omega_0 t_0}) \frac{a}{2\Omega/\gamma},
\end{align*}
\]

(E.27)

where the Rabi frequency \(\Omega\) is defined in Equation (E.18). The intensity reflection and transmission coefficients may then be expressed as

\[
\begin{align*}
    R &= \frac{\langle b_{\text{out},L}^\dagger b_{\text{out},L} \rangle}{\langle b_{\text{in},R}^\dagger b_{\text{in},R} \rangle} = \left[1 + \langle a_L\rangle + \langle a_L^\dagger a_L \rangle \right] R_0, \\
    T &= \frac{\langle b_{\text{out},R}^\dagger b_{\text{out},R} \rangle}{\langle b_{\text{in},R}^\dagger b_{\text{in},R} \rangle} = \left[1 + \langle a_R\rangle + \langle a_R^\dagger a_R \rangle \right] T_0.
\end{align*}
\]

(E.28)

(E.29)

It is straightforward to show that these expressions agree with the classical result in Equation (E.4) and Equation (E.5) in linear response \((\chi_1 = \ldots)\).
\( \chi_2 = 0 \) under the same conditions for which the Heisenberg–Langevin equation is valid. For higher-order correlation functions, it is helpful to note that input fields at later times commute with output fields at earlier times, e.g. \([b_{\text{in},R}(t), b_{\text{out},R}(0)] = 0 \) for \( t > 0 \), as a consequence of causality [171]. We are interested in the normalized two-time correlation function of the transmitted light, which thus evaluates to

\[
g^{(2)}_T(t) = \frac{\langle b_{\text{out},R}(0) b_{\text{out},R}(t) b_{\text{out},R}(t) b_{\text{out},R}(0) \rangle}{\langle b_{\text{out},R}(0) b_{\text{out},R}(0) \rangle \langle b_{\text{out},R}(t) b_{\text{out},R}(t) \rangle}
= \left( \frac{T_0}{T} \right)^2 \left\{ 1 + 2 \left[ \langle a_R(0) \rangle + \text{c.c.} \right]
+ \left[ \langle a_R(t) a_R(0) \rangle + \langle a_R^\dagger(t) a_R(t) \rangle + \langle a_R^\dagger(0) a_R(0) \rangle + \text{c.c.} \right]
+ \left[ \langle a_R^\dagger(t) a_R(t) a_R(0) \rangle + \langle a_R^\dagger(0) a_R(t) a_R(t) \rangle + \text{c.c.} \right]
+ \langle a_R^\dagger(0) a_R^\dagger(t) a_R(t) a_R(0) \rangle \right\}.
\]  

(E.30)

### E.4 Anharmonic oscillator

Above we have shown how to compute the properties of the scattered field when the dynamics of the system are known. We now briefly outline how to obtain the relevant correlation functions for the anharmonic oscillator described in Chapter 7. The Hamiltonian in the rotating frame is given by

\[
H = (\Delta - \delta)a^\dagger a + \frac{\chi_1}{2} a^\dagger a^\dagger a a - i \left( \Omega a^\dagger - \Omega^* a \right).
\]  

(E.31)
while the nonunitary evolution is captured by the sum of the three dissipators

\[ D_0[Q] = \Gamma \left( a^\dagger Q a - \frac{1}{2} \left\{ Q, a^\dagger a \right\} \right) \]  
(linear decay),  
(E.32)

\[ D_1[Q] = \frac{\chi_2}{2} \left( a^\dagger a^\dagger Q a a - \frac{1}{2} \left\{ Q, a^\dagger a^\dagger a a \right\} \right) \]  
(nonlinear decay),  
(E.33)

\[ D_2[Q] = 2\gamma_d \left( a^\dagger a Q a^\dagger a - \frac{1}{2} \left\{ Q, a^\dagger a^\dagger a \right\} \right) \]  
(pure dephasing),  
(E.34)

where we defined

\[ \Delta = \frac{\gamma}{2} \text{Im} \left( r_0 e^{2i k_0 d} \right), \quad \Gamma = \tilde{\gamma} + \gamma' = \gamma \left[ 1 + \text{Re} \left( r_0 e^{2i k_0 d} \right) \right] + \gamma'. \]  
(E.35)

In addition to the linear and nonlinear decay terms, we included the dissipator \( D_2[Q] \) corresponding to pure dephasing at rate \( \gamma_d \).

The time evolution of the oscillator is fully determined by the normal ordered expectation values \( \langle a^m a^n \rangle \). A straightforward calculation yields

\[
\frac{d}{dt} \langle a^m a^n \rangle = - \left[ i(n-m)(\Delta-\delta) + (n+m)\frac{\Gamma}{2} + i(n(n-1)-m(m-1))\frac{\chi_1}{2} \right. \\
+ (n(n-1)+m(m-1))\frac{\chi_2}{4} + (n-m)^2\gamma_d \left. \right] \langle a^m a^n \rangle \\
- n\Omega \langle a^{m+1} a^{n-1} \rangle - m\Omega^* \langle a^{m-1} a^n \rangle \\
- \left[ i(n-m)\chi_1 + (n+m)\frac{\chi_2}{2} \right] \langle a^{m+1} a^{n+1} \rangle.
\]  
(E.36)

We can cast the above equations of motion into matrix form as

\[
\frac{d}{dt} \langle a^m a^n \rangle = \sum_{kl} M_{mn,kl} \langle a^{k} a^{l} \rangle
\]  
(E.37)

To find the steady state, we note that \( \langle a^0 a^0 \rangle = 1 \), which allows us to re-write
the equation as

$$M_{mn,00} + \sum_{(k,l) \neq (0,0)} M_{mn,kl} \langle a^\dagger k a^\dagger l \rangle = 0.$$  \hspace{1cm} (E.38)

Assuming that there exists a unique steady state, as is the case for weak driving, we can numerically solve this equation by matrix inversion in a truncated Fock space.

Once all the normal ordered expectation values are known, two-time correlation functions can be obtained using the quantum regression theorem (valid within the Markov approximation) \[123\]. Applied to our problem, the quantum regression theorem states that

$$\frac{d}{dt} \langle a^\dagger(0)^p a^\dagger(t)^n a(t)^k a(0)^q \rangle = \sum_{kl} M_{mn,kl} \langle a^\dagger(0)^p a^\dagger(t)^k a(t)^l a(0)^q \rangle,$$  \hspace{1cm} (E.39)

which can be readily integrated in a truncated Fock space with the initial conditions determined by the steady-state solution. Hence, the two-time correlation functions directly follow from the one-time expectation values.

**E.5 Pure dephasing**

In Chapter 7, we discussed the role of loss and provided an upper bound on the loss rate \(\gamma'\) for the quantum nonlinearity to be observable. In addition to loss, excitons may also be subject to pure dephasing as described by the dissipative term Equation (E.34). To explore the impact of pure dephasing, we show in Figure E.2 plots analogous to Figure 7.1e and Figure 7.2d, replacing the loss rate \(\gamma'\) by the dephasing rate \(\gamma_d\). The figures clearly indicate that
Figure E.2: (a) Transmission at the Fabry–Pérot resonance as a function of the dephasing rate $\gamma_d$, c.f. Figure 7.1e. (b) $y_T^{(2)}(0)$ as a function of $\gamma_d$ and the transmission coefficient $T_0$ of the mirror in analogy with Figure 7.2d. We set $\gamma' = 0$ in both cases.

Pure dephasing affects the linear and nonlinear response of the system in a qualitatively and quantitatively similar fashion to loss. Hence, the system parameters must satisfy

$$\chi > T_0 \gamma > \gamma_d \quad \quad \quad (E.40)$$

as well as Equation (7.6) in order to exhibit strong quantum nonlinear dynamics.
Appendix F

Supporting material for Chapter 8

F.1 Computational details

To compute the exciton energy, we use the dielectrically screened Coulomb interaction described in Section 8.2 with $r_0 = 5.17 \text{ nm}$ [203]. The Schrödinger equation is diagonalized numerically in a basis of angular momentum eigenstates of the electron. We include angular momentum quantum numbers up to $m = 5$ and employ a nonuniform grid (quadratically increasing spacing) of 1000 radial momenta from 0 to $0.5 \text{ Å}^{-1}$. The electron and hole masses used for the calculation are $m_e = 0.56m_0$, $m_h = 0.59m_0$, where $m_0$ [130] denotes the mass of a free electron. All numerical integrations were performed using a trapezoidal rule, adjusting the grid size to reach convergence.
F.2 Optical decay rates

To compute the emission spectrum and radiative decay rates, we start from the fully quantized light-matter interaction Hamiltonian

\[ H_{\gamma} = \sum_{p,p_z,q,\lambda} \mu \cdot \hat{e}_{p+p_z,\lambda} \sqrt{\frac{\nu_{p+p_z}}{2\varepsilon_0}} \gamma_{p+p_z,\lambda}^\dagger e_{p,q} \hbar + \text{h.c.} \]  

(F.1)

Here, the momenta \( p \) and \( q \) are confined to the plane of the MoSe\(_2\) monolayer (xy plane), while \( p_z \) is perpendicular to it. The operator \( \gamma_{p,\lambda}^\dagger \) creates a photon with total momentum \( p \) and polarization \( \lambda \), where \( \hat{e}_{p,\lambda} \) denotes the associated polarization vector. We further introduced the transition dipole matrix element between the conduction and the valence band, \( \mu \) and the photon dispersion, \( \nu_p = c|p| \). Since the valence band hole is assumed to be in the \( K \) valley, electrons in the \( K' \) do not participate in the decay process.

The spontaneous emission rate \( \Gamma \) of some initial state \( |i\rangle \) can be determined using Fermi’s Golden Rule,

\[ \Gamma = 2\pi \sum_f |\langle f|H_{\gamma}|i\rangle|^2 \delta(\omega_i - \omega_f), \]  

(F.2)

where the sum runs over all final states \( |f\rangle \). By assuming that the photonic part of \( |i\rangle \) is in the vacuum state, this may be written as

\[ \Gamma = \frac{\pi}{\varepsilon_0} \sum_{p,p_z,\lambda} |\mu \cdot \hat{e}_{p+p_z,\lambda}|^2 \nu_{p+p_z} \]  

\[ \times \sum_f |\langle f|e_{q}\hbar_{p-q}|i\rangle|^2 \delta(\omega_i - \omega_f - \nu_{p+p_z}), \]  

(F.3)
where the states $|i\rangle$ and $|f\rangle$ as well as their corresponding energies $\omega_i$ and $\omega_f$ now only include electronic degrees of freedom. We make use of the identity

$$\sum_{\lambda} \hat{e}_{p\lambda} \hat{e}_{p\lambda} = I - \frac{1}{p^2} \mathbf{p}\mathbf{p}$$

and employ the fact that $\mathbf{\mu}$ is in the $xy$ plane to obtain

$$\Gamma = \frac{\pi \mu^2}{\varepsilon_0} \sum_{p, p_z, \lambda} \left( 1 - \frac{|\hat{\mathbf{\mu}} \cdot \mathbf{p}|^2}{p^2 + p_z^2} \right) \nu_{p+p_z}$$

$$\times \sum_f \left| \langle f | \sum_q e_q h_{p-q} |i \rangle \right|^2 \delta(\omega_i - \omega_f - \nu_{p+p_z}),$$

where $\hat{\mathbf{\mu}} = \mathbf{\mu}/|\mathbf{\mu}|$. Next, we switch variables from $(\mathbf{p}, p_z)$ to $(\mathbf{p}, \nu)$, where $\nu = \sqrt{p^2 + p_z^2}$ (having set $c = 1$). This is accomplished in the integrand Equation (F.3) by letting

$$\sum_{p, p_z} \rightarrow \frac{1}{2\pi} \int_{-\infty}^{\infty} dp_z \sum_{\mathbf{p}} \rightarrow \frac{1}{\pi} \int_0^{\infty} d\nu \sum_{|p|<\nu} \frac{\nu}{\sqrt{1 - p^2/\nu^2}}.$$  

Defining the spectral decay rate

$$\Gamma = \int_0^{\infty} d\nu \Gamma(\nu)$$

thus yields

$$\Gamma(\nu) = \frac{\mu^2 \nu}{\varepsilon_0} \sum_{|p|<\nu} \frac{1 - |\hat{\mathbf{\mu}} \cdot \mathbf{p}|^2/\nu^2}{\sqrt{1 - p^2/\nu^2}} \sum_f \left| \langle f | \sum_q e_q h_{p-q} |i \rangle \right|^2 \delta(\omega_i - \omega_f - \nu).$$

As the initial state, we consider the Chevy ansatz, described in Section 8.3,
with momentum $Q$ and energy $E_{\text{pol}}(Q)$:

$$|i\rangle = \left( \alpha Q^x_{Q} + \sum_{|q|<k_F, |k|>k_F} \beta_{Q,k} q^x_{Q+q-k} e_{k} e_{q} \right)|FS\rangle. \quad \text{(F.9)}$$

The simplest accessible final state is an empty Fermi sea, which gives rise to the first contribution to the decay rate,

$$\Gamma_1(\nu) = \frac{\mu^2 \nu}{\varepsilon_0} |\alpha| q^2 |\varphi_Q(r = 0)|^2 \frac{1 - |\hat{\mu} \cdot Q|^2/\nu^2}{\sqrt{1 - |Q|^2/\nu^2}} \Theta(\nu - |Q|) \delta(E_{\text{pol}}(Q) - \nu), \quad \text{(F.10)}$$

where $\varphi_Q(r = 0) = \sum_q \varphi_Q(q)$ is the exciton wavefunction at vanishing separation between the electron and the hole. The dependence on the Fermi energy is implicit. This decay rate is nonzero only if the polaron is inside the light cone, $|Q| < \nu$. It is therefore only relevant for states close to zero momentum but not the roton minimum. The expression further allows us to obtain the decay rate $\Gamma_0$ of an exciton at zero momentum and zero Fermi energy by setting $Q = 0$ and $\alpha_Q = 1$ and integrating over $\nu$. Hence,

$$\Gamma_0 = \frac{\mu^2 \nu}{\varepsilon_0} |\varphi_0(r = 0)|^2. \quad \text{(F.11)}$$

Next, we consider final states in which an electron-hole pair is left behind in the $K$ valley but no in the $K'$ valley. This corresponds to the physical
process denoted by \( \Gamma_3 \) in Section 8.4. It is straightforward to show that

\[
\Gamma_3(\nu) = \frac{\mu^2 \nu}{\varepsilon_0} |\alpha Q|^2 \sum_{|p|<\nu} \frac{1 - |\hat{\mu} \cdot p|^2/\nu^2}{\sqrt{1 - p^2/\nu^2}} \\
\times \sum_{|q|<k_F} |\varphi_Q(Q + q - p)|^2 \delta(\Omega_Q - \varepsilon_{Q+q-p} + \varepsilon_q - \nu).
\]  

(F.12)

The above expression can be simplified by noting that the in-plane photon momentum \( p \) is bounded by \( \nu \), which is small compared to the relevant momentum scales of the TMD such as the Fermi momentum and the inverse Bohr radius. This allows us to set \( p = 0 \) in the second sum such that the first sum can be evaluated directly,

\[
\frac{1}{A} \sum_{|p|<\nu} \frac{1 - |\hat{\mu} \cdot p|^2/\nu^2}{\sqrt{1 - p^2/\nu^2}} = \frac{\nu^2}{3\pi}.
\]  

(F.13)

yielding

\[
\Gamma_3(\nu) \approx \frac{\mu^2 \nu^3}{3\pi \varepsilon_0} |\alpha Q|^2 \sum_{|q|<k_F} |\varphi_Q(Q + q)|^2 \delta(\Omega_Q - \varepsilon_{Q+q} + \varepsilon_q - \nu).
\]  

(F.14)

A similar procedure can be applied to remaining two decay rates. For the process \( \Gamma_2 \), where an electron-hole pair is left behind in \( K' \) but not in \( K \), we obtain

\[
\Gamma_2(\nu) \approx \frac{\mu^2 \nu^3}{3\pi \varepsilon_0} |\varphi_0(\nu = 0)|^2 \sum_{|q|<k_F} |\beta_{Q,q,Q+q}|^2 \delta(\Omega_Q - \varepsilon_{Q+q} + \varepsilon_q - \nu),
\]  

(F.15)

while for the process that leaves behind an excitation in each Fermi sea, the
corresponding spectral decay rate is given by

$$\Gamma_4(\nu) \approx \frac{\mu^2 \nu^3}{3\pi \varepsilon_0} \sum_{|q|<k_F \atop |k|,|k'|>k_F} |\beta_{Q,q,k}|^2 |\varphi_{Q-k+q}(k')|^2 \Theta(k_F - |Q - k - k' + q|)$$

$$\times \delta(\Omega_Q - \varepsilon_k - \varepsilon_{k'} + \varepsilon_q + \varepsilon_{k+k'-q} - \nu). \quad (F.16)$$
Bibliography


M. Sidler, P. Back, O. Cotlet, A. Srivastava, T. Fink, M. Kroner, E. Demler, and A. İmamoğlu, “Fermi polaron-polaritons in charge-tunable...


