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Dynamics of Magnetic Molecules under Electrical Control

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Abstract

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This thesis theoretically studies the dynamics of molecular magnets under electrical control. Molecular magnets are nanoscale magnets that can, e.g., consist of single-molecules or single-atoms. In these magnets, the electronically mediated exchange and transport can be controlled by external fields. In this thesis, we study the effect of electrical control and voltage pulses on the transport properties, spin dynamics and the exchange of the molecular magnets.

Nonequilibrium Green's functions is the method used to describe the underlying electronic structure of the magnetic molecule. The studied systems consists of single-molecule magnets in a tunnel junction between metallic leads. Here, the transport characteristics are derived for charge, spin and heat currents in the system for time-dependent voltage pulses. Furthermore, a generalized spin equation of motion is derived for the molecular spin moment, using nonequilibrium field theory. The equation of motion incorporates nonequilibrium conditions and is of nonadiabatic character. The effective model for the spin moment can be decomposed into effective magnetic field, isotropic Heisenberg interaction, and anisotropic Ising and Dzyaloshinskii-Moriya interactions. These effective fields depends on the electronic structure of the molecule and can be controlled by, e.g., gate and bias voltages.

The thesis encompasses studies on the effect of a sudden on-set of a voltage pulse for a single-molecule magnet and its effect on the spin dynamics and transport properties of the molecule. Different approximations schemes for the spin equation of motion and their regimes of validity are investigated. Moreover, spin-dependent signatures in the heat transport characteristics of the single-molecule magnet are connected to the dynamics of the molecular spin moment. A phase induced switching mechanism of the molecular moment is shown for voltage pulses of varying temporal length. In the stationary limit, it is shown that one can electrically control the interaction and transport of two molecular magnets in a series. Furthermore, investigations on the electrictronically mediated anisotropy in a vibrating single-molecule magnet show that the anisotropy can be tuned by a temperature difference or a voltage bias.

Keywords: Molecular magnets, Spin dynamics, Non-adiabatic effects, Exchange interaction, Thermoelectricity

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List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I **Time-dependent spin and transport properties of a single-molecule magnet in a tunnel junction**
H. Hammar and J. Fransson
Phys. Rev. B **94** *054311 (2016)*

Erratum: Time-dependent spin and transport properties of a single-molecule magnet in a tunnel junction [Phys. Rev. B 94, 054311 (2016)]
H. Hammar and J. Fransson
Accepted for publication in PRB

II **Transient spin dynamics in a single-molecule magnet**
H. Hammar and J. Fransson
Phys. Rev. B **96** *214401 (2017)*

III **Dynamical exchange and phase induced switching of localized molecular spin**
H. Hammar and J. Fransson
Phys. Rev. B **98** *174438 (2018)*

IV **Spin-dependent heat signatures of single-molecule spin dynamics**
H. Hammar, J. D. Vasquez Jaramillo, and J. Fransson
Submitted to PRB

V **Voltage-Induced Switching Dynamics of a Coupled Spin Pair in a Molecular Junction**
T. Saygun, J. Bylin, H. Hammar, and J. Fransson
Nano Lett. **16**, *2824-2829 (2016)*

VI **Electronically Mediated Magnetic Anisotropy in Vibrating Magnetic Molecules**
J. D. Vasquez Jaramillo, H. Hammar, and J. Fransson
ACS Omega **3**, *6546-6553 (2018)*

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My contributions

In paper I-IV, where I am the first author, I had main responsibility for the work, performed the analysis, discussed the results with the co-authors, did the numerical calculations, and wrote the manuscripts. In paper V-VI, I was involved in the theoretical discussion, helped with the numerical implementation, and the analysis of the systems.

Contents

Part I:
Introduction

The first part of this thesis will give an overall introduction and background to put the thesis into context. The focus is to describe the topics of interest and to give a brief overview of the different fields which the thesis touch upon.

1. Introduction

Due to the experimental progress in the past decades, it is now possible to study a vast range of phenomena in the atomic regime. This has led to intriguing possibilities of understanding quantum mechanics on the scale of single atoms and molecules, providing further insights into the physics of nanoscale systems. Experimental techniques enables for control and read-out on the nanoscale, opening up for realizing new types of technologies for future applications, and to the attosecond time-scale, enabling for real-time observation and time-domain control of atomic-scale electron dynamics [1, 2]. Furthermore, techniques for probing ultrafast spin dynamics have been developed [3], facilitating advancement in the study of ultrafast quantum dynamics of small systems. Together with a better understanding of molecules and their magnetization [4], it now provides access to study single-molecule magnets in the fast regime.

The realization of single-molecule magnets and simple quantum systems on the nanoscale have also led to break-throughs on the theoretical side. Due to the simplicity of such systems, the systems degrees of freedom decrease, allowing us to study single phenomena in more detail. Studying these systems far from equilibrium both questions our understanding of thermodynamics and provides new insights into nonequilibrium phenomena [5, 6]. It also interconnects with the active field of forming a field-theoretical description of spin systems and systems out-of-equilibrium [7, 8].

This thesis aims to theoretically investigate molecular magnets in an out-of-equilibrium environment using field theoretical methods. Here, we describe the molecular magnets as a set of distinct energy levels, represented by quantum dots, connected to two large electronic reservoirs through tunneling coupling and to single-spin moments via exchange interaction. The single-spin moment could be an effective spin of a magnetic molecule, while the quantum dot represents the electronic levels of the molecule. Investigations are then done on the electronically mediated exchange with the localized spin moment, the spin dynamics of the localized moment and the transport properties of the molecule.

The studies and accompanying papers in this thesis can be divided into two categories. The first category considers the dynamics of a single-molecule magnet. It treats the transient effects of sudden pulses, non-adiabatic properties of the spin dynamics and the transport properties of the molecule. Control of switching, charge, spin and heat currents using pulses are examined and connected with the dynamics of the exchange interaction in the molecule. The

second category treats the static limit of molecular magnets. Here, studies include control of the exchange interaction in multi-spin systems and the effect of vibrations on the electronically mediated anisotropy of a single-molecular magnet.

The thesis is organized as follows. First, in Chapter 2, the background of the study is introduced, both regarding theory as well as experimental research. In the later chapters, the theoretical part of the study is derived and described. It starts with a short introduction to nonequilibrium Green's functions in Chapter 3. In Chapter 4, the system of focus in this thesis, a single-spin moment connected to the quantum dot, is introduced and the Green's function derived. Thermoelectricity for single-molecule magnets are then described in Chapter 5. In Chapter 6, the theory for the dynamics of the single-spin moment is derived. In Chapter 7 and 8, the results in the papers are briefly presented for the first and second category described above, respectively. Then, in Chapter 9, the thesis is summarized and future prospects are described.

2. Background

This chapter serves as a brief review of the relevant topics related to molecular magnets and to put the thesis into context. Modern research is performed in a vibrant community. Therefore it is highly relevant to go through and understand what has been done in the field before laying out the theory and results. The chapter starts with a short review of nonequilibrium physics, then we go through molecular magnets and spin dynamics. After that the topics of quantum dynamics, thermoelectricity of molecular systems and quantum thermodynamics are addressed.

2.1 Nonequilibrium physics

The field of nonequilibrium physics is about studying systems that are driven out of their relaxed equilibrium state by some external disturbance. It is highly relevant in small quantum systems, such as quantum dots and single molecules, as they can be strongly coupled to the environment and easily disturbed. Nonequilibrium properties are both of interest when probing currents through the system, but also in order to study various thermodynamic properties [9]. The realization of cold atoms in optical cavities, driven by an external field, has also pushed for an deepened exploration of the theory behind driven quantum systems [10–13].

Several theoretical methods to describe nonequilibrium phenomena have been developed. These range from stationary to time-dependent approaches [14], and include, among others, master equations [15], generalized Langevin equations [16], and Keldysh Green's functions techniques [17–19]. Here, topics of interest can be, e.g., vibrating molecules in junctions [20, 21].

In order to deal with the extra complexity provided by treating a system out-of-equilbrium, different numerical techniques have been established. One example of these techniques is the wave function method [22, 23], where one uses a source-sink Schrödinger equation, providing convenient problem in order to simulate time-resolved electron dynamics in multi-terminal devices. Other numerical approaches incorporate nonequilibrium Green's functions within the framework of time-dependent density functional theory [24–26], where one extends the theory to perform ab-initio calculations for different materials out-of-equilibrium.

In this thesis we focus on nonequilibrium Green's functions defined on the Keldysh contour [17–19, 27, 28], since it provides a good analytical tool for

describing nonequilibrium and time-dependent phenomena. Our aim is to go beyond the equilibrium and stationary regime and to achieve an appropriate description of the effects of electrical and time-dependent drive of molecular magnets.

2.2 Molecular magnets

Molecular magnets and molecular spintronics provides interesting prospects for technical applications [29, 30]. These types of devices use the intrinsic spin moment of magnetic molecules for logical operations, and serve as model systems to study various physical phenomena. Within the field of molecular spintronics, much interest have circulated around single-molecule magnets [4], where one make use of a large effective single-spin moment of a molecule or atom.

Experimentally it has been shown that one can control and detect the magnetization of molecules by electrical current [31–38]. This, and other new methods for probing single-molecule spin states [39–41], enable both control and read-out of single molecules. Experiments on magnetic atoms and molecules show interesting effects in their exchange [42–45], large anisotropy of individual molecules [46–49], as well as collective spin excitations and Kondo effect [50–53], thus revealing new kinds of interesting physics on the nanoscale.

When it comes to creating molecular devices, experiments have looked into the possibility of creating quantum mechanical logical gates [54, 55], and to use molecular spintronics for quantum computation [56, 57]. Other interesting developments is that one can engineer and control the magnetic anisotropy of molecular magnets [58, 59] and stabilize the effective spin moment of single atoms for longer times [60]. This, together with other works [61–64], show the way towards realization of single-atom and single-spin memory devices.

On the theoretical side we have witnessed great progress over the course of the past decades. Studies have been performed on the possibilities for electrical control of, e.g., the exchange interaction [65], magnetic anisotropy induced by ferromagnetic leads [66], and electron paramagnetic resonance of single-molecule magnets [67]. Effects of a localized spin and its anisotropy has also been investigated in the terms of the Kondo effect [68–73] and the Pauli spin blockade in molecular dimers [74]. Superconducting spintronics is, moreover, a fertile ground for further research [75–79], enhancing the central effects of spintronics devices. Furthermore, several works have been done within the field of switching dynamics of molecular magnets which we will discuss in Section 2.3.3.

In this thesis, we are primarily interested in molecules consisting of a local spin moment separated from the electronic current mediated by the molecule. As the molecule usually comprises a set of atoms, which gives rise to a

description in terms of molecular orbitals, one talks about the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). This would be in contrast to the valence and conduction band for a crystal structure. A separation between the HOMO and LUMO levels and the local spin moment can be done in, e.g., molecular structures containing transition metal atoms. In these compounds the d-levels of the transition metal, which are deeply localized, constitute the localized magnetic moment. Molecules that show these kinds of properties are, among others, molecular complexes [80–87]. Using this picture, we also neglect the local Coulomb interaction in the molecule. We note that this is a severe simplification, but it is justified since the Coulomb interaction is typically negligible in the sp-orbitals that constitute the conducting levels in the molecular ligand structure.

2.3 Spin dynamics

Spin dynamics is the field of describing the magnetization dynamics of materials. It was first established to describe large scale materials. Then there has been a push towards atomistic systems and to describe fast phenomena in materials. Here we go through the developments in atomistic spin dynamics, ultra-fast spin dynamics and the dynamics of single-molecule magnets.

2.3.1 Atomistic spin dynamics

The usual way of describing the dynamics of the magnetization of materials is to employ the Landau-Lifshitz-Gilbert (LLG) equation of motion [88]. Here, one describes the magnetic moment as a classical spin. This has successfully been applied to describe the magnetization dynamics of different materials. It is also the commonly used approach when calculating properties and dynamics of interesting systems and phenomena, such as skyrmions [89] and magnons [90]. In-depth studies have been performed on the Gilbert damping [91–93], which play an important role in the LLG equation. The model has been extended to take into account other effects, such as temperature, moment of inertia and stochastic forces, by adding extra terms into the equation of motion. For example, by adding a Langevin term to the equation, one can induce, e.g., noise and temperature effects. In order to make use of the LLG equation, one of the assumptions is usually that the material is in quasi-equilibrium and sometimes with a thermal gradient. There are several works that has investigated thermal effects on the spin dynamics using the LLG equation, e.g., [94–98].

2.3.2 Ultra-fast demagnetization

Ultrafast demagnetization was found by experimentalist in the late 1990s [99–101] and has since then gotten a lot of attention, since people are not convinced

of the theoretical picture. The area spans over several fields, including ab-initio methods, such as time-dependent density functional theory, and atomistic spin dynamics [102]. This has led to further investigation of the LLG equation itself in the ultra-fast regime [103, 104], and magnetic interactions in strongly correlated systems [105]. Several proposals have been made for the describing the ultra-fast demagnetization [102, 106, 107], and pushed for further understanding of ultra-fast effects in the spin dynamics. Furthermore, for a more detailed description of ultrafast spin dynamics, several works have been performed in order to calculate dynamical exchange interactions. Extensions have been made to include nonequilibrium and time-dependent interactions when calculating the exchange in materials [105]. The formalism was later extended to study dynamical magnetic susceptibility and exchange parameters [108]. Other studies on dynamical exchange parameters have shown the importance of dynamical exchanges in their calculations [109] and that the exchange interactions quench for ultrafast laser pulses [110]. Also, ab-initio studies using time-dependent density functional theory have been performed on dynamical exchange interactions, where consequences on ultrafast spin dynamics were studied [111]. Experimental techniques have pushed towards probing of ultrafast exchange interactions [112, 113].

2.3.3 Spin dynamics of molecular magnets

In order to describe the spin dynamics of single molecules, it is important to consider nonequilibrium effects since they easily can be disturbed by external forces. Methods using quantum master equations [15, 114–117] and stochastic LLG equation [118, 119] have been thoroughly investigated. Another technique, which will be used in this thesis, is to derive a spin equation of motion from the spin action defined on the Keldysh contour, considering the full nonequilibrium properties of the effective spin moment [91, 120–123]. This provides a general description of the spin dynamics, and one also allows for other types of exchange interactions appearing in the nonequilibrium regime [65, 124–133]. Field-theoretical methods have also shown interesting properties in single-spin systems, such as geometric phases and chaotic behaviors [134, 135]. Magnetic tunnel junctions are of related interest where studies have been performed on systems having noncollinear leads [136, 137] and on the spin-switching by spin-torque [138–140]. So far most approaches do not consider nonadiabatic effects, which are important in molecular magnets as the small system opens up for back-action. In this thesis we try to include nonadiabatic effects and extend the formalism to the time-dependent regime, thus giving time and history dependent parameters in the spin equation of motion, see Chapter 6.

2.4 Quantum dynamics of open systems

Dynamics of open systems is an active area of research [11, 141] where nonequilibrium open systems, such as nanojunctions, quantum dots, and single molecules, have been studied extensively, both experimentally and theoretically. Studies include electron dynamics [142, 143], vibrating quantum dots [144], pulse-enhanced thermoelectric efficiency [145, 146], time-dependent driving of a molecular junction [147], and optoelectronics and spectroscopy [148, 149]. Due to size confinement, the systems exhibit intrinsic out-of-equilibrium properties which can be controlled by pulses and external forces. Hence, such set-ups are well suited for studying non-adiabatic quantum dynamics. This has lead to extensive works of using field theoretical models for driven open quantum systems [12]. Recent theoretical predictions have also suggested that periodical out-of-equilibrium driving can induce temporal phases of matter [150], which subsequently have been experimentally corroborated [151, 152]. Specially interesting in these systems are the possibility of probing non-Markovian effects, i.e., effects dependent on changes in the past, appearing due to their quantum nature. This has several implications and is of interest because of non-locality. The workhorse of the field is the quantum master equation, and work has been done to extend it with nonequilibrium Green's functions [14], which is the language used in this thesis.

2.5 Thermoelectricity of molecular systems

Thermoelectricity in nanosystems, such as single-molecules and nanojunctions, have been under investigation during recent years [153]. Here the focus has been on figuring out the relationships between the heat and electrical currents in these systems and to improve thermoelectric efficiencies. Furthermore, the relation between heat and spin currents has been studied in several different molecular systems and quantum dots [154–161]. It has been shown that strongly correlated phenomena and interference could have interesting effects on the thermoelectric properties [162–167]. Other studies involve the effect of time-dependent control on the energy and heat transfer of molecular systems [145, 146, 168–171] to, e.g., improve the thermoelectric efficiency or design thermal machines.

The discoveries of spin Seebeck and spin Peltier effects have also led to increase the interest in spin-dependent thermoelectric effects [98, 172–175]. It includes investigations of spin-dependent Seebeck and Peltier effects where the heat current is coupled to the spin-dependent electron channels in the material. In the context of molecular magnets, local anisotropies have been suggested to have an effect on the spin-dependent thermoelectric transport properties [157, 158, 176]. Experiments of molecular magnets show thermodynamic signatures of the change of spin configurations in the magnet [177]. Moreover, experimental progress in nanoscale systems has pushed towards the realizations

of devices where one can observe heat using nanothermometry [9, 178, 179]. This, together with the detection of ultrafast spin dynamics with nanoscale resolution [3], opens up the possibility to probe and study the relation between heat and spin dynamics on the nanoscale.

2.6 Quantum thermodynamics

Quantum thermodynamics treats the thermodynamics of microscopic systems, such as single molecules, where quantum effects play a crucial role. The topic has been under recent investigation, since finding viable definitions of quantum thermodynamics for strongly coupled systems is an open problem [180, 181]. Proposals have been done to extend the models to include system-bath coupling and time-dependent drives [182–184], creating an extra component in the heat current named the energy reactance [182]. It does, though, not fully comply with the laws of thermodynamics in all set-ups [185], and there have been further suggestions to improve the description [186, 187]. Using new definitions for quantum thermodynamics in terms of nonequilibrium Green's functions has also been investigated [180]. We will not treat the full quantum thermodynamics of molecular magnets in this thesis, however, the progress in the field is important for further investigations.

Part II:
Theory

In this part of the thesis we go through and develop the theory that is used to describe the transport properties and spin dynamics of a molecular magnet. In Chapter 3 we introduce some basic concepts and nonequilibrium Green's functions which is central for calculating the properties of the molecular magnet. In Chapter 4 we derive the Green's function for a molecular magnet with a single spin and in Chapter 5 we study the thermoelectric properties of such a system. In Chapter 6 we look at the spin dynamics of a molecular magnet and derive a generalized spin equation of motion which we relate to the Landau-Lifshitz-Gilbert equation.

3. Nonequilibrium Green's function

In this chapter we introduce some basic concepts in order to derive properties of the molecular magnet in the following chapter. We use the language of nonequilibrium Green's functions and describe the physics in a second quantized form, i.e., in the language of many-particle states. Note that this overview is meant to be brief in order to introduce the concepts used in the thesis. For more information regarding Green's functions and their properties see, e.g., Ref. [17, 27, 28, 188].

3.1 Commutation and anti-commutation relations

Different quantum mechanical particles follow different statistics. There are mainly two classes, fermions and bosons. Other types of particles also exist, but are not considered in this thesis. Typical examples of fermions are, e.g., electrons, while typical bosonic particles are, e.g., phonons and photons.

3.1.1 Bosons

In second quantized form we can define a bosonic creation $b^\dagger$ and annihilation b operator. This operators will create (annihilate) a bosonic particle acting on a Fock state that counts the number of particles occupying each state. In a bosonic system, the amount of particles occupying each state is not restricted. Therefore, they have the following commutation relations

$$[b_\alpha^\dagger, b_\beta^\dagger] = [b_\alpha, b_\beta] = 0, \tag{3.1}$$
$$[b_\alpha, b_\beta^\dagger] = \delta_{\alpha\beta}.$$

3.1.2 Fermions

Fermions follow the Pauli exclusion principle. Thus, they can't occupy the same state. If we define the fermionic creation $c^\dagger$ and annihilation c operator this will give us the anti-commutation relations

$$\{c_\alpha^\dagger, c_\beta^\dagger\} = \{c_\alpha, c_\beta\} = 0, \tag{3.2}$$
$$\{c_\alpha, c_\beta^\dagger\} = \delta_{\alpha\beta}.$$

3.1.3 Commutators and anti-commutators

In order to evaluate the statistics imposed by the bosonic and fermionic particles, it is useful to rewrite commutators including several operators. Expanding [A, BC] gives

$$
\begin{aligned}
[A, BC] &= ABC - BCA \\
&= ABC + BAC - BAC + BCA \\
&= \{A, B\}C - B\{A, C\}.
\end{aligned}
\tag{3.3}
$$

Similarly

$$
[AB, C] = A\{B, C\} - \{A, C\}B.
\tag{3.4}
$$

Using the same procedure, the expression [AB, CD] can be expressed as follows

$$
\begin{aligned}
[AB, DC] &= [AB, C]D + C[AB, D] \\
&= (A\{B, C\} - \{A, C\}B)D + C(A\{B, D\} - \{A, D\}B).
\end{aligned}
\tag{3.5}
$$

3.2 Heisenberg equation of motion

It is helpful to define the Heisenberg equation of motion in order to derive the Green's functions for the molecular magnet. The Heisenberg picture defines the operators, e.g., the creation and annihilation operators, to be time-dependent acting on stationary state vectors. It is in contrast with the Schrödinger picture, where the operators are stationary and the state vectors are time-dependent, or the interaction picture, where both the operators and state vectors are time-dependent. In the Heisenberg picture, the evolution of a time-dependent operator $A(t)$ is described by the Heisenberg equation of motion

$$
\frac{dA(t)}{dt} = i[\mathcal{H}, A(t)],
\tag{3.6}
$$

where $\mathcal{H}$ the Hamiltonian and we set $\hbar = 1$.

3.3 Green's function

Propagation between two times, t and t', for the time-dependent creation (annihilation) operators $c(t)(c^\dagger(t'))$ can be calculated through the time-ordered Green's function defined as

$$
\begin{aligned}
G(t, t') &= -i \left\langle \mathrm{T}\, c(t)c^\dagger(t') \right\rangle \\
&= -i\theta(t - t') \left\langle c(t)c^\dagger(t') \right\rangle + i\theta(t' - t) \left\langle c^\dagger(t')c(t) \right\rangle,
\end{aligned}
\tag{3.7}
$$

where T denotes the time-ordering operator. The Green's function provides the correlation of the field operators between time t and t'. The spatial Green's function is defined analogously. The Green's function could be understood as the overlap between the fields at time t and t' and is a convenient tool since it can be used to derive the properties and observables of the system of interest.

It is helpful to define the greater and lesser Green's function

$$G^>(t, t') = -i \left\langle c(t) c^\dagger(t') \right\rangle,$$
$$G^<(t, t') = i \left\langle c^\dagger(t') c(t) \right\rangle, \tag{3.8}$$

representing the backwards and forwards propagation, respectively, such that $G(t, t') = \theta(t - t') G^>(t, t') + \theta(t' - t) G^<(t, t')$. In turn we can define the advanced and retarded Green's function as

$$\begin{aligned} G^a &= i\theta(t' - t) \left\langle \left\{ c(t), c^\dagger(t') \right\} \right\rangle \\ &= \theta(t' - t) \left[G^<(t, t') - G^>(t, t') \right], \end{aligned} \tag{3.9}$$

and

$$\begin{aligned} G^r &= -i\theta(t - t') \left\langle \left\{ c(t), c^\dagger(t') \right\} \right\rangle \\ &= \theta(t - t') \left[G^>(t, t') - G^<(t, t') \right]. \end{aligned} \tag{3.10}$$

3.4 Equation of motion for the Green's function

Taking the time-derivative with respect to t of the Green's function in Eq. (3.7) gives the equation of motion for the Green's function

$$\partial_t G(t, t') = -i \left\langle \left\{ c(t), c^\dagger(t') \right\} \right\rangle - \left\langle \mathrm{T}[c(t), \mathcal{H}] c^\dagger(t') \right\rangle. \tag{3.11}$$

When taking the derivative, we used the fact that $\partial_t \theta(t - t') = \delta(t - t')$ and the Heisenberg equation of motion, $i\partial_t c(t) = [c(t), \mathcal{H}]$.

3.5 Green's function in nonequilibrium

For a system in nonequilibrium, the Green's function is extended on a contour in the complex plane. We perform this extension since we cannot be sure that the system is the same at minus and plus infinity, and since we want to end up with a system being the same at the end-points when defining the Green's function. Thus, we define the contour ordered Green's function

$$G(t, t') = (-i) \left\langle \mathrm{T}_c \, c(t) c^\dagger(t') \right\rangle, \tag{3.12}$$

23

C_1

$-\infty$ $+\infty$

C_2
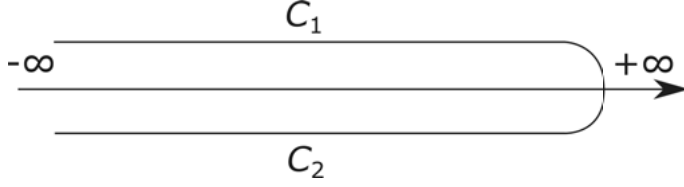
Figure 3.1. The Keldysh contour.

where T_c orders the operators $c(t)$ $(c^\dagger(t'))$ on the Keldysh contour, see Fig. 3.1. We can also define the greater and lesser Green's function depending on the time-ordering as

$$G^> = -i\left\langle c(t)c^\dagger(t')\right\rangle \qquad\qquad t > t' \in C,$$
$$G^< = i\left\langle c^\dagger(t')c(t)\right\rangle \qquad\qquad t < t' \in C. \qquad (3.13)$$

3.6 Analytical continuation

For a Green's function, defined on the Keldysh contour, it is convenient to make use of analytical continuation when it constitutes two Green's functions. Our equation of interest is

$$A(t,t') = \oint_C d\tau\, B(t,\tau)C(\tau,t'). \qquad (3.14)$$

By deforming the contour, see Fig. 3.2, we can rewrite it as

$$A^<(t,t') = \oint_{C_1} d\tau\, B(t,\tau)C^<(\tau,t') + \oint_{C_2} d\tau\, B^<(t,\tau)C(\tau,t'). \qquad (3.15)$$

Due to the deformation, the integration variable τ, is always strictly smaller than t', and we could therefore write $C^<(\tau,t')$ in the first term. Expanding the first term on the real axis, we rewrite it as

$$\oint_{C_1} d\tau\, B(t,\tau)C^<(\tau,t') = \int_{-\infty}^t d\tau\, B^>(t,\tau)C^<(\tau,t') + \int_t^{-\infty} d\tau\, B^<(t,\tau)C^<(\tau,t')$$
$$= \int_{-\infty}^\infty d\tau\, B^r(t,\tau)C^<(\tau,t'), \qquad (3.16)$$

where we have used the connection between the lesser/greater Green's function and the retarded Green's function in Eq. 3.10. Doing the same for the second term, the expression becomes

$$A^<(t,t') = \int d\tau\, \left[B^r(t,\ \tau\ )C^<(\tau,t') + B^<(t,\ \tau\ )C^a(\tau,t')\right]. \qquad (3.17)$$

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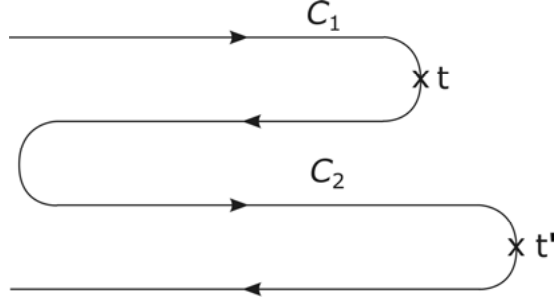
Figure 3.2. The deformed Keldysh contour used in analytical continuation.

Using the same method for the greater Green's function we find similar result, with the difference that one exchanges the lesser functions to greater functions.

For the retarded and advanced Green's function we can use the same tricks that we used for the lesser/greater Green's function, as they are connected through Eq. 3.9-3.10. The retarded component becomes

$$
\begin{aligned}
A^r(t,t') =&\, \theta(t-t')\left[A^>(t,t') - A^<(t,t')\right]\\
=&\, \theta(t-t')\int d\tau\left[B^r(C^> - C^<) - (B^> - B^<)C^a\right]\\
=&\, \theta(t-t')\left[\int_{-\infty}^{t} d\tau (B^> - B^<)(C^> - C^<)\right.\\
&\, \left.+\int_{-\infty}^{t'} d\tau (B^> - B^<)(C^> - C^<)\right]\\
=&\, \int d\tau B^r(t,\tau)C^r(\tau,t').
\end{aligned}
\tag{3.18}
$$

In the case of $A = \oint_C d\tau BCD$ the rules translates as

$$
\begin{aligned}
A^<(t,t') &= \int\int d\tau d\tau'\left[A^r B^r C^< + A^r B^< C^a + A^< B^a C^a\right],\\
A^r(t,t') &= \int\int d\tau d\tau' A^r B^r C^r.
\end{aligned}
\tag{3.19}
$$

3.7 Dyson and Keldysh equation

The Dyson equation is defined as

$$
G(t,t') = G_0(t,t') + \int\int d\tau d\tau' G_0(t,\tau)\Sigma(\tau,\tau')G(\tau',t'),
\tag{3.20}
$$

where $\Sigma(\tau, \tau')$ is the self-energy functional. Using analytical continuation we can define the Keldysh equation by expanding the Dyson equation for the lesser Green's function

$$
\begin{aligned}
G^< &= G_0^< + G_0^r \Sigma^r G^< + G_0^r \Sigma^< G^a + G_0^< \Sigma^a G^a \\
&= (1 + G_0^r \Sigma^r) G_0^< (1 + \Sigma^a G^a) + (G_0^< + G_0^r G_0^<) \Sigma^< G^a + G_0^r \Sigma^r G_0^r \Sigma^r G^<,
\end{aligned}
\tag{3.21}
$$

where we dropped the indication of time-dependence for clarity. We see that by iterating the procedure to infinite order, we get

$$
G^< = (1 + G^r \Sigma^r) G_0^< (1 + \Sigma^a G^a) + G^r \Sigma^< G^a.
\tag{3.22}
$$

3.8 Electron gas

To exemplify the framework with a simple example we choose the free electron gas [27] for which the Hamiltonian is $\mathcal{H} = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} c_{\mathbf{k}}^\dagger c_{\mathbf{k}}$. The Heisenberg equation of motion then becomes

$$
\begin{aligned}
i \frac{dc_{\mathbf{k}}}{dt} &= [c_{\mathbf{k}}, \mathcal{H}] = [c_{\mathbf{k}}, \sum_{\mathbf{k}'} \varepsilon_{\mathbf{k}'} c_{\mathbf{k}'}^\dagger c_{\mathbf{k}'}] \\
&= \sum_{\mathbf{k}'} \varepsilon_{\mathbf{k}'} \left(\{c_{\mathbf{k}}, c_{\mathbf{k}'}^\dagger\} c_{\mathbf{k}'} - c_{\mathbf{k}'}^\dagger \{c_{\mathbf{k}}, c_{\mathbf{k}}\} \right) \\
&= \sum_{\mathbf{k}'} \varepsilon_{\mathbf{k}'} \delta_{k,k'} c_{\mathbf{k}'} = \varepsilon_{\mathbf{k}} c_{\mathbf{k}}.
\end{aligned}
\tag{3.23}
$$

Inserting it into the equation of motion for the Green's function gives

$$
\begin{aligned}
\partial_t G(t, t') &= -i\delta(t - t') \left\langle \{c_{\mathbf{k}}(t), c_{\mathbf{k}}^\dagger(t')\} \right\rangle - \left\langle \mathrm{T}[c_{\mathbf{k}}(t), \mathcal{H}] c_{\mathbf{k}}^\dagger(t') \right\rangle \\
&= -i\delta(t - t') - \varepsilon_{\mathbf{k}} \left\langle \mathrm{T}\, c_{\mathbf{k}}(t) c_{\mathbf{k}}^\dagger(t') \right\rangle.
\end{aligned}
\tag{3.24}
$$

Multiplying with i and identifying $G(t, t') = -i \left\langle \mathrm{T}\, c_{\mathbf{k}}(t) c_{\mathbf{k}}^\dagger(t') \right\rangle$, the whole expression can be rewritten as

$$
(i\partial_t - \varepsilon_{\mathbf{k}}) G(t, t') = \delta(t - t').
\tag{3.25}
$$

For a free electron gas, the time-independent expectation value of the electron operators are $\left\langle c_{\mathbf{k}}^\dagger c_{\mathbf{k}} \right\rangle = f(\varepsilon_{\mathbf{k}})$ and $\left\langle c_{\mathbf{k}} c_{\mathbf{k}}^\dagger \right\rangle = f(-\varepsilon_{\mathbf{k}})$, where $f(\varepsilon_{\mathbf{k}}) = 1/(e^{\varepsilon_{\mathbf{k}} \beta} + 1)$ is the Fermi function and $f(-\varepsilon_{\mathbf{k}}) = 1 - f(\varepsilon_{\mathbf{k}})$. Integrating the Heisenberg equation for constant energy $\varepsilon_{\mathbf{k}}$, one gets $c_{\mathbf{k}}(t) = e^{-i\varepsilon_{\mathbf{k}} t} c_{\mathbf{k}}(0)$. Using these results, we get $\left\langle c_{\mathbf{k}}^\dagger(t') c_{\mathbf{k}}(t) \right\rangle = f(\varepsilon_{\mathbf{k}}) e^{-i\varepsilon_{\mathbf{k}}(t - t')}$ and $\left\langle c_{\mathbf{k}}(t) c_{\mathbf{k}}^\dagger(t') \right\rangle =$

$f(-\varepsilon_{\mathbf{k}})e^{-i\varepsilon_{\mathbf{k}}(t-t')}$. Thus, we can express the Green's function for the free electrons as

$$
\begin{aligned}
G(t,t') &= -i\theta(t-t')\left\langle c_{\mathbf{k}}(t)c_{\mathbf{k}}^{\dagger}(t')\right\rangle + i\theta(t'-t)\left\langle c_{\mathbf{k}}^{\dagger}(t')c_{\mathbf{k}}(t)\right\rangle \\
&= -i\left[\theta(t-t')f(\varepsilon_{\mathbf{k}}) - \theta(t'-t)f(-\varepsilon_{\mathbf{k}})\right]e^{-i\varepsilon_{\mathbf{k}}(t-t')}. \qquad (3.26)
\end{aligned}
$$

The Fourier transform of $G(t)$ is defined as $G(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t}$. As our Green's function is stationary, i.e., $G(t,t') = G(t-t')$, we can write $\tau = t - t'$ and then get the Fourier transform

$$
\begin{aligned}
G(\omega) &= -i\int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau}\left[\theta(\tau)f(\varepsilon_{\mathbf{k}}) - \theta(\tau)f(-\varepsilon_{\mathbf{k}})\right]e^{-i\varepsilon_{\mathbf{k}}(\tau)} \\
&= -i\left[\int_{0}^{\infty} d\tau\, f(\varepsilon_{\mathbf{k}})e^{i\tau(\omega-\varepsilon_{\mathbf{k}}+i\delta)} - \int_{-\infty}^{0} d\tau\, f(-\varepsilon_{\mathbf{k}})e^{i\tau(\omega-\varepsilon_{\mathbf{k}}-i\delta)}\right] \\
&= \frac{f(\varepsilon_{\mathbf{k}})}{\omega - \varepsilon_{\mathbf{k}} + i\delta} + \frac{f(-\varepsilon_{\mathbf{k}})}{\omega - \varepsilon_{\mathbf{k}} - i\delta}. \qquad (3.27)
\end{aligned}
$$

4. Green's function for a single-molecule magnet with a single spin

We now turn to treat the Green's function for a single-molecule magnet with a single-spin moment. A single-molecule magnet has many degrees of freedom and there could be several types of contributions in the Hamiltonian for the system. In this derivation we are primarily interested in the electronic and spin degrees of freedom of the molecular magnet under a time-dependent drive. We restrict the system to include leads that are metal baths of noninteracting electrons with wide-bands, a single-level quantum dot as the electronic level of the molecule and the magnetic moment of the molecule being a single-spin moment coupled via exchange interaction to the quantum dot. The physical motivation of the molecular system is given in Section 2.2 and using that motivation we do not treat the Coulomb interaction in the molecule. For a comprehensive review of transport properties in molecular junctions we refer the reader to Ref. [189].

4.1 Hamiltonian

The system studied is a single-spin moment $\mathbf{S}$ in a tunnel junction interacting with a single-level quantum dot, see Fig. 4.1. The quantum dot is coupled through tunneling coupling to metal contacts with respective chemical potential μ_χ, where $\chi = L, R$ denotes the left/right reservoir. The Hamiltonian for the system becomes

$$\mathcal{H} = \mathcal{H}_\mathrm{L} + \mathcal{H}_\mathrm{R} + \mathcal{H}_\mathrm{T} + \mathcal{H}_\mathrm{QD} + \mathcal{H}_\mathrm{S} + \mathcal{H}_\mathrm{int}. \tag{4.1}$$

We write the electron operator in the reservoirs as $c_{\mathbf{k}\sigma}$ and in the quantum dot as d_σ, where $c_{\mathbf{k}\sigma}^\dagger$ creates an electron in the reservoir with momentum $\mathbf{k}$ and spin σ, and $c_{\mathbf{k}\sigma}$ annihilates it. The same goes for the quantum dot, but as there is only one energy level it is simplified to $d_\sigma^\dagger$ and d_σ. The Hamiltonian for the reservoirs, thus, becomes

$$\mathcal{H}_\chi = \sum_{\mathbf{k}\chi\sigma} (\varepsilon_{\mathbf{k}\chi\sigma} - \mu_\chi(t)) c_{\mathbf{k}\chi\sigma}^\dagger c_{\mathbf{k}\chi\sigma}. \tag{4.2}$$

Here, $\varepsilon_{\mathbf{k}\chi\sigma}$ is the energy levels of the reservoir, $\mathbf{k}$ denotes the momentum vector and σ the spin. The chemical potential depends on a time-dependent voltage
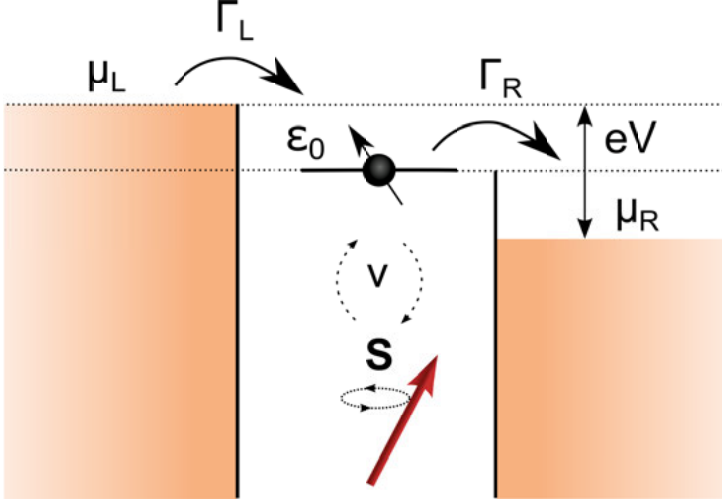
Figure 4.1. The system studied in this chapter, representing a single-molecule magnet. It consist of a single-spin moment **S** interacting with a quantum dot in a tunnel junction. The spin in the quantum dot illustrates the spin of the electrons **s** interacting with the magnetic moment.

$eV(t) = \mu_L(t) - \mu_R(t)$ across the junction. The tunneling Hamiltonian is defined as $\mathcal{H}_T = \mathcal{H}_{TL} + \mathcal{H}_{TR}$, where

$$\mathcal{H}_{T\chi} = T_\chi \sum_{\mathbf{k}\chi\sigma} c^\dagger_{\mathbf{k}\chi\sigma} d_\sigma + H.c., \tag{4.3}$$

i.e., it creates an electron in the reservoir and annihilates it in the quantum dot, and vice versa. The quantum dot has the Hamiltonian

$$\mathcal{H}_{QD} = \sum_\sigma \varepsilon_\sigma d^\dagger_\sigma d_\sigma, \tag{4.4}$$

where $\varepsilon_\sigma = \varepsilon_0 + g\mu_B B\sigma^z_{\sigma\sigma}/2$ is the energy of the electron level in the quantum dot. The second term in the energy arises from that the quantum dot is Zeeman coupled to a magnetic field, $\mathbf{B} = B\hat{\mathbf{z}}$, where g is the g-factor, and μ_B the Bohr constant. The spin system has the Hamiltonian

$$\mathcal{H}_S = -g\mu_B \mathbf{S} \cdot \mathbf{B}, \tag{4.5}$$

where **S** is the spin vector. The interactions between the spin and the quantum dot is given by

$$\mathcal{H}_{int} = -v\mathbf{s} \cdot \mathbf{S}, \tag{4.6}$$

where v is the exchange interacting strength and $\mathbf{s} = \sum_{\sigma\sigma'} d^\dagger_\sigma \boldsymbol{\sigma}_{\sigma\sigma'} d_{\sigma'}/2$ denotes the spin of the electrons in the quantum dot. We can then write the full

Hamiltonian as

$$\mathcal{H} = \sum_{\mathbf{k}\chi\sigma}(\varepsilon_{\mathbf{k}\chi\sigma} - \mu_\chi(t))c^\dagger_{\mathbf{k}\chi\sigma}c_{\mathbf{k}\chi\sigma} + \sum_{\mathbf{k}\chi\sigma}T_\chi\left(c^\dagger_{\mathbf{k}\chi\sigma}d_\sigma + H.c\right)$$

$$+ \sum_\sigma \varepsilon_\sigma d^\dagger_\sigma d_\sigma - g\mu_B \mathbf{S} \cdot \mathbf{B} - v\mathbf{s} \cdot \mathbf{S}. \tag{4.7}$$

4.2 Quantum dot Green's function

The quantum dot Green's function is defined as

$$G_{\sigma\sigma'}(t,t') = -i\left\langle \mathrm{T}\, d_\sigma(t)d^\dagger_{\sigma'}(t')\right\rangle. \tag{4.8}$$

The equation of motion is

$$\partial_t G_{\sigma\sigma'}(t,t') = -i\left\langle \{d_\sigma(t), d^\dagger_{\sigma'}(t')\}\right\rangle - \left\langle \mathrm{T}[d_\sigma(t), \mathcal{H}]d^\dagger_{\sigma'}(t')\right\rangle. \tag{4.9}$$

The anti-commutation relations for fermions give $\{d_\sigma, d^\dagger_{\sigma'}\} = \delta_{\sigma\sigma'}$ and $\{d_\sigma, d_{\sigma'}\} = \{d^\dagger_\sigma, d^\dagger_{\sigma'}\} = \{d_\sigma, c_{\mathbf{k}\chi\sigma'}\} = \{d_\sigma, c^\dagger_{\mathbf{k}\chi\sigma'}\} = 0$. Evaluating the term $[d_\sigma(t), \mathcal{H}]$ by using Eq. 3.4 gives

$$[d_\sigma, \mathcal{H}_\chi] = \sum_{\mathbf{k}\chi\sigma}(\varepsilon_{\mathbf{k}\chi\sigma'} - \mu_\chi(t))[d_\sigma, c^\dagger_{\mathbf{k}\chi\sigma'}c_{\mathbf{k}\chi\sigma'}] = 0,$$

$$[d_\sigma, \mathcal{H}_{T\chi}] = \sum_{\mathbf{k}\chi\sigma'}T_\chi[d_\sigma, c^\dagger_{\mathbf{k}\chi\sigma'}d_{\sigma'} + H.c.] = \sum_{\mathbf{k}\chi}T_\chi c_{\mathbf{k}\chi\sigma},$$

$$[d_\sigma, \mathcal{H}_{QD}] = \sum_{\sigma'}\varepsilon_{\sigma'}[d_\sigma, d^\dagger_{\sigma'}d_{\sigma'}] = \varepsilon_\sigma d_\sigma,$$

$$[d_\sigma, \mathcal{H}_S] = 0,$$

$$[d_\sigma, \mathcal{H}_{int}] = -v\sum_{ss'}[d_\sigma, d^\dagger_s \boldsymbol{\sigma}_{ss'} \cdot \mathbf{S}d_{s'}] = -v\sum_{s'}\boldsymbol{\sigma}_{\sigma s'} \cdot \mathbf{S}d_{s'}. \tag{4.10}$$

Inserting the results into the equation of motion, yields the expression

$$\partial_t G_{\sigma\sigma'}(t,t') = -i\delta_{\sigma\sigma'}\delta(t-t')$$

$$-\left\langle \mathrm{T}\left(\sum_{\mathbf{k}\chi}T_\chi c_{\mathbf{k}\chi\sigma}(t) + \varepsilon_\sigma d_\sigma(t) - v\sum_s \boldsymbol{\sigma}_{\sigma s} \cdot \mathbf{S}d_s(t)\right)d^\dagger_{\sigma'}(t')\right\rangle. \tag{4.11}$$

We can now identify the following Green's functions in the previous expression

$$G_{\mathbf{k}\chi\sigma\sigma'}(t,t') = -i\left\langle \mathrm{T}\, c_{\mathbf{k}\chi\sigma}(t)d^\dagger_{\sigma'}(t')\right\rangle, \tag{4.12}$$

$$G_{\sigma\sigma'}(t,t') = -i\left\langle \mathrm{T}\, d_\sigma(t)d^\dagger_{\sigma'}(t')\right\rangle. \tag{4.13}$$

By multiplying with i gives

$$i\partial_t G_{\sigma\sigma'}(t,t') = \delta_{\sigma\sigma'}\delta(t-t') + \sum_{\mathbf{k}\chi} T_\chi G_{\mathbf{k}\chi\sigma\sigma'}(t,t')$$
$$+ \varepsilon_\sigma G_{\sigma\sigma'}(t,t') - v\left\langle \mathbf{S}\cdot\boldsymbol{\sigma}_{\sigma\sigma'}\right\rangle G_{\sigma\sigma'}(t,t'). \qquad (4.14)$$

In the last step we did the approximation $-i\left\langle \mathrm{T}\sum_s \boldsymbol{\sigma}_{\sigma s}\cdot\mathbf{S}d_s(t)d_{\sigma'}^\dagger(t')\right\rangle \approx \left\langle \mathbf{S}\cdot\boldsymbol{\sigma}_{\sigma\sigma'}\right\rangle(-i)\left\langle \mathrm{T}\,d_\sigma(t)d_{\sigma'}^\dagger(t')\right\rangle.$

4.3 Bare Green's function

In order to solve the Eq. (4.14), we start with solving the equation

$$i\partial_t g_{\sigma\sigma'}(t,t') = \delta_{\sigma\sigma'}\delta(t-t') + \varepsilon_\sigma g_{\sigma\sigma'} + \sum_{\mathbf{k}\chi} T_\chi G_{\mathbf{k}\chi\sigma\sigma'}(t,t'). \qquad (4.15)$$

Here, we defined $g_{\sigma\sigma'}(t,t') = -i\left\langle \mathrm{T}\,d_\sigma(t)d_{\sigma'}^\dagger(t')\right\rangle$ as the bare quantum dot Green's function and as the solution to this equation. This equation represents the quantum dot with a time-dependent applied bias voltage without any interaction with the localized magnetic moment. The derivation is an extension of the time-dependent transport in a quantum dot, Ref. [19], in order to include spin degrees of freedom.

First, we compute the equation of motion for the tunneling Green's function $G_{\mathbf{k}\chi\sigma\sigma'}(t,t')$. It is

$$\partial_t G_{\mathbf{k}\chi\sigma\sigma'}(t,t') = -i\left\langle \{c_{\mathbf{k}\chi\sigma}(t), d_{\sigma'}^\dagger(t')\}\right\rangle - \left\langle \mathrm{T}[c_{\mathbf{k}\chi\sigma}(t),\mathcal{H}]d_{\sigma'}^\dagger(t')\right\rangle. \qquad (4.16)$$

Evaluating the Heisenberg equation gives $[c_{\mathbf{k}\chi\sigma}(t),\mathcal{H}] = (\varepsilon_{\mathbf{k}\chi\sigma}-\mu_\chi(t))c_{\mathbf{k}\chi\sigma} + T_\chi d_\sigma$. Inserting it into the equation of motion gives

$$i\partial_t G_{\mathbf{k}\chi\sigma\sigma'}(t,t') = (\varepsilon_{\mathbf{k}\chi\sigma}-\mu_\chi(t))G_{\mathbf{k}\chi\sigma\sigma'}(t,t') + T_\chi g_{\sigma\sigma'}(t,t'), \qquad (4.17)$$

where we multiplied with i and identified the Green's functions as above. We move the first term on the right hand side to the left hand side

$$(i\partial_t - \varepsilon_{\mathbf{k}\chi\sigma} + \mu_\chi(t))G_{\mathbf{k}\chi\sigma\sigma'}(t,t') = T_\chi g_{\sigma\sigma'}(t,t'). \qquad (4.18)$$

By introducing the Green's function for the leads, $g_{\mathbf{k}\chi\sigma}(t,t') = -i\left\langle \mathrm{T}\,c_{\mathbf{k}\chi\sigma}^\dagger(t')c_{\mathbf{k}\chi\sigma}(t)\right\rangle$, that follows $(i\partial_t - \varepsilon_{\mathbf{k}\chi\sigma} + \mu_\chi(t))g_{\mathbf{k}\chi\sigma}(t,t') = \delta(t-t')$ one can identify the term in the brackets on the left hand side as the inverse of the lead Green's function. Operating with the lead Green's function from the right gives

$$G_{\mathbf{k}\chi\sigma\sigma'}(t,t') = T_\chi \int d\tau\, g_{\sigma\sigma'}(t,\tau)g_{\mathbf{k}\chi\sigma}(\tau,t'). \qquad (4.19)$$

Inserting the expression into Eq. (4.15) gives

$$(i\partial_t - \varepsilon_\sigma)g_{\sigma\sigma'}(t,t') = \delta_{\sigma\sigma'}\delta(t-t') + \sum_{\mathbf{k}\chi} T_\chi^2 \int d\tau\, g_{\sigma\sigma'}(t,\tau)g_{\mathbf{k}\chi\sigma}(\tau,t'). \quad (4.20)$$

Making use of the Born approximation we can solve the previous equation with introducing the Green's function $g_{\sigma\sigma'}^{(0)}(t,t')$ as the solution to $(i\partial_t - \varepsilon_\sigma)g_{\sigma\sigma'}^{(0)}(t,t') = \delta(t-t')$. It gives the Dyson equation

$$g_{\sigma\sigma'}(t,t') = \delta_{\sigma\sigma'}g_{\sigma\sigma'}^{(0)}(t,t') + \iint d\tau d\tau'\, g_{\sigma\sigma'}(t,\tau)\Sigma(\tau,\tau')g_{\sigma\sigma'}^{(0)}(\tau',t'). \quad (4.21)$$

Now it is convenient to resort to the lesser/greater and retarded/advanced Green's functions. It is for $g_{\sigma\sigma'}^{(0)}(t,t')$ the following

$$g_{\sigma\sigma'}^{(0)r/a}(t,t') = \mp i\theta(\pm t \mp t')\left\langle \left\{d_\sigma(t), d_{\sigma'}^\dagger(t')\right\}\right\rangle = \mp i\theta(\pm t \mp t')e^{-i\varepsilon_\sigma(t-t')}, \quad (4.22)$$

and

$$g_{\sigma\sigma'}^{(0)</>}(t,t') = \pm i\left\langle d_\sigma(t), d_{\sigma'}^\dagger(t')\right\rangle = \pm i f(\pm\varepsilon_\sigma)e^{-i\varepsilon_\sigma(t-t')}. \quad (4.23)$$

Analogously, the lead Green's functions becomes

$$g_{\mathbf{k}\chi\sigma}^{r/a}(t,t') = \mp i\theta(\pm t \mp t')e^{-i\varepsilon_{\mathbf{k}\chi\sigma}(t-t')-i\int_{t'}^t d\tau \mu_\chi(\tau)}, \quad (4.24)$$

and

$$g_{\mathbf{k}\chi\sigma}^{</>}(t,t') = \pm i f(\pm\varepsilon_{\mathbf{k}\chi\sigma})e^{-i\varepsilon_{\mathbf{k}\chi\sigma}(t-t')-i\int_{t'}^t d\tau \mu_\chi(\tau)}. \quad (4.25)$$

Making use of the wide band limit, the retarded self-energy in the Dyson equation (4.21) can be rewritten as

$$\begin{aligned}
\Sigma^r(t,t') &= \sum_{\mathbf{k}\chi} T_\chi^2 g_{\mathbf{k}\chi\sigma}^r(t,t') \\
&= -i\sum_{\mathbf{k}\chi} T_\chi^2 \theta(t-t')e^{-i\varepsilon_{\mathbf{k}\chi\sigma}(t-t')-i\int_{t'}^t d\tau \mu_\chi(\tau)} \\
&= \sum_{\mathbf{k}\chi} T_\chi^2 e^{-i\int_{t'}^t d\tau \mu_\chi(\tau)} \int \frac{d\omega}{2\pi} \frac{e^{-i\omega(t-t')}}{\omega - \varepsilon_{\mathbf{k}\chi\sigma} + i\delta} \\
&= \sum_\chi T_\chi^2 e^{-i\int_{t'}^t d\tau \mu_\chi(\tau)} \int \frac{d\omega}{2\pi} \int d\varepsilon_{\chi\sigma} \frac{\rho(\varepsilon_{\chi\sigma})e^{-i\omega(t-t')}}{\omega - \varepsilon_{\chi\sigma} + i\delta} \\
&\approx -i\sum_\chi \pi\rho_{\chi\sigma}T_\chi^2 e^{-i\int_{t'}^t d\tau \mu_\chi(\tau)} \int \frac{d\omega}{2\pi} e^{-i\omega(t-t')} \\
&= -i\sum_\chi (\Gamma_\sigma^\chi/2)e^{-i\int_{t'}^t d\tau \mu_\chi(\tau)}\delta(t-t') \\
&= -i\sum_\chi \Gamma_\sigma^\chi \delta(t-t')/2. \quad (4.26)
\end{aligned}$$

Here, we used the Fourier transform of the free electron Green's function,

$$-i \sum_{\mathbf{k}\chi} \theta(t - t') e^{-i\varepsilon_{\mathbf{k}\chi\sigma}(t-t')} = \sum_{\mathbf{k}\chi} \int \frac{d\omega}{2\pi} \frac{e^{-i\omega(t-t')}}{\omega - \varepsilon_{\mathbf{k}\chi\sigma} + i\delta}, \qquad (4.27)$$

and defined the tunneling coupling constant

$$\Gamma_\sigma^\chi = 2T_\chi^2 \sum_{\mathbf{k}} \delta(\omega - \varepsilon_{\mathbf{k}\sigma}) = 2T_\chi^2 \int d\varepsilon_{\chi\sigma} \rho(\varepsilon_\sigma) \delta(\omega - \varepsilon_{\chi\sigma}) = 2\pi T_\chi^2 \rho_{\chi\sigma}. \qquad (4.28)$$

In the integration over $\varepsilon_{\chi\sigma}$ only the principal value is left due to the wide-band limit ($\omega \to \infty$) and the density of states is assumed constant $\rho_{\chi\sigma}(\omega) = \rho_{\chi\sigma}$.

We can also derive the lesser/greater self-energies as

$$\Sigma^{</>}(t, t') = \sum_{\mathbf{k}\chi} T_\chi^2 g_{\mathbf{k}\chi\sigma}^{</>}(t, t')$$

$$= \pm i \sum_{\mathbf{k}\chi} T_\chi^2 f(\pm \varepsilon_{\mathbf{k}\chi\sigma}) e^{-i\varepsilon_{\mathbf{k}\chi\sigma}(t-t') - i \int_{t'}^t d\tau \mu_\chi(\tau)}$$

$$= \pm i \sum_\chi \Gamma_\sigma^\chi \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t-t') - i \int_{t'}^t d\tau \mu_\chi(\tau)}. \qquad (4.29)$$

Here, we replaced $\sum_{\mathbf{k}} T_\chi^2 f(\pm \varepsilon_{\mathbf{k}\chi\sigma}) e^{-i\varepsilon_{\mathbf{k}\chi\sigma}(t-t')} = \Gamma_\sigma^\chi \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t-t')}$.

Now, if we insert the Green's function in Eq. (4.22) and the self-energy in Eq. (4.26), we can calculate the Dyson equation in Eq. (4.21). It is important to note Eq. (4.21) is defined on the Keldysh contour and we perform the analytical continuation of Eq. (3.18). This yields for the retarded Green's function

$$g_{\sigma\sigma'}^r(t, t') = -i\theta(t - t') e^{-i\varepsilon_\sigma(t-t')} \delta_{\sigma\sigma'} + \iint d\tau d\tau' g_{\sigma\sigma'}^r(t, \tau)$$

$$\times \left(-i \sum_{\chi\sigma} \Gamma_\sigma^\chi / 2 \delta(\tau - \tau') \right) \left(-i\theta(\tau' - t') e^{-i\varepsilon_\sigma(\tau'-t')} \right)$$

$$= -i\theta(t - t') e^{-i\varepsilon_\sigma(t-t')} \delta_{\sigma\sigma'}$$

$$- i \sum_{\chi\sigma} \Gamma_\sigma^\chi / 2 \int d\tau g_{\sigma\sigma'}^r(t, \tau) \left(-i\theta(\tau - t') e^{-i\varepsilon_\sigma(\tau-t')} \right). \qquad (4.30)$$

The solution for this equation becomes

$$g_\sigma^r(t, t') = -i\theta(t - t') e^{-i(\varepsilon_\sigma - i\Gamma_\sigma/2)(t-t')}, \qquad (4.31)$$

where we define $\Gamma_\sigma = \sum_\chi \Gamma_{\sigma\chi}$.

By defining the coupling parameters $\Gamma_0^\chi = \sum_\sigma \Gamma_\sigma^\chi$ and $\mathbf{\Gamma}_1^\chi = \sum_\sigma \sigma_{\sigma\sigma}^z \Gamma_\sigma^\chi \hat{\mathbf{z}}$ and introducing the spin-polarization in the leads $p_\chi \in [-1, 1]$, such that

$\Gamma_{\sigma}^{\chi} = \Gamma_0^{\chi}(1 + \sigma_{\sigma\sigma}^z p_{\chi})/2$, we can write $\mathbf{\Gamma}_1^{\chi} = p_{\chi}\Gamma_0^{\chi}\hat{\mathbf{z}}$. With this notation we can introduce the coupling matrix $\mathbf{\Gamma} = \Gamma_0\sigma^0 + \mathbf{\Gamma}_1 \cdot \boldsymbol{\sigma}$, where $\Gamma_0 = \sum_{\chi} \Gamma_0^{\chi}$ and $\mathbf{\Gamma}_1 = \sum_{\chi} \mathbf{\Gamma}_1^{\chi}$. Analogously, we write the retarded/advanced and lesser/greater self-energies as $\mathbf{\Sigma}^{r/a} = \Sigma_0^{r/a}\sigma^0 + \mathbf{\Sigma}_1^{r/a} \cdot \boldsymbol{\sigma}$ and $\mathbf{\Sigma}^{</>} = \Sigma_0^{</>}\sigma^0 + \mathbf{\Sigma}_1^{</>} \cdot \boldsymbol{\sigma}$, where

$$\Sigma_0^{r/a}(t,t') = (\pm i)\delta(t-t')\Gamma_0/2, \tag{4.32}$$

$$\mathbf{\Sigma}_1^{r/a}(t,t') = (\pm i)\delta(t-t')\mathbf{\Gamma}_1/2, \tag{4.33}$$

$$\Sigma_0^{</>}(t,t') = (\pm i)\sum_{\chi}\Gamma_0^{\chi}\int \frac{d\omega}{2\pi}f(\pm\omega)e^{-i\omega(t-t')-i\int_{t'}^t d\tau \mu_{\chi}(\tau)}, \tag{4.34}$$

$$\mathbf{\Sigma}_1^{</>}(t,t') = (\pm i)\sum_{\chi}\mathbf{\Gamma}_1^{\chi}\int \frac{d\omega}{2\pi}f(\pm\omega)e^{-i\omega(t-t')-i\int_{t'}^t d\tau \mu_{\chi}(\tau)}. \tag{4.35}$$

Using this notation we partion the bare Green's functions in terms of its charge and magnetic components according to $\mathbf{g} = g_0\sigma^0 + \boldsymbol{\sigma} \cdot \mathbf{g}_1$. The retarded/advanced form of $\mathbf{g}$ can then be written

$$g_0^{r/a}(t,t') = (\mp i)\theta(\pm t \mp t')\sum_{\sigma}e^{-i(\varepsilon_{\sigma}\mp i\Gamma_{\sigma}/2)(t-t')}/2, \tag{4.36a}$$

$$\mathbf{g}_1^{r/a}(t,t') = (\mp i)\theta(\pm t \mp t')\sum_{\sigma}\sigma_{\sigma\sigma}^z e^{-i(\varepsilon_{\sigma}\mp i\Gamma_{\sigma}/2)(t-t')}\hat{\mathbf{z}}/2. \tag{4.36b}$$

Analogously, the lesser/greater form of $\mathbf{g}$ is given by the Keldysh equation in Eq. (3.22)

$$\mathbf{g}^{</>}(t,t') = \iint d\tau d\tau' \mathbf{g}^r(t,\tau)\mathbf{\Sigma}^{</>}(\tau,\tau')\mathbf{g}^a(\tau',t')$$

$$= g_0^{</>}(t,t')\sigma_0 + \boldsymbol{\sigma} \cdot \mathbf{g}_1^{</>}(t,t'), \tag{4.37}$$

where

$$g_0^{</>}(t,t') = \iint d\tau d\tau' \left(g_0^r\Sigma_0^{</>}g_0^a + \mathbf{g}_1^r\Sigma_0^{</>} \cdot \mathbf{g}_1^a \right.$$

$$\left. + g_0^r\mathbf{\Sigma}_1^{</>} \cdot \mathbf{g}_1^a + \mathbf{g}_1^r \cdot \mathbf{\Sigma}_1^{</>}g_0^a \right), \tag{4.38}$$

$$\mathbf{g}_1^{</>}(t,t') = \iint d\tau d\tau' \left(g_0^r\mathbf{\Sigma}_1^{</>}g_0^a + \mathbf{g}_1^r \cdot \mathbf{\Sigma}_1^{</>}\mathbf{g}_1^a \right.$$

$$\left. + g_0^r\Sigma_0^{</>}\mathbf{g}_1^a + \mathbf{g}_1^r\Sigma_0^{</>}g_0^a \right). \tag{4.39}$$

Here, and further on, we sometimes suppress the time-dependence of the propagators for clarity.

4.4 Dressed quantum dot Green's function

By using the bare Green's function, we can now write the dressed quantum dot Green's function for the full system including the interactions with the local

spin moment. We achieve this goal by defining it as the first order expansion in terms of the local moment, that is,

$$\begin{aligned} \mathbf{G}(t,t') &= \mathbf{g}(t,t') + \delta\mathbf{G}(t,t') \\ &= \mathbf{g}(t,t') - v \oint_C d\tau \mathbf{g}(t,\tau) \langle \mathbf{S}(\tau) \rangle \cdot \boldsymbol{\sigma} \mathbf{g}(\tau,t'), \end{aligned} \tag{4.40}$$

where $\mathbf{g}$ is the bare Green's function and $\delta\mathbf{G}$ is the correction from the interactions with the local magnetic moment. This is analogous to the Dyson equation with the self-energy defined as $\Sigma = -v \langle \mathbf{S}(\tau) \rangle \cdot \boldsymbol{\sigma}$. As above, we write $\mathbf{G} = \mathbf{G}_0 \sigma^0 + \boldsymbol{\sigma} \cdot \mathbf{G}_1$, where $G_0 = g_0 + \delta G_0$ and $\mathbf{G}_1 = \mathbf{g}_1 + \delta\mathbf{G}_1$, and the corrections are given by

$$\delta G_0(t,t') = -v \oint_C d\tau \Big(g_0 \langle \mathbf{S} \rangle \cdot \mathbf{g}_1 + \mathbf{g}_1 \cdot \langle \mathbf{S} \rangle g_0 + i[\mathbf{g}_1 \times \langle \mathbf{S} \rangle] \cdot \mathbf{g}_1 \Big), \tag{4.41}$$

$$\delta\mathbf{G}_1(t,t') = -v \oint_C d\tau \Big(g_0 \langle \mathbf{S} \rangle g_0 + (\mathbf{g}_1 \cdot \langle \mathbf{S} \rangle) \mathbf{g}_1 + i[\mathbf{g}_1 \times \langle \mathbf{S} \rangle] g_0$$
$$+ i g_0 [\langle \mathbf{S} \rangle \times \mathbf{g}_1] + i[\mathbf{g}_1 \times \langle \mathbf{S} \rangle] \times \mathbf{g}_1 \Big). \tag{4.42}$$

Here, we have used the identity $(\mathbf{A} \cdot \boldsymbol{\sigma})(\mathbf{B} \cdot \boldsymbol{\sigma}) = \mathbf{A} \cdot \mathbf{B} \sigma^0 + i[\mathbf{A} \times \mathbf{B}] \cdot \boldsymbol{\sigma}$, which gives

$$\begin{aligned} \mathbf{g} \langle \mathbf{S} \rangle \cdot \boldsymbol{\sigma} \mathbf{g} &= (g_0 \sigma^0 + \mathbf{g}_1 \cdot \boldsymbol{\sigma})(\langle \mathbf{S} \rangle \cdot \boldsymbol{\sigma})(g_0 \sigma^0 + \mathbf{g}_1 \cdot \boldsymbol{\sigma}) \\ &= \Big(\mathbf{g}_1 \cdot \langle \mathbf{S} \rangle + (g_0 \langle \mathbf{S} \rangle + i[\mathbf{g}_1 \times \langle \mathbf{S} \rangle]) \cdot \boldsymbol{\sigma} \Big) \Big(g_0 \sigma^0 + \mathbf{g}_1 \cdot \boldsymbol{\sigma} \Big), \\ &= \Big[\mathbf{g}_1 \cdot \langle \mathbf{S} \rangle g_0 + g_0 \langle \mathbf{S} \rangle \cdot \mathbf{g}_1 + i([\mathbf{g}_1 \times \langle \mathbf{S} \rangle] \cdot \mathbf{g}_1) \Big] \sigma^0 \\ &\quad + \Big[g_0 \langle \mathbf{S} \rangle g_0 + (\mathbf{g}_1 \cdot \langle \mathbf{S} \rangle) \mathbf{g}_1 + i[\mathbf{g}_1 \times \langle \mathbf{S} \rangle] g_0 \\ &\quad + i g_0 [\langle \mathbf{S} \rangle \times \mathbf{g}_1] + i([\mathbf{g}_1 \times \langle \mathbf{S} \rangle] \times \mathbf{g}_1) \Big] \cdot \boldsymbol{\sigma}. \end{aligned} \tag{4.43}$$

Performing the analytical continuation the retarded/advanced form of the correction to the dressed Green's function becomes

$$\delta G_0^{r/a}(t,t') = -v \int d\tau \Big(g_0^{r/a} \langle \mathbf{S} \rangle \cdot \mathbf{g}_1^{r/a} + \mathbf{g}_1^{r/a} \cdot \langle \mathbf{S} \rangle g_0^{r/a}$$
$$+ i[\mathbf{g}_1^{r/a} \times \langle \mathbf{S} \rangle] \cdot \mathbf{g}_1^{r/a} \Big), \tag{4.44}$$

$$\delta\mathbf{G}_1^{r/a}(t,t') = -v \int d\tau \Big(g_0^{r/a} \langle \mathbf{S} \rangle g_0^{r/a} + (\mathbf{g}_1^{r/a} \cdot \langle \mathbf{S} \rangle) \mathbf{g}_1^{r/a} + i[\mathbf{g}_1^{r/a} \times \langle \mathbf{S} \rangle] g_0^{r/a}$$
$$+ i g_0^{r/a} [\langle \mathbf{S} \rangle \times \mathbf{g}_1^{r/a}] + i[\mathbf{g}_1^{r/a} \times \langle \mathbf{S} \rangle] \times \mathbf{g}_1^{r/a} \Big). \tag{4.45}$$

The lesser/greater form of the correction becomes

$$\delta \mathbf{G}^{</>}(t,t') = - v \int d\tau \Big(\mathbf{g}^r(t,\tau) \langle \mathbf{S}(\tau) \rangle \cdot \boldsymbol{\sigma} \mathbf{g}^{</>}(\tau,t')$$

$$+ \mathbf{g}^{</>}(t,\tau) \langle \mathbf{S}(\tau) \rangle \cdot \boldsymbol{\sigma} \mathbf{g}^a(\tau,t') \Big), \qquad (4.46)$$

and decomposing into the charge and magnetic components we have

$$\delta G_0^{</>}(t,t') = - v \int d\tau \Big(g_0^r \langle \mathbf{S} \rangle \cdot \mathbf{g_1}^{</>} + g_0^{</>} \langle \mathbf{S} \rangle \cdot \mathbf{g}_1^a$$

$$+ \mathbf{g}_1^r \cdot \langle \mathbf{S} \rangle g_0^{</>} + \mathbf{g}_1^{</>} \cdot \langle \mathbf{S} \rangle g_0^a$$

$$+ i \left[\mathbf{g}_1^r \times \langle \mathbf{S} \rangle \right] \cdot \mathbf{g}_1^{</>} + i \left[\mathbf{g}_1^{</>} \times \langle \mathbf{S} \rangle \right] \cdot \mathbf{g}_1^a \Big), \qquad (4.47)$$

$$\delta \mathbf{G}_1^{</>}(t,t') = - v \int d\tau \Big(g_0^r \langle \mathbf{S} \rangle g_0^{</>} + g_0^{</>} \langle \mathbf{S} \rangle g_0^a$$

$$+ (\mathbf{g}_1^r \cdot \langle \mathbf{S} \rangle) \mathbf{g}_1^{</>} + (\mathbf{g}_1^{</>} \cdot \langle \mathbf{S} \rangle) \mathbf{g}_1^a + i \left[\mathbf{g}_1^r \times \langle \mathbf{S} \rangle \right] g_0^{</>}$$

$$+ i \left[\mathbf{g}_1^{</>} \times \langle \mathbf{S} \rangle \right] g_0^a + i g_0^r \left[\langle \mathbf{S} \rangle \times \mathbf{g}_1^{</>} \right] + i g_0^{</>} \left[\langle \mathbf{S} \rangle \times \mathbf{g}_1^a \right]$$

$$+ i \left[\mathbf{g}_1^r \times \langle \mathbf{S} \rangle \right] \times \mathbf{g}_1^{</>} + i \left[\mathbf{g}_1^{</>} \times \langle \mathbf{S} \rangle \right] \times \mathbf{g}_1^a \Big). \qquad (4.48)$$

4.5 Time-independent Green's functions

For time-independent processes we can assume that the Green's functions can be written as $G(t,t') = G(t - t')$ and we can perform a Fourier transform. Applying it on the bare Green's function gives

$$g_0^{r/a}(\omega) = \frac{1}{2} \sum_\sigma g_\sigma^{r/a}(\omega), \qquad (4.49)$$

$$\mathbf{g}_1^{r/a}(\omega) = \frac{1}{2} \sum_\sigma \sigma_{\sigma\sigma}^z g_\sigma^{r/a}(\omega), \hat{\mathbf{z}}, \qquad (4.50)$$

where

$$g_\sigma^{r/a}(\omega) = \frac{1}{\omega - \varepsilon_\sigma \pm i\Gamma_\sigma/2}, \qquad (4.51)$$

and the self-energies become

$$\Sigma_0^{</>}(\omega) = (\pm i) \sum_\chi \Gamma_0^\chi f_\chi(\pm\omega), \qquad (4.52)$$

$$\Sigma_1^{</>}(\omega) = (\pm i) \sum_\chi \mathbf{\Gamma}_1^\chi f_\chi(\pm\omega). \qquad (4.53)$$

In Fourier space, the lesser/greater Green's function is defined as

$$g_0^{</>}(\omega) = g_0^r \Sigma_0^{</>} g_0^a + g_1^r \Sigma_0^{</>} g_1^a + g_0^r \Sigma_1^{</>} g_1^a + g_1^r \Sigma_1^{</>} g_0^a, \qquad (4.54)$$

$$\mathbf{g_1}^{</>}(\omega) = \left(g_0^r \Sigma_1^{</>} g_0^a + g_1^r \Sigma_1^{</>} g_1^a + g_0^r \Sigma_0^{</>} g_1^a + g_1^r \Sigma_0^{</>} g_0^a\right)\hat{\mathbf{z}}. \quad (4.55)$$

Solving these equations gives

$$g_0^{</>}(\omega) = (\pm i)\frac{1}{2}\sum_{\chi\sigma}\left(\frac{\Gamma_0^\chi f_\chi(\pm\omega)}{(\omega-\epsilon_\sigma)^2+(\Gamma_\sigma/2)^2} + \sigma_{\sigma\sigma}^z\frac{\Gamma_S^\chi f_\chi(\pm\omega)}{(\omega-\epsilon_\sigma)^2+(\Gamma_\sigma/2)^2}\right),$$
$$\quad (4.56)$$

$$g_1^{</>}(\omega) = (\pm i)\frac{1}{2}\sum_{\chi\sigma}\left(\frac{\Gamma_S^\chi f_\chi(\pm\omega)}{(\omega-\epsilon_\sigma)^2+(\Gamma_\sigma/2)^2} + \sigma_{\sigma\sigma}^z\frac{\Gamma_0^\chi f_\chi(\pm\omega)}{(\omega-\epsilon_\sigma)^2+(\Gamma_\sigma/2)^2}\right)\hat{\mathbf{z}}.$$
$$\quad (4.57)$$

Finally, doing the Fourier transform on the correction gives

$$\delta G_0^{</>}(\omega) = -v\left(g_0^r\langle\mathbf{S}\rangle\cdot\mathbf{g_1}^{</>} + g_0^{</>}\langle\mathbf{S}\rangle\cdot\mathbf{g_1}^a + \mathbf{g_1}^r\cdot\langle\mathbf{S}\rangle g_0^{</>}\right.$$
$$\left. + \mathbf{g_1}^{</>}\cdot\langle\mathbf{S}\rangle g_0^a + i[\mathbf{g_1}^r\times\langle\mathbf{S}\rangle]\cdot\mathbf{g_1}^{</>} + i\left[\mathbf{g_1}^{</>}\times\langle\mathbf{S}\rangle\right]\cdot\mathbf{g_1}^a\right),$$
$$\quad (4.58)$$

$$\delta\mathbf{G_1}^{</>}(\omega) = -v\left(g_0^r\langle\mathbf{S}\rangle g_0^{</>} + g_0^{</>}\langle\mathbf{S}\rangle g_0^a + i[\mathbf{g_1}^r\times\langle\mathbf{S}\rangle]g_0^{</>}\right.$$
$$+ (\mathbf{g_1}^r\cdot\langle\mathbf{S}\rangle)\mathbf{g_1}^{</>} + (\mathbf{g_1}^{</>}\cdot\langle\mathbf{S}\rangle)\mathbf{g_1}^a$$
$$+ i\left[\mathbf{g_1}^{</>}\times\langle\mathbf{S}\rangle\right]g_0^a + ig_0^r\left[\langle\mathbf{S}\rangle\times\mathbf{g_1}^{</>}\right] + ig_0^{</>}[\langle\mathbf{S}\rangle\times\mathbf{g_1}^a]$$
$$\left. + i[\mathbf{g_1}^r\times\langle\mathbf{S}\rangle]\times\mathbf{g_1}^{</>} + i\left[\mathbf{g_1}^{</>}\times\langle\mathbf{S}\rangle\right]\times\mathbf{g_1}^a\right). \quad (4.59)$$

4.6 Non-polarized case

In the case of non-polarized leads, i.e., $\Gamma_S = 0$, and with a vanishing external magnetic field, the Green's functions are reduced. The bare Green's function becomes

$$g^{r/a}(\omega) = \frac{1}{\omega - \varepsilon_0 \pm i\Gamma_0/4}, \quad (4.60)$$

and the self-energy becomes

$$\Sigma^{</>}(\omega) = (\pm i)\sum_\chi \Gamma_0^\chi f_\chi(\pm\omega). \quad (4.61)$$

In Fourier space, the lesser/greater Green's function is defined as

$$g^{</>}(\omega) = g^r \Sigma^{</>} g^a, \quad (4.62)$$

and inserting the retarded/advanced Green's function and the self-energy it becomes

$$g^{</>}(\omega) = (\pm i) \sum_\chi \frac{\Gamma_0^\chi f_\chi(\pm\omega)}{(\omega - \epsilon_0)^2 + (\Gamma_0/4)^2}.$$

(4.63)

Finally, the retarded/advanced dressed Green's function becomes

$$\mathbf{G}^{r/a}(\omega) = g^{r/a}\sigma_0 - v g_0^{r/a} \langle \mathbf{S} \rangle g_0^{r/a} \cdot \boldsymbol{\sigma},$$

(4.64)

and the lesser/greater

$$\mathbf{G}^{</>}(\omega) = g^{</>}\sigma_0 - v \left(g_0^r \langle \mathbf{S} \rangle g_0^{</>} + g_0^{</>} \langle \mathbf{S} \rangle g_0^a \right) \cdot \boldsymbol{\sigma}.$$

(4.65)

4.7 Particle number and local magnetic occupation

The local particle number of the QD is defined as

$$n(t) = \left\langle \psi^\dagger(t)\psi(t) \right\rangle = \sum_\sigma \left\langle d_\sigma^\dagger(t)d_\sigma(t) \right\rangle = \text{Im sp}\mathbf{G}^<(t,t)$$

$$= \frac{1}{2\pi}\text{Im sp} \int d\omega \mathbf{G}^<(\omega) = \frac{1}{\pi}\text{Im} \int d\omega G_0^<(\omega),$$

(4.66)

where we used the notation of spinors $\psi = (d_\uparrow, d_\downarrow)$. The local magnetic occupation is defined as

$$\mathbf{m}(t) = \langle \mathbf{s}(t) \rangle = \frac{1}{2} \left\langle \psi(t)^\dagger \boldsymbol{\sigma}\psi(t) \right\rangle = \frac{1}{2}\text{Im sp}\boldsymbol{\sigma}\mathbf{G}^<(t,t)$$

$$= \frac{1}{4\pi}\text{Im sp}\boldsymbol{\sigma} \int d\omega \mathbf{G}^<(\omega) = \frac{1}{2\pi}\text{Im} \int d\omega \mathbf{G}_1^<(\omega).$$

(4.67)

In the case of non-polarized leads and a vanishing external field it is

$$\mathbf{m}(t) = -\frac{v}{2\pi}\text{Im} \int d\omega \left(g_0^r \langle \mathbf{S} \rangle g_0^< + g_0^< \langle \mathbf{S} \rangle g_0^a \right).$$

(4.68)

4.8 Currents through the single-molecule magnet

In this section we go through the currents flowing through the system. We define it as the change of particles and energy in respective lead, thus, the particle current becomes

$$I_\chi^N = \left\langle \frac{dN_\chi}{dt} \right\rangle = -\frac{i}{\hbar} \sum_{\mathbf{k}\sigma} \left\langle \left[c_{\mathbf{k}\sigma\chi}^\dagger c_{\mathbf{k}\sigma\chi}, \mathcal{H} \right] \right\rangle,$$

(4.69)

the charge current

$$I_\chi^C = -eI_\chi^N = -e \left\langle \frac{dN_\chi}{dt} \right\rangle = \frac{ie}{\hbar} \sum_{\mathbf{k}\sigma} \left\langle \left[c_{\mathbf{k}\sigma\chi}^\dagger c_{\mathbf{k}\sigma\chi}, \mathcal{H} \right] \right\rangle,$$

(4.70)

the spin current

$$I_\chi^S = -e \sum_{\mathbf{k}\sigma\sigma'} \frac{d}{dt} \left\langle c_{\mathbf{k}\sigma\chi}^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} c_{\mathbf{k}\sigma'\chi} \right\rangle = \frac{ie}{\hbar} \sum_{\mathbf{k}\sigma\sigma'} \left\langle \left[c_{\mathbf{k}\sigma\chi}^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} c_{\mathbf{k}\sigma'\chi}, \mathcal{H} \right] \right\rangle, \quad (4.71)$$

the energy current

$$I_\chi^E = \left\langle \frac{d\mathcal{H}_\chi}{dt} \right\rangle = -\frac{i}{\hbar} \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}\sigma} \left\langle \left[c_{\mathbf{k}\sigma\chi}^\dagger c_{\mathbf{k}\sigma\chi}, \mathcal{H} \right] \right\rangle, \quad (4.72)$$

and the heat current

$$I_\chi^Q = I_\chi^E - \mu_\chi I_\chi^N = -\frac{i}{\hbar} \sum_{\mathbf{k}\sigma} (\varepsilon_{\mathbf{k}\chi\sigma} - \mu_\chi) \left\langle \left[c_{\mathbf{k}\sigma\chi}^\dagger c_{\mathbf{k}\sigma\chi}, \mathcal{H} \right] \right\rangle. \quad (4.73)$$

We can easily see that the important quantity is $\frac{i}{\hbar} \sum_{\mathbf{k}\sigma} \left\langle \left[c_{\mathbf{k}\sigma\chi}^\dagger c_{\mathbf{k}\sigma\chi}, \mathcal{H} \right] \right\rangle$. Evaluating the term $\left[c_{\mathbf{k}\sigma\chi}^\dagger c_{\mathbf{k}\sigma\chi}, \mathcal{H} \right]$ by using Eq. (3.5) gives the only non-vanishing term

$$\left[c_{\mathbf{k}\sigma\chi}^\dagger c_{\mathbf{k}\sigma\chi}, \mathcal{H}_{T\chi} \right] = \sum_{\mathbf{k}'\sigma'\chi'} T_{\chi'} [c_{\mathbf{k}\sigma\chi}^\dagger c_{\mathbf{k}\sigma\chi}, c_{\mathbf{k}'\sigma'\chi'}^\dagger d_{\sigma'} + H.c.]$$

$$= T_\chi \left(c_{\mathbf{k}\chi\sigma}^\dagger d_\sigma - d_\sigma^\dagger c_{\mathbf{k}\chi\sigma} \right). \quad (4.74)$$

Here we can identify the transfer Green's function $\mathbf{G}_{\mathbf{k}\chi\sigma\sigma'}^<(t,t) = i \left\langle c_{\mathbf{k}\chi\sigma}(t) d_{\sigma'}^\dagger(t) \right\rangle$ and $\left[\mathbf{G}_{\mathbf{k}\chi\sigma\sigma'}^<(t,t) \right]^* = -i \left\langle d_{\sigma'}^\dagger(t) c_{\mathbf{k}\chi\sigma}(t) \right\rangle$ which is defined in Eq. (4.19). Seeing that $\mathbf{G}_{\mathbf{k}\chi\sigma\sigma'}^<(t,t) = - \left[\mathbf{G}_{\mathbf{k}\chi\sigma\sigma'}^<(t,t) \right]^*$ we thus get

$$\frac{i}{\hbar} \sum_{\mathbf{k}\sigma} \left\langle \left[c_{\mathbf{k}\sigma\chi}^\dagger c_{\mathbf{k}\sigma\chi}, \mathcal{H} \right] \right\rangle = \frac{i}{\hbar} \sum_{\mathbf{k}\sigma} T_\chi \left(c_{\mathbf{k}\chi\sigma}^\dagger d_\sigma - d_\sigma^\dagger c_{\mathbf{k}\chi\sigma} \right)$$

$$= \frac{2}{\hbar} \sum_{\mathbf{k}\sigma} T_\chi \mathbf{G}_{\mathbf{k}\chi\sigma\sigma'}^<(t,t). \quad (4.75)$$

Applying the analytical continuation rules in Eq. (3.17) to the Keldysh equation of the transfer Green's function gives

$$\mathbf{G}_{\mathbf{k}\chi\sigma\sigma'}^<(t,t') = T_\chi \oint_C d\tau\, g_{\mathbf{k}\chi\sigma}(t,\tau) \mathbf{G}(\tau,t)$$

$$= T_\chi \int d\tau \left(g_{\mathbf{k}\chi\sigma}^r(t,\tau) \mathbf{G}^<(\tau,t) + g_{\mathbf{k}\chi\sigma}^<(t,\tau) \mathbf{G}^a(\tau,t') \right)$$

$$= -iT_\chi \int_{-\infty}^t d\tau \left[\mathbf{G}^<(\tau,t) - f(\varepsilon_{\mathbf{k}\chi\sigma}) \mathbf{G}^a(\tau,t) \right]$$

$$\times e^{-i\varepsilon_{\mathbf{k}\chi\sigma}(t-\tau) - i \int_\tau^t d\tau' \mu_\chi(\tau')}, \quad (4.76)$$

where we inserted the retarded and lesser Green's functions for the leads defined in Eq. (4.24) and (4.25). Rewriting the terms in the brackets using Eq. (3.9) gives

$$
\begin{aligned}
\mathbf{G}^<(\tau,t) - f(\varepsilon_{\mathbf{k}\chi\sigma})\mathbf{G}^a(\tau,t) =& \mathbf{G}^<(\tau,t) - f(\varepsilon_{\mathbf{k}\chi\sigma})\theta(t-\tau) \\
& \times \left[\mathbf{G}^<(\tau,t) - \mathbf{G}^>(\tau,t)\right] \\
=& \mathbf{G}^>(\tau,t)f(\varepsilon_{\mathbf{k}\chi\sigma})\theta(t-\tau) \\
& + \mathbf{G}^<(\tau,t)(1 - f(\varepsilon_{\mathbf{k}\chi\sigma})\theta(t-\tau)), \quad (4.77)
\end{aligned}
$$

and

$$
\begin{aligned}
\frac{2}{\hbar}\sum_{\mathbf{k}\sigma} T_\chi \mathbf{G}^<_{\mathbf{k}\chi\sigma\sigma'}(t,t) =& -\frac{2}{\hbar}\sum_{\mathbf{k}\sigma} T_\chi^2 \int_{-\infty}^{t} d\tau \, \left[\mathbf{G}^>(\tau,t)f(\varepsilon_{\mathbf{k}\chi\sigma})\right. \\
& \left. + \mathbf{G}^<(\tau,t)(1 - f(\varepsilon_{\mathbf{k}\chi\sigma}))\right] e^{-i\varepsilon_{\mathbf{k}\chi\sigma}(t-\tau) - i\int_\tau^t d\tau' \mu_\chi(\tau')} \\
=& -\frac{2}{\hbar}\sum_{\sigma} \int_{-\infty}^{t} d\tau \, \left[\Sigma_\chi^<(t,\tau)\mathbf{G}^>(\tau,t)\right. \\
& \left. - \Sigma_\chi^>(t,\tau)\mathbf{G}^<(\tau,t)\right]. \quad (4.78)
\end{aligned}
$$

In the last step we identified the self-energies given in Eq. (4.29).

In the case of the energy current in Eq. (4.72) we identify that the expression we solved for is multiplied by $\sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}\sigma}$. Furthermore, in our identification of the self-energies we made use of the wide-band limit and integrated over all energies. In order to do the same and include the energies of the energy current we thus need to define a specific "energy current self-energy" as

$$
\begin{aligned}
\Sigma_{E\chi}^{</>}(t,t') =& \pm i \sum_{\mathbf{k}} T_\chi^2 \varepsilon_{\mathbf{k}\chi\sigma} f(\pm\varepsilon_{\mathbf{k}\chi\sigma}) e^{-i\varepsilon_{\mathbf{k}\chi\sigma}(t-t') - i\int_{t'}^t d\tau \mu_\chi(\tau)} \\
=& \pm i\Gamma_\sigma^\chi \int \frac{d\omega}{2\pi} \omega f(\pm\omega) e^{-i\omega(t-t') - i\int_{t'}^t d\tau \mu_\chi(\tau)}. \quad (4.79)
\end{aligned}
$$

Finally, this gives the currents

$$I_\chi^N = \frac{2}{\hbar} \sum_\sigma \int_{-\infty}^t d\tau \left[\Sigma_\chi^<(t,\tau) \mathbf{G}^>(\tau,t) - \Sigma_\chi^>(t,\tau) \mathbf{G}^<(\tau,t) \right], \tag{4.80}$$

$$I_\chi^C = -\frac{2e}{\hbar} \sum_\sigma \int_{-\infty}^t d\tau \left[\Sigma_\chi^<(t,\tau) \mathbf{G}^>(\tau,t) - \Sigma_\chi^>(t,\tau) \mathbf{G}^<(\tau,t) \right], \tag{4.81}$$

$$I_\chi^S = -\frac{2e}{\hbar} \sum_\sigma \boldsymbol{\sigma} \int_{-\infty}^t d\tau \left[\Sigma_\chi^<(t,\tau) \mathbf{G}^>(\tau,t) - \Sigma_\chi^>(t,\tau) \mathbf{G}^<(\tau,t) \right], \tag{4.82}$$

$$I_\chi^E = \frac{2}{\hbar} \int_{-\infty}^t d\tau \left[\Sigma_{E\chi}^<(t,\tau) \mathbf{G}^>(\tau,t) - \Sigma_{E\chi}^>(t,\tau) \mathbf{G}^<(\tau,t) \right], \tag{4.83}$$

$$I_\chi^Q = \frac{2}{\hbar} \int_{-\infty}^t d\tau \left[\left(\Sigma_{E\chi}^<(t,\tau) - \mu_\chi \Sigma_\chi^<(t,\tau) \right) \mathbf{G}^>(\tau,t) \right.$$
$$\left. - \left(\Sigma_{E\chi}^>(t,\tau) - \mu_\chi \Sigma_\chi^>(t,\tau) \right) \mathbf{G}^<(\tau,t) \right]. \tag{4.84}$$

4.9 Time-independent currents

As in Section 4.5, we can perform a Fourier transform of the currents for time-independent processes. Performing the transform on the particle current gives

$$-\frac{2}{\hbar} \sum_\sigma \int_{-\infty}^t d\tau \left[\Sigma^<(t,\tau) \mathbf{G}^>(\tau,t) - \Sigma^>(t,\tau) \mathbf{G}^<(\tau,t) \right]$$

$$= -\frac{2}{\hbar} \sum_\sigma \int_{-\infty}^t d\tau \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} \left[\Sigma^<(\omega) e^{-i\omega(t-\tau)} \mathbf{G}^>(\omega') e^{-i\omega'(\tau-t)} \right.$$
$$\left. - \Sigma^>(\omega) e^{-i\omega(t-\tau)} \mathbf{G}^<(\omega') e^{-i\omega'(\tau-t)} \right]$$

$$= -\frac{2}{\hbar} \sum_\sigma \int_{-\infty}^t d\tau \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} \left[\Sigma^<(\omega) \mathbf{G}^>(\omega') \right.$$
$$\left. - \Sigma^>(\omega) \mathbf{G}^<(\omega') \right] e^{-i(\omega-\omega')(t-\tau)}$$

$$= -\frac{2}{\hbar} \sum_\sigma \int \frac{d\omega}{2\pi} \int \frac{d\omega'}{2\pi} \left[\Sigma^<(\omega) \mathbf{G}^>(\omega') - \Sigma^>(\omega) \mathbf{G}^<(\omega') \right] \pi\delta(\omega - \omega')$$

$$= -\frac{1}{\hbar} \sum_\sigma \int \frac{d\omega}{2\pi} \left[\Sigma^<(\omega) \mathbf{G}^>(\omega) - \Sigma^>(\omega) \mathbf{G}^<(\omega) \right]. $$

$$\tag{4.85}$$

Here, we used the Kramer-Kronig relations, i.e., $\operatorname{Re} f(\omega) = \frac{1}{\pi} \int d\omega' \frac{\operatorname{Im} f(\omega')}{\omega'-\omega}$. In our case we used the fact that $\frac{1}{\omega-\omega'+i\delta} = \frac{1}{\omega-\omega'} - i\pi\delta(\omega - \omega')$.

This gives the currents in their time-independent form

$$I_\chi^N = -\frac{1}{\hbar} \sum_\sigma \int \frac{d\omega}{2\pi} \left[\mathbf{\Sigma}_\chi^<(\omega)\mathbf{G}^>(\omega) - \mathbf{\Sigma}_\chi^>(\omega)\mathbf{G}^<(\omega) \right], \tag{4.86}$$

$$I_\chi^C = -\frac{e}{\hbar} \sum_\sigma \int \frac{d\omega}{2\pi} \left[\mathbf{\Sigma}_\chi^<(\omega)\mathbf{G}^>(\omega) - \mathbf{\Sigma}_\chi^>(\omega)\mathbf{G}^<(\omega) \right], \tag{4.87}$$

$$I_\chi^S = -\frac{e}{\hbar} \sum_\sigma \boldsymbol{\sigma} \int \frac{d\omega}{2\pi} \left[\mathbf{\Sigma}_\chi^<(\omega)\mathbf{G}^>(\omega) - \mathbf{\Sigma}_\chi^>(\omega)\mathbf{G}^<(\omega) \right], \tag{4.88}$$

$$I_\chi^E = -\frac{1}{\hbar} \sum_\sigma \int \frac{d\omega}{2\pi} \omega \left[\mathbf{\Sigma}_\chi^<(\omega)\mathbf{G}^>(\omega) - \mathbf{\Sigma}_\chi^>(\omega)\mathbf{G}^<(\omega) \right], \tag{4.89}$$

$$I_\chi^Q = -\frac{1}{\hbar} \sum_\sigma \int \frac{d\omega}{2\pi} (\omega - \mu_\chi) \left[\mathbf{\Sigma}_\chi^<(\omega)\mathbf{G}^>(\omega) - \mathbf{\Sigma}_\chi^>(\omega)\mathbf{G}^<(\omega) \right]. \tag{4.90}$$

4.10 Time-dependent currents for pulses

We are now interested in describing the time-dependent currents for different pulses over the junction. We start by rewriting our Green's function for treating the different pulses. We first do this for the case of non-polarized leads and a degenerate quantum dot, i.e., $p_\chi = \mathbf{\Gamma}_1 = 0$, $\Gamma_\uparrow^\chi = \Gamma_\downarrow^\chi = \Gamma_0^\chi/2$ and a vanishing external field B. This leads to the simplification of the bare Green's functions, such that they can be expressed as

$$g^{</>}(t,t') = \iint d\tau d\tau' g^r(t,\tau)\Sigma^{</>}(\tau,\tau')g^a(\tau',t'), \tag{4.91}$$

where the self-energy and retarded/advanced Green's function are defined as

$$\Sigma^{</>}(t,t') = (\pm i) \sum_\chi \Gamma_0^\chi \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t-t') - i \int_{t'}^t d\tau \mu_\chi(\tau)}, \tag{4.92}$$

$$g^{r/a}(t,t') = (\mp i)\theta(\pm t \mp t') e^{-i(\varepsilon_0 \mp i\Gamma_0/4)(t-t')}. \tag{4.93}$$

The dressed quantum dot Green's function that takes the local magnetic moment into account becomes

$$\mathbf{G}^{</>}(t,t') = g^{</>}(t,t') - v \int d\tau \left(g^r(t,\tau)g^{</>}(\tau,t') \right.$$

$$\left. + g^{</>}(t,\tau)g^a(\tau,t') \right) \langle \mathbf{S} \rangle \cdot \boldsymbol{\sigma}. \tag{4.94}$$

In order to compute the effects of the pulses, the time-integration kernel in the currents can be written in a more convenient form. The pulse information is considered in the integral $\int_{t'}^t d\tau \mu_\chi(\tau)$, which can be rewritten as $\int_{t'}^t d\tau \mu_\chi(\tau) = \int_{-\infty}^t d\tau \mu_\chi(\tau) - \int_{-\infty}^{t'} d\tau \mu_\chi(\tau)$. This leads to that the integration over τ and τ'

in the self-energy can be separated into two parts. We rewrite the self-energy as

$$\Sigma^{</>}(t,t') = (\pm i)\sum_\chi \Gamma_0^\chi K_\chi^{</>}(t,t'),$$ (4.95)

where we defined

$$K_\chi^{</>}(t,t') = \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t-t')-ie\int_{t'}^t d\tau \Delta_\chi(\tau)}.$$ (4.96)

We note that the integration can be performed over $\exp[-i\omega t - i\int_{-\infty}^t d\tau \mu_\chi(\tau)]$ and $\exp[i\omega t' + i\int_{-\infty}^{t'} d\tau \mu_\chi(\tau)]$ separately. This leads to the separation of the bare Green's function as

$$g_0^{</>}(t,t') = (\pm i)\sum_\chi \Gamma_0^\chi \int \frac{d\omega}{2\pi} f(\pm\omega) A_\chi(\omega,t) B_\chi(\omega,t')$$ (4.97)

where

$$A_\chi(\omega,t) = (-i)\int_{-\infty}^t d\tau e^{-i(\varepsilon_0-i\Gamma_0/4)(t-\tau)-i\omega\tau-i\int_{-\infty}^\tau ds\Delta_\chi(s)},$$ (4.98)

$$B_\chi(\omega,t') = i\int_{-\infty}^t d\tau' e^{i(\varepsilon_0+i\Gamma_0/4)(t'-\tau')+i\omega\tau'+i\int_{-\infty}^{\tau'} ds\Delta_\chi(s)}.$$ (4.99)

The spin-dependent part of the Green's function becomes

$$\mathbf{G}_1^{</>}(t,t') = (\mp i)v \sum_\chi \Gamma_0^\chi \int \frac{d\omega}{2\pi} f(\pm\omega)\Big(C_\chi(\omega,t)B_\chi(\omega,t')$$

$$+ A_\chi(\omega,t)D_\chi(\omega,t')\Big)\langle\mathbf{S}\rangle,$$ (4.100)

where we defined

$$C_\chi(\omega,t) = \int d\tau g^r(t,\tau) A_\chi(\omega,\tau)$$

$$= -\int_{-\infty}^t d\tau e^{-i(\varepsilon_0-i\Gamma_0/4)(t-\tau)}$$

$$\times \left(\int_{-\infty}^\tau d\tau' e^{-i(\varepsilon_0-i\Gamma_0)(\tau-\tau')-i\omega\tau'-ie\int_{-\infty}^{\tau'} ds\Delta_\chi(s)}\right),$$ (4.101)

$$D_\chi(\omega,t') = \int d\tau g^a(t,\tau) B_\chi(\omega,\tau)$$

$$= -\int_{-\infty}^{t'} d\tau e^{i(\varepsilon_0+i\Gamma_0/4)(t'-\tau)}$$

$$\times \left(\int_{-\infty}^\tau d\tau' e^{i(\varepsilon_0+i\Gamma_0)(\tau-\tau')+i\omega\tau'+ie\int_{-\infty}^{\tau'} ds\Delta_\chi(s)}\right).$$ (4.102)

The charge and spin current can be written as

$$I^C(t) = -\frac{4e}{\hbar}\Gamma_0^L \text{Im} \int_{-\infty}^t dt' \left(K_L^>(t,t') G_0^<(t',t) + K_L^<(t,t') G_0^>(t',t) \right),$$

(4.103)

$$\mathbf{I^S}(t) = -\frac{4e}{\hbar}\Gamma_0^L \text{Im} \int_{-\infty}^t dt' \left(K_L^>(t,t') \mathbf{G}_1^<(t',t) + K_L^<(t,t') \mathbf{G}_1^>(t',t) \right).$$

(4.104)

4.10.1 Current for a step-like bias voltage

A step-like bias voltage at time t_0 gives that $\Delta_\chi(\tau)$ becomes $\Delta_\chi\theta(t - t_0)$. We can now calculate the current using the theory above. We get that

$$K_\chi^{</>}(t,t') = \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t-t')-i\int_{t'}^t ds\Delta_\chi\theta(s-t_0)}$$

$$= \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t-t')-i\Delta_\chi((t-t_0)\theta(t-t_0)-(t'-t_0)\theta(t'-t_0))}$$

(4.105)

This yields

$$A_\chi(\omega,t) = (-i) \int_{-\infty}^t d\tau e^{-i(\varepsilon_0-i\Gamma_0/4)(t-\tau)-i\omega\tau-i\Delta_\chi(\tau-t_0)\theta(\tau-t_0)}, \quad (4.106)$$

$$B_\chi(\omega,t') = i \int_{-\infty}^{t'} d\tau' e^{i(\varepsilon_0+i\Gamma_0/4)(t'-\tau')+\omega\tau'+i\Delta_\chi(\tau'-t_0)\theta(\tau'-t_0)}. \quad (4.107)$$

Solving A - D we get

$$A_\chi(\omega,t) = \theta(t_0 - t)\frac{e^{-i\omega t}}{\omega - \varepsilon_0 + i\Gamma_0/4}$$

$$+ \theta(t - t_0) \left(\frac{e^{-i(\varepsilon_0-i\Gamma_0/4)(t-t_0)-i\omega t_0}}{\omega - \varepsilon_0 + i\Gamma_0/4} \right.$$

$$\left. + \frac{e^{-i\Delta_\chi(t-t_0)-i\omega t} - e^{-i(\varepsilon_0-i\Gamma_0/4)(t-t_0)-i\omega t_0}}{\omega + \Delta_\chi - \varepsilon_0 + i\Gamma_0/4} \right), \quad (4.108)$$

$$B_\chi(\omega, t') = \theta(t_0 - t')\frac{e^{+i\omega t'}}{\omega - \varepsilon_0 - i\Gamma_0/4}$$

$$+ \theta(t - t_0)\left(\frac{e^{-i(\varepsilon_0 + i\Gamma_0/4)(t_0 - t') + i\omega t_0}}{\omega - \varepsilon_0 - i\Gamma_0/4}\right.$$

$$\left. + \frac{e^{i\Delta_\chi(t' - t_0) + i\omega t'} - e^{-i(\varepsilon_0 + i\Gamma_0/4)(t_0 - t') + i\omega t_0}}{\omega + \Delta_\chi - \varepsilon_0 - i\Gamma_0/4}\right), \qquad (4.109)$$

$$C_\chi(\omega, t) = \theta(t_0 - t)\frac{e^{-i\omega t}}{(\omega - \varepsilon_0 + i\Gamma_0/4)(\omega - \varepsilon_0 + i\Gamma_0/4)}$$

$$+ \theta(t - t_0)\left(\frac{e^{-i(\varepsilon_0 - i\Gamma_0/4)(t - t_0) - i\omega t_0}}{(\omega - \varepsilon_0 + i\Gamma_0/4)(\omega - \varepsilon_0 + i\Gamma_0/4)}\right.$$

$$\left. + \frac{e^{-i\omega t - i\Delta_\chi(t - t_0)} - e^{-i(\varepsilon_0 - i\Gamma_0/4)(t - t_0) - i\omega t_0}}{(\omega + \Delta_\chi - \varepsilon_0 + i\Gamma_0/4)(\omega + \Delta_\chi - \varepsilon_0 + i\Gamma_0/4)}\right), \quad (4.110)$$

$$D_\chi(\omega, t') = \theta(t_0 - t)\frac{e^{+i\omega t'}}{(\omega - \varepsilon_0 - i\Gamma_0/4)(\omega - \varepsilon_0 - i\Gamma_0/4)}$$

$$+ \theta(t - t_0)\left(\frac{e^{i(\varepsilon_0 + i\Gamma_0/4)(t' - t_0) + i\omega t_0}}{(\omega - \varepsilon_0 - i\Gamma_0/4)(\omega - \varepsilon_0 - i\Gamma_0/4)}\right.$$

$$\left. + \frac{e^{i\omega t' + i\Delta_\chi(t' - t_0)} - e^{i(\varepsilon_0 + i\Gamma_0/4)(t' - t_0) + i\omega t_0}}{(\omega + \Delta_\chi - \varepsilon_0 - i\Gamma_0/4)(\omega + \Delta_\chi - \varepsilon_0 - i\Gamma_0/4)}\right). \quad (4.111)$$

4.10.2 Current for a rectangular bias pulse

A rectangular bias pulse applied at time t_0 and stopped at time t_1 gives an extension of the previous solution for the step-like bias voltage. We then get

$$K_\chi^{</>}(t, t') = \begin{cases} \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t - t')}, & t, t' < t_0 \\ \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t - t') - i\Delta_\chi(t_0 - t')} & t < t_0 < t' < t_1 \\ \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t - t') - i\Delta_\chi(t - t_0)} & t' < t_0 < t < t_1 \\ \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t - t') - i\Delta_\chi(t - t_0)} & t_0 < t, t' < t_1 \\ \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t - t') - i\Delta_\chi(t - t_1)} & t_0 < t < t_1 < t' \\ \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t - t') - i\Delta_\chi(t_1 - t')} & t_0 < t' < t_1 < t \\ \int \frac{d\omega}{2\pi} f(\pm\omega) e^{-i\omega(t - t')} & t_1 < t, t' \end{cases}$$

Solving A and B we get for $t, t' < t_0$

$$A_{\sigma,\chi}(\omega, t) = \frac{e^{-i\omega t}}{\omega - \varepsilon_0 + i\Gamma_0/4}, \tag{4.112}$$

$$B_{\sigma,\chi}(\omega, t') = \frac{e^{+i\omega t'}}{\omega - \varepsilon_0 - i\Gamma_0/4}, \tag{4.113}$$

and for $t_0 < t, t' < t_1$

$$A_\chi(\omega, t) = \frac{e^{-i(\varepsilon_0 - i\Gamma_0/4)(t-t_0) - i\omega t_0}}{\omega - \varepsilon_0 + i\Gamma_0/4} + \frac{e^{-i\Delta_\chi(t-t_0) - i\omega t} - e^{-i(\varepsilon_0 - i\Gamma_0/4)(t-t_0) - i\omega t_0}}{\omega + \Delta_\chi - \varepsilon_0 + i\Gamma_0/4}, \tag{4.114}$$

$$B_\chi(\omega, t') = \frac{e^{-i(\varepsilon_0 + i\Gamma_0/4)(t_0-t') + i\omega t_0}}{\omega - \varepsilon_0 - i\Gamma_0/4} + \frac{e^{i\Delta_\chi(t'-t_0) + i\omega t'} - e^{-i(\varepsilon_0 + i\Gamma_0/4)(t_0-t') + i\omega t_0}}{\omega + \Delta_\chi - \varepsilon_0 - i\Gamma_0/4}, \tag{4.115}$$

and for $t_1 < t, t'$

$$\begin{aligned}
A_\chi(\omega, t) = & e^{-i(\varepsilon_0 - i\Gamma_0/4)t} \\
& \times \left(\frac{e^{i(\varepsilon_0 - i\Gamma_0/4 - \omega)t_0} + e^{i(\varepsilon_0 - i\Gamma_0/4 - \omega)t} - e^{i(\varepsilon_0 - i\Gamma_0/4 - \omega)t_1}}{\omega - \varepsilon_0 + i\Gamma_0/4} \right. \\
& \left. + \frac{e^{i(\varepsilon_0 - i\Gamma_0/4 - \omega)t_1 - i\Delta_\chi(t_1-t_0)} - e^{i(\varepsilon_0 - i\Gamma_0/4 - \omega)t_0}}{\omega + \Delta_\chi - \varepsilon_0 + i\Gamma_0/4} \right),
\end{aligned} \tag{4.116}$$

$$\begin{aligned}
B_\chi(\omega, t') = & e^{i(\varepsilon_0 + i\Gamma_0/4)t'} \\
& \times \left(\frac{e^{-i(\varepsilon_0 + i\Gamma_0/4 - \omega)t_0} + e^{-i(\varepsilon_0 + i\Gamma_0/4 - \omega)t'} - e^{-i(\varepsilon_0 - i\Gamma_0/4 - \omega)t_1}}{\omega - \varepsilon_0 - i\Gamma_0/4} \right. \\
& \left. + \frac{e^{-i(\varepsilon_0 + i\Gamma_0/4 - \omega)t_1 + i\Delta_\chi(t_1-t_0)} - e^{-i(\varepsilon_0 + i\Gamma_0/4 - \omega)t_0}}{\omega + \Delta_\chi - \varepsilon_0 - i\Gamma_0/4} \right). \tag{4.117}
\end{aligned}$$

The different parameters, C and D, in the Green's function then becomes for $t, t' < t_0$

$$C_\chi(\omega, t) = \frac{e^{-i\omega t}}{(\omega - \varepsilon_0 + i\Gamma_0/4)(\omega - \varepsilon_0 + i\Gamma_0/4)}, \tag{4.118}$$

$$D_\chi(\omega, t') = \frac{e^{+i\omega t'}}{(\omega - \varepsilon_0 - i\Gamma_0/4)(\omega - \varepsilon_0 - i\Gamma_0/4)}, \tag{4.119}$$

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and for $t_0 < t, t' < t_1$

$$
\begin{aligned}
C_\chi(\omega, t) =& \frac{e^{-i(\varepsilon_0 - i\Gamma_0/4)(t-t_0) - i\omega t_0}}{(\omega - \varepsilon_0 + i\Gamma_0/4)(\omega - \varepsilon_0 + i\Gamma_0/4)} \\
&+ \frac{e^{-i\omega t - i\Delta_\chi(t-t_0)} - e^{-i(\varepsilon_0 - i\Gamma_0/4)(t-t_0) - i\omega t_0}}{(\omega + \Delta_\chi - \varepsilon_0 + i\Gamma_0/4)(\omega + \Delta_\chi - \varepsilon_0 + i\Gamma_0/4)}, \quad (4.120)
\end{aligned}
$$

$$
\begin{aligned}
D_\chi(\omega, t') =& \frac{e^{i(\varepsilon_0 + i\Gamma_0/4)(t'-t_0) + i\omega t_0}}{(\omega - \varepsilon_0 - i\Gamma_0/4)(\omega - \varepsilon_0 - i\Gamma_0/4)} \\
&+ \frac{e^{i\omega t' + i\Delta_\chi(t'-t_0)} - e^{i(\varepsilon_0 + i\Gamma_0/4)(t'-t_0) + i\omega t_0}}{(\omega + \Delta_\chi - \varepsilon_0 - i\Gamma_0/4)(\omega + \Delta_\chi - \varepsilon_0 - i\Gamma_0/4)}, \quad (4.121)
\end{aligned}
$$

and for $t_1 < t, t'$

$$
\begin{aligned}
C_\chi(\omega, t) =& e^{-i(\varepsilon_0 - i\Gamma_0/4)t} \\
&\times \left(\frac{e^{i(\varepsilon_0 - i\Gamma_0/4 - \omega)t_0} + e^{i(\varepsilon_0 - i\Gamma_0/4 - \omega)t} - e^{i(\varepsilon_0 - i\Gamma_0/4 - \omega)t_1}}{(\omega - \varepsilon_0 + i\Gamma_0/4)(\omega - \varepsilon_0 + i\Gamma_0/4)} \right. \\
&\left. + \frac{e^{i(\varepsilon_0 - i\Gamma_0/4 - \omega)t_1 - i\Delta_\chi(t_1 - t_0)} - e^{i(\varepsilon_0 - i\Gamma_0/4 - \omega)t_0}}{(\omega + \Delta_\chi - \varepsilon_0 + i\Gamma_0/4)(\omega + \Delta_\chi - \varepsilon_0 + i\Gamma_0/4)} \right), \quad (4.122)
\end{aligned}
$$

$$
\begin{aligned}
D_\chi(\omega, t') =& e^{i(\varepsilon_0 + i\Gamma_0/4)t'} \\
&\times \left(\frac{e^{-i(\varepsilon_0 + i\Gamma_0/4 - \omega)t_0} + e^{-i(\varepsilon_0 + i\Gamma_0/4 - \omega)t'} - e^{-i(\varepsilon_0 - i\Gamma_0/4 - \omega)t_1}}{(\omega - \varepsilon_0 - i\Gamma_0/4)(\omega - \varepsilon_0 - i\Gamma_0/4)} \right. \\
&\left. + \frac{e^{-i(\varepsilon_0 + i\Gamma_0/4 - \omega)t_1 + i\Delta_\chi(t_1 - t_0)} - e^{-i(\varepsilon_0 + i\Gamma_0/4 - \omega)t_0}}{(\omega + \Delta_\chi - \varepsilon_0 - i\Gamma_0/4)(\omega + \Delta_\chi - \varepsilon_0 - i\Gamma_0/4)} \right). \quad (4.123)
\end{aligned}
$$

4.10.3 Time-dependent current with polarized leads

Generalizing the previous treatment to polarized leads is just an extension of the previous procedure. As the expressions become rather lengthy but straightforward we do not show it in this thesis.

5. Thermoelectricity of a single-molecule magnet

The thermoelectric effects considered in this thesis can be classified into different types of phenomena. We have either electrically, spin or thermally driven effects in the system.

First, an electrical bias voltage will drive a charge current in a conducting material. This charge current can generate a thermal bias through the Peltier effect. A thermal bias can generate an electrical bias through the Seebeck effect. This are considered the conventional thermoelectric effects and were found in the 19th century.

Secondly, regarding the spin-dependent thermoelectric effects, we have a spin bias that can drive a spin current. This spin current can generate a thermal bias in the system through the spin Peltier effect. It is classified as a spin Peltier effect if it is driven by a collective motion of the magnetic structure, while it is called a spin-dependent Peltier effect if it is driven by the transport of charges.

On the other hand a thermal bias can generate a spin Seebeck effect. It is called spin Seebeck if it is driven by a collective motion of the magnetic structure, and spin-dependent Seebeck effect if it is driven by the independent electric spin-up and spin-down channels.

In this chapter we go through some basic concepts regarding thermoelectricity of a single-molecule magnet. For more information regarding thermoelectricity in the context of atomic and molecular junctions we refer the reader to the review of Ref. [153]. For a review of spin caloritronics see Ref. [174].

5.1 Thermoelectricity in a single-molecule magnet

A single-molecule magnet might exhibit both conventional thermoelectric effects and spin thermoelectric effects of both kinds. In this thesis, we will study spin-dependent Seebeck and Peltier effect due to the net transport of spins related to the charges in the system. Spin Seebeck and spin Peltier has also been studied in single-molecule magnets and it has been shown that they can exhibit pure spin currents [157, 158, 176]. The case is also true for a quantum dot under a magnetic field [160] or connected to ferromagnetic leads [154].

5.2 Heat current

Using the generic separation of a matrix $\mathbf{A} = A_0\sigma^0 + \boldsymbol{\sigma} \cdot \mathbf{A}_1$, we partition the particle and energy current from the previous chapter into a spin-independent

and spin-dependent part according to $I_\chi^N(t) = I_{0\chi}^N(t) + I_{1\chi}^N(t)$, where

$$I_{0\chi}^N(t) = \frac{4}{\hbar} \int_{-\infty}^{t} dt' \left(\Sigma_{0\chi}^> G_0^< + \Sigma_{0\chi}^< G_0^> \right), \tag{5.1a}$$

$$I_{1\chi}^N(t) = \frac{4}{\hbar} \int_{-\infty}^{t} dt' \left(\mathbf{\Sigma}_{1\chi}^> \cdot \mathbf{G}_1^< + \mathbf{\Sigma}_{1\chi}^< \cdot \mathbf{G}_1^> \right). \tag{5.1b}$$

Analougsly, the spin-independent and spin-dependent part of the energy current becomes

$$I_{0\chi}^E(t) = \frac{4}{\hbar} \int_{-\infty}^{t} \left(\Sigma_{E0\chi}^> G_0^< + \Sigma_{E0\chi}^< G_0^> \right) dt', \tag{5.2a}$$

$$I_{1\chi}^E(t) = \frac{4}{\hbar} \int_{-\infty}^{t} \left(\mathbf{\Sigma}_{E1\chi}^> \cdot \mathbf{G}_1^< + \mathbf{\Sigma}_{E1\chi}^< \cdot \mathbf{G}_1^> \right) dt'. \tag{5.2b}$$

Note that we here only considers the heat current, related to the Peltier and spin-dependent Peltier effect, in terms of the current exiting each lead. As the system is strongly coupled, this means that it does not correspond to the heat current in the molecule due to the strong system-bath coupling. Thus, further considerations need to be made for considering the quantum thermodynamics of the molecular magnet, as stated in Section 2.6.

5.3 Fourier and Peltier heat

The expressions above relate both to the Fourier and Peltier heat flowing through the molecule. The Fourier heat describes the heat flow due to a temperature difference, while the Peltier heat relates to a heat flow due to the electric and spin current. In the case of the same temperature in the system, we can ignore the Fourier heat and only consider the Peltier heat current. In that case, $I_{0\chi}^Q(t)$ represents the heat current generated by the Peltier effect, and $I_{1\chi}^Q(t)$ the heat current generated by the spin-dependent Peltier effect.

5.4 Seebeck coefficient and Peltier coefficient

In linear response, we can define the Seebeck coefficient for a molecular magnet and relate it to the Peltier coefficient [158, 166]. As previously stated, the Seebeck effect is a resulting voltage difference due to a thermal gradient over the junction. The charge Seebeck coefficient is thus defined as

$$S_C = -\frac{\Delta V}{\Delta T}. \tag{5.3}$$

Here, ΔV is the thermoelectric voltage over the junction, generated by the thermal gradient ΔT. This is also called the thermopower, and is the transfer

of charge due to a thermal gradient, i.e., the conventional thermoelectric effect. Analogously, the spin Seebeck coefficient is defined as

$$S_S = -\frac{\Delta V_S}{\Delta T}.$$ (5.4)

Here, ΔV_S is the spin voltage over the junctions, generated by the thermal gradient ΔT. The spin voltage corresponds to a nonequilibrium spin accumulation at the interfaces between the leads and the quantum dot making the chemical potential spin-polarized. The spin voltage can then drive a spin current through the system without any transport of charges.

As the Seebeck and Peltier effect are the result of the same effect, they are related through the second Thomson relation as $\Pi_C = TS_C$ and $\Pi_S = TS_S$, for an absolute temperature T.

6. Spin dynamics of a single-molecule magnet

6.1 General concepts and background

A single-molecule magnet can be represented by its intrinsic spin moment, either by a quantum or a classical spin. In order to give the proper description, there are several things to consider in the system. Among such are:

- Is the intrinsic spin moment of the molecule large enough in order to be considered classical?
- Is it strongly correlated to the electronic structure, i.e., does one need to treat it with the Anderson model and consider Kondo screening?
- Is the system small such that nonequilibrium conditions need to be treated?

In this thesis, we are considering the case of a classical spin that is connected by exchange interaction with the electronic background without strong correlations. We will discuss the exchange interaction and strongly correlated models, such as the Anderson model, briefly. The main focus is the spin dynamics of the classical spin and how to incorporate quantum and nonequilibrium effects into the description. For more information regarding the basic concepts of magnetism in condensed matter see, e.g., Ref. [190].

6.1.1 Exchange interaction

Exchange interaction is an interaction between identical particles, mediated by the overlap of the one-particle wave functions. It is related to the Coulomb interaction and Pauli exclusion principle of fermionic particles, such as electrons, and is part of the mediating exchange between different spins in a material. In the case of single-molecule magnets, the electrons of the embedded spin, i.e., the spin moment, interact via exchange interaction with the surrounding electrons. The exchange between different spins is thereby mediated by an electron gas. When the spins in a single-molecule magnet can be treated classically, e.g., in the case of a transition metal atom in a phthalocyanine, the electron degrees of freedom can be integrated out. The effective exchange is then approximated by an exchange integral between the localized and the delocalized electrons, i.e., the electrons of the molecular magnet and the surrounding electrons.

6.1.2 Kondo model

The Kondo model describes a quantum impurity coupled to a large reservoir of noninteracting electrons, i.e., a fermi gas. The quantum impurity is represented

by a spin coupled to the electrons by an antiferromagnetic exchange v. The antiferromagnetic exchange v is an exchange integral and originates from the exchange interaction described in the previous section. The Hamiltonian for the Kondo model reads

$$\mathcal{H}_\chi = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} - v\mathbf{s} \cdot \mathbf{S}. \tag{6.1}$$

Here, $c_{\mathbf{k}\sigma}^\dagger$ ($c_{\mathbf{k}\sigma}$) is the electron creation (annihilation) operator which creates (annihilates) an electron with momentum $\mathbf{k}$ and spin σ, v is the exchange interaction strength and $\mathbf{s} = \sum_{\sigma\sigma'} c_\sigma^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} c_{\sigma'}/2$ represent the spin states of the surrounding electrons. In the context of a single-molecule magnet, the magnetic impurity $\mathbf{S}$ can be interpreted as the spin moment of the magnet. Evaluating the sum representing $\mathbf{s}$ gives

$$\sum_{\sigma\sigma'} c_\sigma^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} c_{\sigma'}/2 = \begin{pmatrix} c_\uparrow^\dagger & c_\downarrow^\dagger \end{pmatrix} \begin{pmatrix} \boldsymbol{\sigma}_{\uparrow\uparrow} & \boldsymbol{\sigma}_{\uparrow\downarrow} \\ \boldsymbol{\sigma}_{\downarrow\uparrow} & \boldsymbol{\sigma}_{\downarrow\downarrow} \end{pmatrix} \begin{pmatrix} c_\uparrow \\ c_\downarrow \end{pmatrix}$$

$$= c_\uparrow^\dagger \boldsymbol{\sigma}_{\uparrow\uparrow} c_\uparrow + c_\uparrow^\dagger \boldsymbol{\sigma}_{\uparrow\downarrow} c_\downarrow + c_\downarrow^\dagger \boldsymbol{\sigma}_{\downarrow\uparrow} c_\uparrow + c_\downarrow^\dagger \boldsymbol{\sigma}_{\downarrow\downarrow} c_\downarrow$$

$$= \left(c_\uparrow^\dagger c_\downarrow + c_\downarrow^\dagger c_\uparrow, -i c_\uparrow^\dagger c_\downarrow + i c_\downarrow^\dagger c_\uparrow, c_\uparrow^\dagger c_\uparrow - c_\downarrow^\dagger c_\downarrow \right), \tag{6.2}$$

where $\boldsymbol{\sigma}_{\sigma\sigma'}$ is the vector of Pauli matrices, i.e., $(\sigma_x, \sigma_y, \sigma_z)$, where, for instance, $\boldsymbol{\sigma}_{\uparrow\uparrow} = (\sigma_{\uparrow\uparrow}^x, \sigma_{\uparrow\uparrow}^y, \sigma_{\uparrow\uparrow}^z)$. Thus, in the z-direction, s_z represents the difference between the spin-up and spin-down states of the surrounding electrons.

6.1.3 Strongly correlated models and effects

When the interaction between the localized electrons of the local spin moment of the molecular magnet and the delocalized ones are strong, the Kondo model does not suffice. In that case, one need to use the Anderson model. The Hamiltonian of the Anderson model is

$$\mathcal{H}_\chi = \sum_\sigma \varepsilon_\sigma d_\sigma^\dagger d_\sigma + U d_\uparrow^\dagger d_\uparrow d_\downarrow^\dagger d_\downarrow + \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}\sigma} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \sum_{\sigma,\mathbf{k}} V_{\mathbf{k}} (d_\sigma^\dagger c_{\mathbf{k}\sigma} + c_{\mathbf{k}\sigma}^\dagger d_\sigma).$$

$$\tag{6.3}$$

Here, $d_\sigma^\dagger$ (d_σ) is the impurity creation (annihilation) operator which creates (annihilates) an electron with spin σ. U is the on-site Coulomb repulsion and $V_{\mathbf{k}}$ is the coupling between the impurity and the conduction electrons.

The Anderson model suits for strongly correlated problems and can be used in order to describe effects such as Kondo screening. The Kondo screening is an effect where impurities increase resistivity as the spin of the electrons scatter on the impurities, resulting in a zero-bias Kondo peak, and can be present in, e.g., molecular magnets [51, 52, 73].

Methods for solving models with electron-electron interaction includes, among others, numerical renormalization group (NRG) [73, 191] and Hubbard

operators [192]. In the former, one uses renormalization to rewrite the conduction band to a chain of interacting states with an interaction strength that exponentially decays for each state. This makes the infinite problem to a finite one and allows to solve the impurity problem. In the latter case, one rewrites the Hamiltonian with Hubbard operators and then calculates the Green's functions for these operators. As we are not considering strongly correlated effects of the molecular moment in this thesis we will not use these approaches. Using Hubbard operators could be a suitable extension of the current work in order to include electron-electron interactions, see, e.g., Ref. [192, 193].

6.2 Single-molecule magnet with a classical spin and its spin dynamics

In this section, we focus on deriving the spin equation of motion for a molecular magnet with a classical spin. We start by considering the spin-spin interaction from the Keldysh action. After that, we add other contributions to create an effective action of the spin. We, thus, derive a generalized spin equation of motion following Ref. [65, 124, 126, 127, 192]. Lastly, we show how we can simplify the generalized spin equation of motion and get the commonly used phenomenological equation Landau-Lifshitz-Gilbert (LLG) [128]. For more information about field theory of condensed matter see, e.g., Ref. [7, 8, 194].

6.2.1 Effective spin-spin interaction

For calculating the effective spin-spin interaction in an electronic background we start by deriving an expression for the effective interaction. We are interested in the interaction between spins in a nonequilibrium environment, thus, we start from a field theoretical approach on the Keldysh contour.

The partition function can be defined as a path integral over the bosonic and fermionic degress of freedom as

$$\mathcal{Z} = \mathcal{Z}_0^{-1} \int \mathcal{D}\eta \int \mathcal{D}(\psi, \bar{\psi}) e^{i\mathcal{S}[\psi, \bar{\psi}, \eta]}, \tag{6.4}$$

where the Keldysh action is given by

$$\mathcal{S}[\psi, \bar{\psi}, \eta] = \int dt \bar{\psi}(t) \left(i\hbar \frac{\partial}{\partial t} - \mathcal{H}_0 - \mathcal{H}_I \right) \psi(t). \tag{6.5}$$

Here, $\psi(t)$ denotes the fermionic fields (Grassman variables) and is a spinor specified by the upper and lower Keldysh components $\psi(t) = (\psi_u(t), \psi_l(t))^T$ on the Keldysh contour. The Hamiltonian $\mathcal{H}_0$ denotes the Hamiltonian for the fermionic degrees of freedom, excluding the interaction with the spins, whereas the Hamiltonian $\mathcal{H}_I$ contains the electron-spin interaction and the spin degrees

of freedom. The bosonic field operator $\eta(t)$ for the spins is constructed such that $\eta(t) = (\eta_1(t), \eta_2(t), \eta_3(t)) \in S^2$.

Performing the integral over the fermionic degrees of freedom gives

$$
\begin{aligned}
\mathcal{Z} &= \mathcal{Z}_0^{-1} \int \mathcal{D}\eta \det \left| (-i) \left(i\hbar \frac{\partial}{\partial t} - \mathcal{H}_0 - \mathcal{H}_I \right) \right| \\
&= \mathcal{Z}_0^{-1} \int \mathcal{D}\eta \det \left| (-i) \left(G^{-1} - \mathcal{H}_I \right) \right| \\
&= \mathcal{Z}_0^{-1} \int \mathcal{D}\eta \exp \left[\ln \left(\det \left| (-i) \left(G^{-1} - \mathcal{H}_I \right) \right| \right) \right] \\
&= \mathcal{Z}_0^{-1} \int \mathcal{D}\eta e^{-\mathcal{S}_{eff}^I[\eta]},
\end{aligned}
\tag{6.6}
$$

where we defined $G^{-1} = i\hbar \frac{\partial}{\partial t} - \mathcal{H}_0$ as the bare fermionic Green's function and

$$
\mathcal{S}_{eff}^I[\eta] = -\ln \left(\det \left| (-i) \left(G^{-1} - \mathcal{H}_I \right) \right| \right).
\tag{6.7}
$$

$\mathcal{S}_{eff}^I[\eta]$ represents the effective action for the spin interactions and can be expanded as

$$
\begin{aligned}
\mathcal{S}_{eff}^I[\eta] &= -\ln \left(\det \left| (-i) \left(G^{-1} - \mathcal{H}_I \right) \right| \right) \\
&= -\mathrm{Tr} \left(\ln \left| (-i) G^{-1} \left(1 - G\mathcal{H}_I \right) \right| \right) \\
&= -\mathrm{Tr} \left(\ln \left| (-i) G^{-1} \right| \right) - \mathrm{Tr} \left(\ln \left| (1 - G\mathcal{H}_I) \right| \right) \\
&= -\mathrm{Tr} \left(\ln \left| (-i) G^{-1} \right| \right) + \mathrm{Tr} \left(G\mathcal{H}_I \right) + \frac{1}{2} \mathrm{Tr} \left(G\mathcal{H}_I \right) \left(G\mathcal{H}_I \right) + ...
\end{aligned}
\tag{6.8}
$$

In the last step, we used the Taylor expansion of the natural logarithm. We limit our discussion to the second order, ignoring higher order terms.

In the case of spin-spin interactions given by the Kondo model, the interaction Hamiltonian will become $\mathcal{H}_I = -v\boldsymbol{\sigma} \cdot \mathbf{S}$, where $\mathbf{S}$ denotes the spin, v the exchange interaction strength and where we have integrated out the fermionic degrees of freedom. As the Green's function G contains the fermionic degrees of freedom, the combined product $G\mathcal{H}_I$ can be written as $-v\mathbf{s} \cdot \mathbf{S}$ where $\mathbf{s} = \psi^\dagger \boldsymbol{\sigma} \psi / 2 = \sum_{\sigma\sigma'} d_\sigma^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} d_{\sigma'} / 2$.

We now evaluate the effective action for the spin interactions given by the Kondo model. The first term can be ignored as it only contains fermionic degrees of freedom. Evaluating the second term of the effective action gives

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the interaction with the effective local electronic spin moment

$$\text{Tr}\left(G(t,t)\mathcal{H}_I(t)\right) = -v\oint_C dt\,\langle\text{T}\,\mathbf{s}(t)\cdot\mathbf{S}(t)\rangle$$

$$= -v\oint_C dt\,\left\langle\text{T}\sum_{\sigma\sigma'}(d_\sigma^\dagger\boldsymbol{\sigma}_{\sigma\sigma'}d_{\sigma'})(t)/2\cdot\mathbf{S}(t)\right\rangle$$

$$= -\frac{v}{2}\sum_{\sigma\sigma'}\oint_C dt\,\left\langle\text{T}(d_\sigma^\dagger d_{\sigma'})(t)\right\rangle\boldsymbol{\sigma}_{\sigma\sigma'}\cdot\mathbf{S}(t)$$

$$= i\frac{v}{2}\sum_{\sigma\sigma'}\oint_C dt\,G_{\sigma\sigma'}^<(t,t^+)\boldsymbol{\sigma}_{\sigma\sigma'}\cdot\mathbf{S}(t)$$

$$= i\frac{v}{2}\sum_{\sigma\sigma'}\int_{-\infty}^\infty dt\,G_{\sigma\sigma'}^<(t,t^+)\boldsymbol{\sigma}_{\sigma\sigma'}\cdot(\mathbf{S}^u(t)-\mathbf{S}^l(t))$$

$$= i\frac{v}{2}\int_{-\infty}^\infty dt\,\text{sp}\boldsymbol{\sigma}\mathbf{G}^<(t,t)\cdot\mathbf{S}^q(t)$$

$$= -v\int_{-\infty}^\infty dt\,\mathbf{m}(t)\cdot\mathbf{S}^q(t). \tag{6.9}$$

Here, we replaced Tr with $\oint_C dt < x >$, T is the time-ordering operator and and sp is the trace over spin space. The spin operators $\mathbf{S}^c$ and $\mathbf{S}^q$, represent the classical and quantum spin operators, defined as $\mathbf{S}^c = (\mathbf{S}^u + \mathbf{S}^l)/2$ and $\mathbf{S}^q = \mathbf{S}^u - \mathbf{S}^l$. Here, the superscripts u (l) denotes the spin operators on the upper and lower part of the Keldysh contour, respectively, and we have performed a rotation in Keldysh space in order to get the classical and quantum spin operators. We defined the local magnetic occupation as $\mathbf{m}(t) = \langle\mathbf{s}(t)\rangle = \frac{1}{2}\langle\psi(t)^\dagger\boldsymbol{\sigma}\psi(t)\rangle = -\frac{i}{2}\text{sp}\boldsymbol{\sigma}\mathbf{G}^<(t,t) = \frac{1}{2}\text{Im}\,\text{sp}\boldsymbol{\sigma}\mathbf{G}^<(t,t)$ where $\mathbf{G}^<(t,t)$ is the equal-time lesser Green's function in spin space.

The third term of the effective action gives the spin-spin interaction through the electronic background

$$\frac{1}{2}\text{Tr}\left(G(\tau,t)\mathcal{H}_I(t)\right)\left(G(\tau,t')\mathcal{H}_I(t')\right)$$

$$= \frac{1}{2}v^2\oint_C dt\,\langle\text{T}\,\mathbf{s}(t)\cdot\mathbf{S}(t)\rangle\oint_{C'} dt'\,\langle\text{T}\,\mathbf{s}(t')\cdot\mathbf{S}(t')\rangle$$

$$= \frac{v^2}{2}\oint_C\oint_{C'} dt\,dt'\mathbf{S}(t)\cdot\text{sp}\left(\boldsymbol{\sigma}\mathbf{G}(t,t')\boldsymbol{\sigma}\mathbf{G}(t',t)\right)\cdot\mathbf{S}(t'). \tag{6.10}$$

The term $\text{sp}\left(\boldsymbol{\sigma}\mathbf{G}(t,t')\boldsymbol{\sigma}\mathbf{G}(t',t)\right)$ is the electronically mediated spin-spin interaction and will be investigated in more detail. Note that $\mathbf{S}$ is here a contour ordered operator and $\mathbf{G}(t,t')$ is a contour ordered Green's function and needs to be expanded onto the upper and lower branch in order to be properly addressed, see Chapter 12 in Ref. [192] for more detail.

6.2.2 Effective spin action

We define the effective spin action for the free spin in order to derive the spin equation of motion. It is done on the Keldysh contour as the system is treated in nonequilibrium. For a spin system, the effective action is defined as

$$\mathcal{S}_{eff} = \mathcal{S}_{\text{WZWN}} + \oint_C dt\mathcal{H}. \tag{6.11}$$

Here, $\mathcal{S}_{\text{WZWN}} = \int dt\mathbf{S}^q(t) \cdot [\mathbf{S}^c(t) \times \partial_t\mathbf{S}^c(t)]/|\mathbf{S}|^2$ is the Wess-Zumino-Witten-Novikov (WZWN) term. This term originates from taking the path integral of the quantum mechanical spins over the sphere S_2 describing the topological Berry phase accumulated by the local spins. For more information, see Chapter 7 in Ref. [194].

Following the derivation that is presented in Chapter 12 in Ref. [192], the effective action can then be written as

$$\mathcal{S}_{eff} = \mathcal{S}_{\text{WZWN}} - g\mu_B \int dt\mathbf{B}(t) \cdot \mathbf{S}^q(t) - v \int dt\mathbf{m}(t) \cdot \mathbf{S}^q(t)$$
$$+ \frac{1}{e} \iint dtdt'\mathbf{j}(t,t') \cdot \mathbf{S}^q(t) + \frac{1}{e} \iint dtdt'\mathbf{S}^q(t) \cdot \mathbb{J}(t,t') \cdot \mathbf{S}^c(t')$$
$$+ \frac{1}{e} \iint dtdt'\mathbf{S}^q(t) \cdot \mathbb{J}^K(t,t') \cdot \mathbf{S}^q(t'). \tag{6.12}$$

Here, the second term denotes the Zeeman coupling to a magnetic field and $\mathbf{B}(t)$ is the external magnetic field. The last three terms originates from the previously derived spin-spin interaction $\text{sp}(\boldsymbol{\sigma}\mathbf{G}\boldsymbol{\sigma}\mathbf{G})$ after performing the Keldysh rotation. The fourth term, $\mathbf{j}(t,t') = iev\theta(t-t')\langle[s^{(0)}(t), s(t')]\rangle$, provides the magnetic field due to the electron flow where $s^{(0)} = \sum_\sigma \varepsilon_\sigma d_\sigma^\dagger d_{\sigma'}/2$ represents the charge flow. This field can be approximated as

$$\mathbf{j}(t,t') \approx iev\theta(t-t')\text{sp}\boldsymbol{\epsilon}\left(\mathbf{G}^<(t,t')\boldsymbol{\sigma}\mathbf{G}^>(t',t)\right.$$
$$\left. -\mathbf{G}^>(t,t')\boldsymbol{\sigma}\mathbf{G}^<(t',t)\right)/4. \tag{6.13}$$

Here, $\boldsymbol{\epsilon} = \text{diag}\{\varepsilon_\uparrow, \varepsilon_\downarrow\}$ represent the electron energy states and we did the approximation

$$\langle \text{T}\, s^0(t)s(t')\rangle = \frac{1}{4}\sum_{\sigma ss'}\varepsilon_\sigma\langle \text{T}\, d_\sigma^\dagger(t)d_\sigma(t)d_s^\dagger(t')\sigma_{ss'}d_{s'}(t')\rangle$$
$$= \frac{1}{4}\sum_{\sigma ss'}\varepsilon_\sigma\sigma_{ss'}\left(-\langle \text{T}\, d_\sigma(t)d_s^\dagger(t')\rangle\langle \text{T}\, d_{s'}(t')d_\sigma^\dagger(t)\rangle\right.$$
$$\left. +\langle \text{T}\, d_\sigma^\dagger(t)d_\sigma(t)\rangle\langle \text{T}\, d_s^\dagger(t')d_{s'}(t')\rangle\right)$$
$$\approx -\frac{(i)^2}{4}\sum_{\sigma ss'}\varepsilon_\sigma\sigma_{ss'}\mathbf{G}_{\sigma s}(t,t')\mathbf{G}_{s'\sigma}(t',t)$$
$$= \frac{1}{4}\text{sp}\boldsymbol{\epsilon}\mathbf{G}(t,t')\boldsymbol{\sigma}\mathbf{G}(t',t). \tag{6.14}$$

Here, the correlated contribution of the electrons is assumed to be negligible.

The fifth term, which involves the field $\mathbb{J}(t,t') = i2ev^2\theta(t - t')\langle[\boldsymbol{s}(t), \boldsymbol{s}(t')]\rangle$, carries the memory of magnetic anisotropy and exchange interactions for the local magnetic moment. It can be approximated as

$$\mathbb{J}(t,t') \approx \frac{ie}{2}v^2\theta(t-t')\mathrm{sp}\boldsymbol{\sigma}\left(\mathbf{G}^<(t,t')\boldsymbol{\sigma}\mathbf{G}^>(t',t)\right.$$
$$\left. -\mathbf{G}^>(t,t')\boldsymbol{\sigma}\mathbf{G}^<(t',t)\right), \tag{6.15}$$

where we did the analogues approximation

$$\langle\mathrm{T}\,\boldsymbol{s}(t)\boldsymbol{s}(t')\rangle = \frac{1}{4}\sum_{\sigma\sigma'ss'}\langle\mathrm{T}\,d_\sigma^\dagger(t)\sigma_{\sigma\sigma'}d_{\sigma'}(t)d_s^\dagger(t')\sigma_{ss'}d_{s'}(t')\rangle$$
$$= \frac{1}{4}\sum_{\sigma\sigma'ss'}\sigma_{\sigma\sigma'}\sigma_{ss'}\left(-\langle\mathrm{T}\,d_{\sigma'}(t)d_s^\dagger(t')\rangle\langle\mathrm{T}\,d_{s'}(t')d_\sigma^\dagger(t)\rangle\right.$$
$$\left. +\langle\mathrm{T}\,d_\sigma^\dagger(t)d_{\sigma'}(t)\rangle\langle\mathrm{T}\,d_s^\dagger(t')d_{s'}(t')\rangle\right)$$
$$\approx -\frac{(i)^2}{4}\sum_{\sigma\sigma'ss'}\sigma_{\sigma\sigma'}\sigma_{ss'}\mathbf{G}_{\sigma s}(t,t')\mathbf{G}_{s'\sigma}(t',t)$$
$$= \frac{1}{4}\mathrm{sp}\boldsymbol{\sigma}\mathbf{G}(t,t')\boldsymbol{\sigma}\mathbf{G}(t',t). \tag{6.16}$$

The last term, which involves the Keldysh component, $\mathbb{J}^K(t,t') = iev^2\langle\{\boldsymbol{s}(t), \boldsymbol{s}(t')\}\rangle$, defines the electronically mediated interactions between the spin operators $\mathbf{S}^q(t)$ and $\mathbf{S}^q(t')$. It carries the quantum-quantum correlations and is usually viewed as a quantum fluctuation. By doing a Hubbard-Stratonovich transformation, that will linearize the equation, one introduces a stochastic field represented by the Gaussian random variables $\xi(t)$. This can be treated by a Fokker-Planck type of equation, where one get a contribution of the form $\gamma\mathbf{S}(t) \times \xi(t)$ in the spin equation of motion. Under certain conditions this contribution can be interpreted as a random magnetic field acting on the spin and the random variable ξ is defined by the electronic correlations through $(g\mu_B)^2\langle\xi(t)\xi(t')\rangle = -i2\mathbb{J}^K(t,t')/e$. In the wide band limit, used in this thesis, it can be shown that the stochastic fields is of Gaussian white noise character, and we choose to omit this contribution as it will result in a thermal smearing of the results. Although, for a more complete description of the problem, it can be of importance, and it is important to be aware of the fact that we do not take it into consideration when analyzing the results.

6.2.3 Spin equation of motion

We are interested in the dynamics of the spin moment and its exchange interaction with the quantum dot. Thus, we want to focus on the equation of motion for the local spin moment. It is derived from the effective action of the

spin, defined in the previous section. By taking the functional derivative of the effective action and setting it to zero gives

$$0 = \frac{\mathcal{S}_{eff}}{\delta \mathbf{S}^q(t)} = \frac{1}{S^2}\mathbf{S}^c(t) \times \dot{\mathbf{S}}^\mathbf{c}(t) - g\mu_B \mathbf{B}(t) - v\mathbf{m}(t)$$

$$+ \frac{1}{e}\int dt'\Big(\mathbf{j}(t,t') + \mathbf{J}(t,t') \cdot \mathbf{S}^c(t')\Big). \qquad (6.17)$$

Here, we omit the quantum-quantum fluctuations carried in the term $\frac{1}{e}\iint dt dt' \mathbf{S}^q(t) \cdot \mathbb{J}^K(t,t') \cdot \mathbf{S}^q(t')$, as discussed in the previous section. We can drop the superscript and take the cross product from the left with $\mathbf{S}(t)\times$ to get

$$0 = \frac{1}{S^2}\mathbf{S}(t) \times \Big[\mathbf{S}(t) \times \dot{\mathbf{S}}(t)\Big] - g\mu_B \mathbf{S}(t) \times \mathbf{B}^{\text{eff}}(t) + \frac{1}{e}\int dt' \mathbf{S}(t) \times J(t,t') \cdot \mathbf{S}(t'),$$

$$(6.18)$$

where an effective magnetic field is defined as $\mathbf{B}^{\text{eff}}(t) = \mathbf{B}(t) + \frac{v}{g\mu_B}\mathbf{m}(t) - \frac{1}{eg\mu_B}\int dt'\mathbf{j}(t,t')$. Assuming that the length of the spin is constant and that it can be treated classically, we set $\partial_t |\mathbf{S}(t)|^2 = 0$, such that the first term can be simplified to $-\dot{\mathbf{S}}(t)$ and moved to the left hand side. The resulting equation of motion becomes

$$\dot{\mathbf{S}}(t) = -g\mu_B \mathbf{S}(t) \times \mathbf{B}^{\text{eff}}(t) + \frac{1}{e}\mathbf{S}(t) \times \int dt' \mathbb{J}(t,t') \cdot \mathbf{S}(t'). \qquad (6.19)$$

This current mediated interaction can be decomposed into an isotropic Heisenberg, J_H, anisotropic Dzyaloshinski-Moriya (DM), $\mathbf{D}$, and Ising, $\mathbb{I}$, interactions. This can be seen from the product $\mathbf{S} \cdot \mathbb{J} \cdot \mathbf{S}$, which is the corresponding contribution in the effective spin model to $\mathbf{S}(t) \times \mathbb{J}(t,t') \cdot \mathbf{S}(t')$ in the spin equation of motion. Using the general partitioning $\mathbf{G} = G_0\sigma^0 + \mathbf{G}_1 \cdot \boldsymbol{\sigma}$, where G_0 and $\mathbf{G}_1$ describes the electronic charge and spin, it is straight forward to see that

$$\text{sp}\mathbf{S} \cdot \boldsymbol{\sigma}\mathbf{G}\boldsymbol{\sigma}\mathbf{G} \cdot \mathbf{S}$$
$$= \text{sp}\mathbf{S} \cdot \boldsymbol{\sigma}(G_0\sigma^0 + \mathbf{G}_1 \cdot \boldsymbol{\sigma})\boldsymbol{\sigma}(G_0\sigma^0 + \mathbf{G}_1 \cdot \boldsymbol{\sigma}) \cdot \mathbf{S}$$
$$= \text{sp}\Big(\mathbf{S} \cdot \mathbf{G}_1 + [SG_0 + i\mathbf{S} \times \mathbf{G}_1] \cdot \boldsymbol{\sigma}\Big)\Big(\mathbf{G}_1 \cdot \mathbf{S} + [G_0\mathbf{S} - i\mathbf{G}_1 \times \mathbf{S}] \cdot \boldsymbol{\sigma}\Big),$$
$$(6.20)$$

where we have used the identity mentioned in Section 4.4. As the Pauli matrices are traceless, the above expression reduces to

$$2\Big(\mathbf{S} \cdot (\mathbf{G}_1\mathbf{G}_1) \cdot \mathbf{S} + [S G_0 + i\mathbf{S} \times \mathbf{G}_1] \cdot [G_0\mathbf{S} - i\mathbf{G}_1 \times \mathbf{S}]\Big). \qquad (6.21)$$

After a little more algebra we obtain the Heisenberg (J_H), anisotropic Ising ($\mathbb{I}$) and anisotropic Dzyaloshinskii-Moriya (**D**) interactions

$$
\begin{aligned}
J_H(t,t') = {} & iev^2\theta(t-t')\Big(G_0^<(t,t')G_0^>(t',t) \\
& -G_0^>(t,t')G_0^<(t',t) - \mathbf{G}_1^<(t,t')\cdot\mathbf{G}_1^>(t',t) \\
& +\mathbf{G}_1^>(t,t')\cdot\mathbf{G}_1^<(t',t)\Big),
\end{aligned}
\tag{6.22a}
$$

$$
\begin{aligned}
\mathbb{I}(t,t') = {} & iev^2\theta(t-t')\Big(\mathbf{G}_1^<(t,t')\mathbf{G}_1^>(t',t) \\
& -\mathbf{G}_1^>(t,t')\mathbf{G}_1^<(t',t) + [\mathbf{G}_1^<(t,t')\mathbf{G}_1^>(t',t) \\
& -\mathbf{G}_1^>(t,t')\mathbf{G}_1^<(t',t)]^t\Big),
\end{aligned}
\tag{6.22b}
$$

$$
\begin{aligned}
\mathbf{D}(t,t') = {} & -ev^2\theta(t-t')\Big(G_0^<(t,t')\mathbf{G}_1^>(t',t) \\
& -G_0^>(t,t')\mathbf{G}_1^<(t',t) - \mathbf{G}_1^<(t,t')G_0^>(t',t) \\
& +\mathbf{G}_1^>(t,t')G_0^<(t',t)\Big).
\end{aligned}
\tag{6.22c}
$$

This leads to that we can partition the current mediated spin-spin interaction in the spin equation of motion into

$$
\begin{aligned}
\mathbf{S}(t)\times\mathbb{J}(t,t')\cdot\mathbf{S}(t') = {} & J_H(t,t')\mathbf{S}(t)\times\mathbf{S}(t') \\
& + \mathbf{S}(t)\times\mathbb{I}(t,t')\cdot\mathbf{S}(t') \\
& - \mathbf{S}(t)\times\mathbf{D}(t,t')\times\mathbf{S}(t').
\end{aligned}
\tag{6.23}
$$

It can be noted that in the case of a spin-independent Green's function, i.e., $\mathbf{G}_1 = 0$, there is only Heisenberg interaction. In the case where one treats the back-action from the local magnetic moment in the quantum dot there will always be spin-dependence in the Green's function as it induces a local Zeeman split in the quantum dot, see Eq. (4.40).

Calculating the current $\mathbf{j}(t,t')$ gives

$$
\begin{aligned}
\mathbf{j}(t,t') = {} & 2vie\theta(t-t')\left(\left[\varepsilon_0 G_0^<(t,t') + \Delta\hat{\mathbf{z}}\cdot\mathbf{G}_1^<(t,t')\right]\mathbf{G}_1^>(t',t)\right. \\
& - \left[\varepsilon_0 G_0^>(t,t') + \Delta\hat{\mathbf{z}}\cdot\mathbf{G}_1^>(t,t')\right]\mathbf{G}_1^<(t',t) \\
& + \left[\varepsilon_0\mathbf{G}_1^<(t,t') + \Delta\hat{\mathbf{z}} + i\hat{\mathbf{z}}\times\mathbf{G}_1^<(t,t')\right]G_0^>(t',t) \\
& - \left[\varepsilon_0\mathbf{G}_1^>(t,t') + \Delta\hat{\mathbf{z}} + i\hat{\mathbf{z}}\times\mathbf{G}_1^>(t,t')\right]G_0^<(t',t) \\
& - i\left[\varepsilon_0\mathbf{G}_1^<(t,t') + \Delta\hat{\mathbf{z}} + i\hat{\mathbf{z}}\times\mathbf{G}_1^<(t,t')\right]\times\mathbf{G}_1^>(t',t) \\
& \left. + i\left[\varepsilon_0\mathbf{G}_1^>(t,t') + \Delta\hat{\mathbf{z}} + i\hat{\mathbf{z}}\times\mathbf{G}_1^>(t,t')\right]\times\mathbf{G}_1^<(t',t)\right),
\end{aligned}
\tag{6.24}
$$

where $\Delta = g\mu_B B_z/2$ is defined.

Furthermore, the local magnetic occupation can be simplified as $\mathbf{m}(t) = \frac{1}{2}\text{Im sp}\boldsymbol{\sigma}\mathbf{G}^<(t,t) = \text{Im}\mathbf{G}_1^<(t,t)$.

6.2.4 The effective field and exchange

The generalized spin equation of motion is quite complex and constitutes of several parts. In order to get a clear description we go through the different terms of the equation in this section.

The effective magnetic field $\mathbf{B}^{\text{eff}}(t)$ constitutes of three different parts. The first one, $\mathbf{B}(t)$, is a simple Zeeman coupling to an external magnetic field, which makes the spin precess in the corresponding field direction. The second term, $\mathbf{m}(t)$, is the local magnetic occupation of the quantum dot. It provides a local field similar to the external field for the spin to precess. The third term, given by $\mathbf{j}(t, t')$, corresponds to the field generated by the current flowing through the dot.

The field generated by the current is the most important term when considering high currents and can be of three to four orders of magnitude larger than the local dot occupation. For low currents, the local dot magnetic occupation is of more importance as it interacts more strongly with the localized spin moment in the molecule.

The exchange interaction between the spins, described by the spin-spin susceptibility tensor, $\mathbb{J}(t, t')$, can be partitioned into three different parts, as stated in the previous section. Effectively this corresponds to the Hamiltonian

$$\mathscr{H} = \mathbf{S} \cdot (\mathbf{J}_H \mathbf{S} + \mathbb{I} \cdot \mathbf{S} + \mathbf{D} \times \mathbf{S}) . \tag{6.25}$$

Here, the first term corresponds to a Heisenberg-like interaction and is therefore a scalar interaction which is minimized as the two spins are parallel for a negative $\mathbf{J}_H$. It is isotropic, i.e., direction independent, and will create a degenerate ground-state of spin-up and spin-down solution for a single spin.

The second term, $\mathbb{I}$, is a tensorial quantity and corresponds to a Ising-like interaction. It will introduce an uniaxial anisotropy in the system, creating an easy axis for the spins to align. In the case of a single spin, there needs to be a magnetization in the local environment for it to effect the spin dynamics, either from an external magnetic field or polarized leads. This is due to that $\mathbb{I} \propto \mathbf{G}_1 \mathbf{G}_1 \propto \mathbf{S}\mathbf{S}$ if there is no magnetization, i.e., it will want to align with itself.

The third term, $\mathbf{D}$, is a Dzyaloshinskii-Moriya-like interaction and corresponds to a vector. This will apply a spin-transfer torque to the spin, partly due to the flow of spins in the system. This term usually arises as one includes spin-orbit coupling, although, in this case it appears as one breaks time-reversal and inversion symmetry of the out-of-eqilibrium system. Therefore it will provide an effective torque on the local spin, either through a pulse or a spin current.

6.2.5 Landau-Lifshitz-Gilbert equation

In this section, we will show how we can derive the LLG equation from the generalized equation of motion. The extended LLG equation is defined as

$$\dot{\mathbf{S}} = \mathbf{S} \times (-\gamma\mathbf{B} + \hat{\mathbf{G}}\dot{\mathbf{S}} + \hat{\mathbf{I}}\ddot{\mathbf{S}}), \qquad (6.26)$$

where $\hat{\mathbf{G}}$ and $\hat{\mathbf{I}}$ is the Gilbert damping and the moment of inertia tensor, respectively. The difference between this equation and the previously derived generalized spin equation of motion, is that the parameters, in the spin equation of motion itself, is time-dependent and depends on the history of the system. Usually, in the treatment of LLG, one solves for a history-independent and time-independent parameters.

In order to retrieve the LLG equation from the spin equation of motion, we perform a Taylor expension of the spin, i.e., $\mathbf{S}(t') = \mathbf{S}(t) - (t - t')\dot{\mathbf{S}}(t) + (t - t')^2\ddot{\mathbf{S}}(t)/2$, and get that

$$\frac{1}{e}\int \mathbb{J}(t,t') \cdot \mathbf{S}(t')dt' \approx \frac{1}{e}\left(\int \mathbb{J}(t,t')dt'\mathbf{S}(t) - \int \mathbb{J}(t,t')(t-t')dt'\dot{\mathbf{S}}(t) \right.$$
$$\left. + \int \mathbb{J}(t,t')(t-t')^2 dt'\ddot{\mathbf{S}}(t)/2\right). \qquad (6.27)$$

Here, the second term corresponds to the Gilbert damping and the third term to the moment of inertia. Just considering the Gilbert damping, the spin equation of motion simplifies to

$$\dot{\mathbf{S}}(t) = \mathbf{S}(t) \times \left(-g\mu_B\mathbf{B}_1^{\text{eff}}(t) - \frac{1}{e}\int \mathbb{J}(t,t')(t-t')dt'\dot{\mathbf{S}}(t)\right), \qquad (6.28)$$

where the first term is defined as $\mathbf{B}_1^{\text{eff}}(t) = \mathbf{B}^{\text{eff}}(t) - \frac{1}{eg\mu}\int \mathbb{J}(t,t')dt'\mathbf{S}(t)$. We identify the factor in front of the first term as γ, the second term as the damping tensor and define it as $\hat{\mathbf{G}} = -\frac{1}{e}\int \mathbb{J}(t,t')(t-t')dt'$. Thus, the equation can be written on the form $\dot{\mathbf{S}} = \mathbf{S} \times (-\gamma\mathbf{B} + \hat{\mathbf{G}}\dot{\mathbf{S}})$.

The big difference between this LLG equation and the generalized spin equation of motion is that the full history of the spin is discarded and that it is approximated to the first or second order. In many cases this is a valid approximation, although in the present study, the focus is to get all effects, even the ones depending on the history of the spin. So far, the parameters are still treated to be time-dependent, although, they are usually treated as constant in atomistic spin dynamics calculations. In the next section we will look at the further simplification and see how one can derive constant parameters for the LLG equation.

6.2.6 LLG with constant exchange coupling

For slow dynamics, the exchange parameters in the LLG equation can be considered constant. For the most simple case, the LLG equation simplifies to

$$\dot{\mathbf{S}}(t) = \mathbf{S}(t) \times \left(-g\mu_B \mathbf{B}_1^{\text{eff}} + \hat{\mathbf{G}} \cdot \dot{\mathbf{S}}(t) \right). \tag{6.29}$$

First, we derive the parameters in the effective magnetic field, $\mathbf{B}_1^{\text{eff}}(t) = \mathbf{B}^{\text{eff}}(t) - \int \mathbb{J}(t,t')dt'\mathbf{S}(t)$. In the time-independent limit, the electron spin-spin correlation function can be Fourier transformed into energy space

$$\mathbb{J}(\epsilon) = \frac{e}{2}v^2 \int \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi} \frac{1}{\omega + \epsilon - \omega' + i\delta} \text{sp}\boldsymbol{\sigma} \Big(\mathbf{G}^<(\omega)\boldsymbol{\sigma}\mathbf{G}^>(\omega')$$
$$- \mathbf{G}^>(\omega)\boldsymbol{\sigma}\mathbf{G}^<(\omega') \Big). \tag{6.30}$$

Here, we used the fact that in the stationary limit, the Green's function can be rewritten as $G(t,t') = G(t-t') = G(\tau)$, and δ was added in order for the integration to converge as $\tau = t-t'$ goes to infinity, $\lim\limits_{\tau \to \infty} \exp(i(\omega' - \epsilon - \omega)\tau - \delta\tau)$.

If we take the limit $\epsilon \to 0$, we get for the internal field

$$\begin{aligned}
\mathbf{j}(t,t') = \ & -2v \int \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi} \frac{1}{\omega + \epsilon - \omega' + i\delta} \\
& \left([\varepsilon_0 G_0^<(\omega) + \Delta\hat{\mathbf{z}} \cdot \mathbf{G}_1^<(\omega)] \mathbf{G}_1^>(\omega') \right. \\
& - [\varepsilon_0 G_0^>(\omega) + \Delta\hat{\mathbf{z}} \cdot \mathbf{G}_1^>(\omega)] \mathbf{G}_1^<(\omega') \\
& + [\varepsilon_0 \mathbf{G}_1^<(\omega) + \Delta\hat{\mathbf{z}} + i\hat{\mathbf{z}} \times \mathbf{G}_1^<(\omega)] G_0^>(\omega') \\
& - [\varepsilon_0 \mathbf{G}_1^>(\omega) + \Delta\hat{\mathbf{z}} + i\hat{\mathbf{z}} \times \mathbf{G}_1^>(\omega)] G_0^<(\omega') \\
& -i [\varepsilon_0 \mathbf{G}_1^<(\omega) + \Delta\hat{\mathbf{z}} + i\hat{\mathbf{z}} \times \mathbf{G}_1^<(\omega)] \times \mathbf{G}_1^>(\omega') \\
& +i [\varepsilon_0 \mathbf{G}_1^>(\omega) + \Delta\hat{\mathbf{z}} + i\hat{\mathbf{z}} \times \mathbf{G}_1^>(\omega)] \\
& \left. \times \mathbf{G}_1^<(\omega'), \right.
\end{aligned} \tag{6.31}$$

and for the decomposed exchange interaction

$$J^{(H)} = - v^2 \int \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi} \frac{1}{\omega + \epsilon - \omega' + i\delta} \left(G_0^<(\omega) G_0^>(\omega') - G_0^>(\omega) G_0^<(\omega') \right.$$
$$\left. - \mathbf{G}_1^<(\omega) \cdot \mathbf{G}_1^>(\omega') + \mathbf{G}_1^>(\omega) \cdot \mathbf{G}_1^<(\omega') \right), \tag{6.32a}$$

$$\mathbb{I} = - v^2 \int \frac{d\omega}{2\pi} \frac{d\omega'}{2\pi} \frac{1}{\omega + \epsilon - \omega' + i\delta} \left(\mathbf{G}_1^<(\omega) \mathbf{G}_1^>(\omega') - \mathbf{G}_1^>(\omega) \mathbf{G}_1^<(\omega') \right.$$
$$\left. + \left[\mathbf{G}_1^<(\omega) \mathbf{G}_1^>(\omega') - \mathbf{G}_1^>(\omega) \mathbf{G}_1^<(\omega') \right]^t \right), \tag{6.32b}$$

$$\mathbf{D} = \frac{v^2}{2} \mathrm{Re} \int \frac{d\omega}{2\pi} \left(G_0^<(\omega + \epsilon) \mathbf{G}_1^>(\omega) - G_0^>(\omega + \epsilon) \mathbf{G}_1^<(\omega) \right.$$
$$\left. - \mathbf{G}_1^<(\omega + \epsilon) G_0^>(\omega) + \mathbf{G}_1^>(\omega + \epsilon) G_0^<(\omega) \right). \tag{6.32c}$$

Here, Kramer-Kronig relations were used in the last row.

In the time-independent limit the Gilbert damping can be derived from

$$\hat{\mathbf{G}} = -\frac{1}{e} \int \mathbb{J}(t, t')(t - t') dt' = -\frac{1}{e} lim_{\epsilon \to 0} i \partial_\epsilon \mathbb{J}(\epsilon). \tag{6.33}$$

Following a similar procedure as for the effective magnetic field, one can get the Gilbert damping in terms of Heisenberg, Ising and Dzyaloshinskii-Moriya interaction.

Part III:
Results

In this part, we will go through the results of the thesis which have been published in the accompanying papers. The results are based onto the theory defined in the previous part, where the majority of the contribution is derived. In some of the papers, further developments were made by co-authors and will be discussed in respective section. Chapter 7 treats Paper I-IV which considers the time-dependent transport characteristics of a dynamic single-molecule magnet. Chapter 8 considers the results of Paper V-VI, where electrical control of single- and multi-molecular systems is performed, and the effect on their exchange and anisotropy are considered.

# 7. Transport and spin dynamics in a single-molecule magnet

This chapter treats the developments in the thesis regarding dynamic properties of single-molecule magnets. More specifically, it considers a single-molecule magnet under the influence of time-dependent pulses. The calculations rely on the theory derived in the previous part of the thesis. There, the dynamical charge and spin-transport in a single-molecule magnet is considered, together with dynamical exchange fields and the dynamics of the magnetic moment. The results are divided into four separate works with different focus. All are briefly presented in this chapter. For more information see the papers.

First, in Paper I, general results for time-dependent spin and transport properties are calculated. It includes a thorough investigation of the system, including the stationary limit, the effect of the different exchange fields, the effect of changing the tunneling and exchange coupling as well as bias and gate voltage. Paper II investigates the difference of using a generalized spin equation of motion and the Landau-Lifshitz-Gilbert equation when calculating single-molecule spin dynamics. Paper III shows the emergence of a phase-induced switching phenomena due to applied pulses and dynamic exchange fields. The induced switching depends on the applied voltage and temporal length of the pulse. Lastly, Paper IV considers spin-dependent heat signatures of single-molecule spin dynamics driven by the spin-dependent Peltier effect.

7.1 Paper I: Time-dependent spin and transport properties of a single-molecule magnet in a tunnel junction

In Part II, the theory of a system representing a single-molecule magnet in a tunnel junction was derived. In Paper I, this theory is used to compute the result for such a system in the case of a sudden on-set of the voltage bias, see Fig. 7.1. In this transient regime, we can study the transient properties of the system.

The analysis starts with considering how the system properties can be tuned in the stationary limit, i.e., when there is no time-dependence. We show that by tuning the gate and bias voltage one can tune the effective exchange interaction of the molecule. The exchange interaction is decomposed into
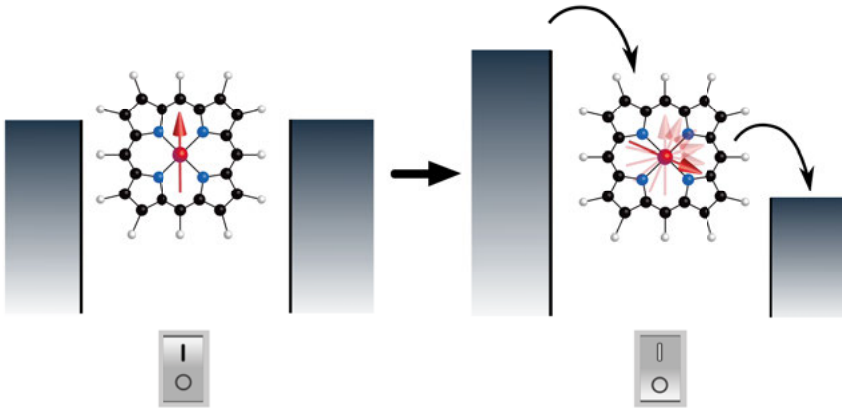
Figure 7.1. The system studied in Paper I representing a single-molecule magnet in a tunnel junction. At a time t_0 their is a sudden on-set of a bias voltage and the transient dynamics is then studied.

isotropic Heisenberg and anisotropic Ising and DM-interaction, following the procedure in section 6.2.4, which all can be tuned.

The results in the stationary limit is then extended to the time-domain by applying an abrupt on-set of a voltage bias. This initiates the dynamics of the molecule, calculated using the generalized spin equation of motion. The effective exchange fields are then calculated and a clear time-dependence in the effective exchange interaction emerges. The time-dependent exchange is clearly different than in the stationary limit. Specially, e.g., the DM-interaction is of finite character in the transient regime, although, it tends towards zero in the long-time limit. This is because the system exhibits broken time-reversal symmetry in the time-domain, due to the sudden pulse. Thus, it is of importance to treat the full dynamic exchange fields when studying pulses.

For non-magnetic leads, the system and the resulting charge current, spin currents and spin dynamics are then considered. First, the effect of different external nonequilibrium forces are investigated, such as applied gate and bias voltage. Secondly, the effect of changing the molecular interactions are investigated, such as the local exchange coupling and tunneling coupling. The evolution of the magnetic moment and the currents are then considered in order to give a description of the dynamic evolution of the system. There is a clear relation depending on the different parameters that control the dynamics. E.g., the bias and gate voltage tune the effective exchange and the resulting solutions, while the exchange coupling tunes the interaction rate and the tunneling coupling tunes the damping of the system.

The last part of the paper studies the case of ferromagnetic leads. The leads will then inject a spin-polarized current into the system, which will result in

larger anisotropies and different dynamics. There is a clear signature in the spin current depending on the different polarization of the leads as expected. This leads to a change in the potential landscape of the molecular spin, such as it alters the resulting spin dynamics. The results show that the interaction is highly anisotropic and depends on the direction of the current. That means, one can control the spin moment by driving current through one lead or the other, in agreement with previous studies [66].

In summary, we have in the paper studied the transient response and the time evolution of a local magnetic moment in a tunnel junction. We have shown that non-trivial exchange interaction appears in the time-dependent domain, especially for small time scales. Anisotropic effects occur due to time-dependence which will effect the direction of the magnetic moment. A large effective internal magnetic field occurs for small time scales and adjusts the evolution of the local magnetic moment, an effect not usually considered as it vanishes for the stationary solution. Considering time-dependent exchange interaction is thus important in small time-scale calculations and shows potential for a deeper understanding of the exchange interaction.

7.2 Paper II: Transient spin dynamics in a single-molecule magnet

In Paper II, the validity of different approximation schemes for calculating the spin dynamics of a single-molecule magnet are investigated. The main motivation is to investigate how a generalized spin equation of motion compares to the commonly used Landau-Lifshitz-Gilbert equation. The paper considers the case of transient response to an applied bias voltage over a junction with non-magnetic leads containing a single-molecule magnet.

The three different approximations used in the paper include the following. First, the generalized spin equation of motion (generalized SEOM), where the spin is treated classically using the Born-Oppenheimer approximation, for systems not in the Anderson limit where strong correlations need to be considered. Second, a time-dependent Landau-Lifshitz-Gilbert equation (tdLLG), where the generalized spin equation of motion has been Taylor expanded following the procedure in 6.2.5, keeping the interaction parameters time-dependent. Third, a Landau-Lifshitz-Gilbert equation with constant parameters (LLG), where the parameters of the equation are calculated in the stationary limit and used in order to simulate the dynamics.

The results are summarized in Fig. 7.2. It shows that for longer time-scales and smaller exchange couplings, the LLG equation suffice. When approaching stronger coupling and faster dynamics, quantum effects and the underlying dynamics of the junction needs to be considered. It is an interplay of the local exchange coupling and tunneling coupling that determines the need for more inclusive description of the underlying dynamics, and the regimes scale with
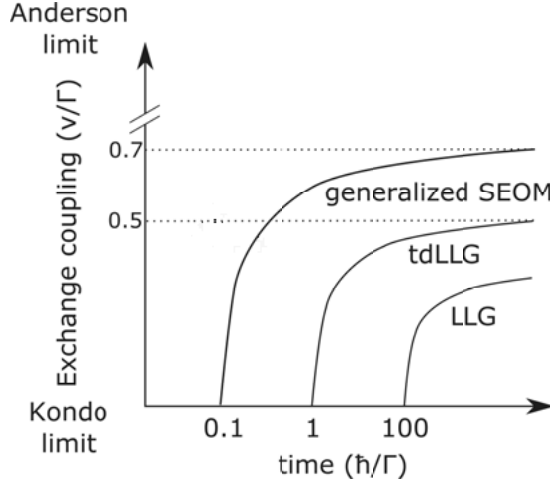
Figure 7.2. Diagram showing regimes of validity for the different approximation schemes used in Paper II. The regimes scale with time t as $t^{1/4}$. Going from slower to faster time-scales, and from low to high exchange coupling, one needs to extend the LLG equation to incorporate quantum effects. Here, the generalized SEOM denotes the general approach used in the paper, and tdLLG denotes a LLG equation with time-dependent parameters. The horizontal dotted lines indicates the limits of the exchange coupling in terms of the model parameters.

time t as $t^{1/4}$. Thus, for fast dynamics and somewhat strongly coupled systems, the generalized SEOM is needed for a full description of the dynamics.

7.3 Paper III: Dynamical exchange and phase induced switching of localized molecular spin

In Paper III, the focus is on studying the effect of a bias pulse of varying length over a junction containing a single-molecule magnet. The paper studies the effect of the dynamical exchange, which results in a phase induced switching of a localized molecular spin, see Fig. 7.3.

The phase is defined as $\varphi \equiv eV(t_1 - t_0)/\hbar$ where e is the electron charge, V is the applied bias voltage, t_0 is the time the pulse starts, t_1 is the time when the pulse ends and $\hbar$ is Plancks constant divided by 2π. The main results are shown in Fig. 7.4. Fig. 7.4 clearly shows that for $\varphi \in (2\pi, 4\pi) \mod 4\pi$ the spin flips and aligns with the magnetic field that points in the positive z-direction, while it does not for $\varphi \in (0, 2\pi) \mod 4\pi$.

The results are explained by dynamical exchange interaction, internal transient fields and self-interactions on the localized spin moment through the generalized spin equation of motion. Furthermore, the limits of the phase-induced switching is investigated. The results show that the uniaxial anisotropy and
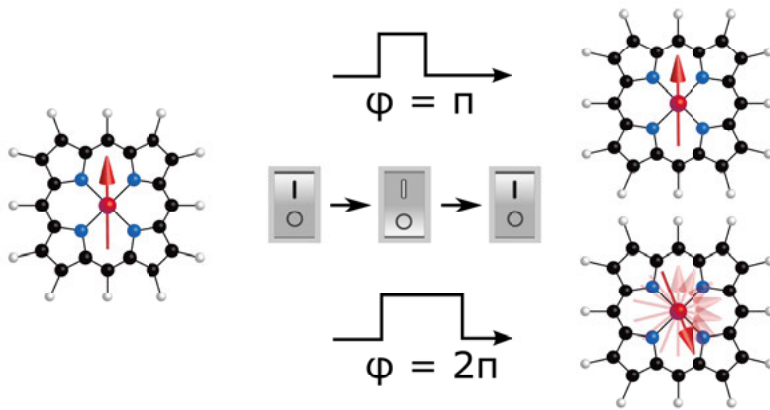
Figure 7.3. The system studied in Paper III due to pulses of varying length. A switching occurs if the pulse has a certain phase.
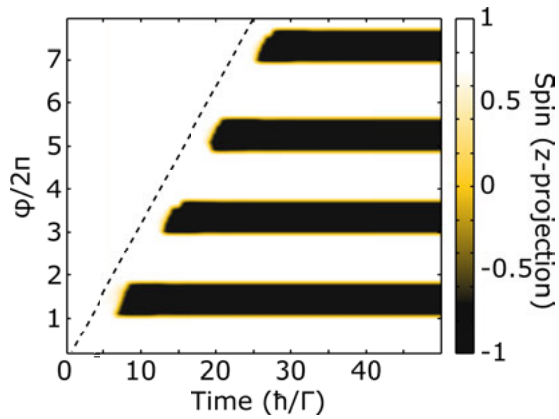

Figure 7.4. Main results of Paper III, which shows the resulting evolution of S_z, showing the spin flip for different pulse lengths, here plot against $\varphi/2\pi$. The dotted line indicates when the pulse ends.

exchange coupling have to be sufficiently large to overcome temperature fluctuations and damping mechanisms of the spin moment. There are also upper bounds on the temperature and the magnetic field for the switching to occur.

7.4 Paper IV: Spin-dependent heat signatures of single-molecule spin dynamics

Paper IV is considering thermoelectric transport through a single-molecule magnet, specially spin-dependent, and relating it to the spin dynamics of the molecular spin. The theory used is presented in Chapter 5 of this thesis. The system is investigated after applying a sudden on-set of a bias voltage.

The paper shows that one can relate the generated heat in the molecule to its charge and spin degrees of freedom. It shows that the currents can be controlled by a bias voltage and that one can create a reversal of the net heat transfer. The net reversal can be described by the presence of a magnetic field and the coupling to the magnetic moment, which creates a local Zeeman splitting in the quantum dot. This creates an energy difference for the spin-up and spin-down electrons tunneling to the junction, creating a net heat transfer. Furthermore, there is a clear relation between the spin heat current and the anisotropies of the magnetic molecule, and both can be controlled by both tunneling coupling and the local exchange interaction.

The conclusions of the paper is that the heat transfer in the molecule is related to both the charge and spin degrees of freedom. The latter is then connected to the spin-dependent Peltier effect, which can be related to the spin dynamics of the magnetic molecule.

8. Electrical control of molecular multi-spin systems and vibrating magnetic molecules

The previous chapter treated the dynamics of a single-molecule magnet and its related transport properties. This chapter treats similar systems, although, in the stationary limit. Approaching the systems in the stationary limit simplifies the treatment and means that we can consider more complicated set-ups, such as systems consisting of multiple spins and the effect of vibrations. The underlying theory is the same as in Part II of the thesis and the equations are considered in the stationary limit.

There are two papers treated in this chapter. First, Paper V treats the switching dynamics of a molecular dimer by an externally applied bias voltage. It considers the effect of non-magnetic transport through a molecular spin pair and the effects on the indirect exchange between the spins. Paper VI treats the electronically mediated magnetic anisotropy in a vibrating single-molecule magnet and the effect of vibrations on the molecular anisotropy.

8.1 Paper V: Voltage-Induced Switching Dynamics of a Coupled Spin Pair in a Molecular Junction

Paper V treats the effect of an externally applied voltage bias on a molecular spin pair coupled through electronic exchange. The system is modelled as two spins separately connected to two degenerate quantum dots. These two quantum dots are then connected to two separate metallic non-magnetic leads and between themselves. The quantum dots provide the electronic structure for which the two spins interact, much like the case of the quantum dot in a single-molecule magnet as treated in the previous chapter. As the electronic structure is non-magnetic, the interaction between the two spins is of isotropic Heisenberg interaction. By applying a bias voltage over the junction, the interaction between the two spins can be tuned, and this tuning is the main investigation of the paper.

The results in the paper show that there are three main regimes for an applied bias voltage. First, there is a ferromagnetic regime, where the two spins create a spin triplet state. This leads to that the molecular spin-projected density of states become delocalized in the molecular structure. In this regime, there is a finite charge current through the junction. The second regime is the antiferromagnetic regime where the two spins create a spin singlet state. This

leads to that the spin-projected density of states becomes strongly localized on one of the molecules. The strong localization creates a blockade of charge transport through the junction. The third regime occurs when the voltage bias is large enough to diminish the interaction between the spins, leading to four states that are equally probable (1/4), and the electronic structure becomes completely delocalized. In this regime there is a large charge transport.

By tuning the levels of the quantum dots, the interaction and charge transport can be changed. Adjusting both levels, using a gate voltage, the interactions in the molecule can be tuned. The gate voltage introduces an antiferromagnetic region at zero bias voltage, and splits the ferromagnetic peaks in the exchange. As described before, this changes the transport in the molecular structure. Similarly, one can create a rectifier by adjusting the levels with respect to each other, increasing the localization in the molecules. This creates a strictly ferromagnetic (antiferromagnetic) interaction for negative (positive) bias voltage.

8.2 Paper VI: Electronically Mediated Magnetic Anisotropy in Vibrating Magnetic Molecules

Paper VI treats the effect of vibrations on the electronically mediated magnetic anisotropy in a single-molecule magnet. The paper considers a molecular magnet between two leads coupled to a vibrational mode through electron-phonon coupling. The electronically mediated anisotropy is calculated from the molecular electronic structure using the apporach introduced in Chapter 6. Here, the focus lies on calculating the uniaxial anisotropy D. In the set-up, it is the same as the Ising component in the zz-direction, i.e., $D = \mathbb{I}_{zz}$, of the current mediated exchange interaction $\mathbb{J}$ in Chapter 6, as the magnetic properties are all aligned with the global z-direction. In the paper, it is shown that the expression for the uniaxial anisotropy can be divided into a part corresponding to the electronic states near the Fermi surface and a part corresponding to the occupied electron density (Fermi sea). Furthermore, the anisotropy depends on the spin imbalances in the molecular electronic system.

The coupling to the vibrations is treated by doing a separation using the Lang-Firsov transformation. The decoupling separates the Green's function for the full system to a Green's function for the electrons and one for the phonons. This approximation is valid for weak couplings, thus, restricts the applicability of the results to the weak coupling regime.

The results show that the anisotropy can be changed from easy-axis to easy-plane by applying a temperature difference or a voltage bias across the junction. For increasing coupling strength between the molecular vibrations and the electrons, the anisotropy is locked into favoring easy-plane anisotropy. Furthermore, for unequal spin polarization in the leads, the character of the anisotropy is determined by the properties of the weaker ferromagnet. This

dominance can be interchanged with the stronger ferromagnet by applying either a temperature or voltage bias on the system.

9. Summary and outlook

Experimental progress has led to the realization of magnets consisting of single atoms or molecules, which can be controlled by external fields, e.g., electric or magnetic fields. To study the molecular magnets response requires an understanding of their properties under nonequilibrium conditions. In this thesis, we perform a theoretical investigation on external control of transport properties, spin dynamics and exchange interaction of magnetic molecules consisting of a single-spin moment.

The language used for describing the electronic properties is nonequilibrium Green's functions. We show how to derive the Green's functions for a single-molecule magnet in a tunnel junction under the influence of a time-dependent voltage pulse. The molecular magnet is mounted between metallic leads of normal- or ferromagnetic character, and is under the influence of an external magnetic field. The resulting observables are the charge, spin and heat currents of the system.

The spin dynamics of a single-molecule magnet is derived from nonequilibrium field theory. The fields acting on the spin are derived from treating the spin on the Keldysh contour. These exchange fields can be decomposed into effective magnetic field, isotropic Heisenberg interaction, and anisotropic Ising and Dzyaloshinskii-Moriya interactions. The interactions describe the effective fields due to the electronic structure of the molecule on the molecular spin system. The resulting equation of motion for the spin will be of nonadiabatic character and incorporate nonequilibrium conditions.

In Paper I-IV, we study the dynamics of a single-molecule magnet under the influence of an external pulse. In Paper I, the transient response of a sudden on-set of a bias voltage is studied. We investigate how the molecular magnet responds to different nonequilibrium conditions, the effect on the charge and spin currents and the spin dynamics of the molecular spin moment. In Paper II, we compare three different approximation schemes for the spin dynamics of a single-molecule magnet, and study their regimes of validity. They include the generalized spin equation of motion developed in this thesis, and the Landau-Lifshitz-Gilbert equation with time-dependent and stationary parameters. In Paper III, we study the temporal effect of a voltage pulse and find a phase induced switching of the localized molecular spin. We, furthermore, study regimes where this phase induced switching occurs. Then, in Paper IV, we investigate the heat transport of the molecular magnet and connect it to the spin dynamics of the molecular spin moment.

The effect of electrical control in the stationary limit is studied in Paper V-VI. In Paper V, it is studied for a dimer consisting of two single-molecule

magnets coupled through the tunnelling electrons in a tunnel junction. Here, the effective switching dynamics is studied. Paper VI considers the effect of vibrations on the electronically mediated magnetic anisotropy of a single-molecule magnet. It is shown that the anisotropy can be tuned by a temperature difference, or a voltage bias, and that the molecular vibrations can lock the sign of the anisotropy of the molecule.

The theoretical studies and results of this thesis is mainly of interest for molecular magnets. It would be interesting to generalize the study to quantum mechanical spins where the electrons participating in the transport constitutes the molecular spin. Furthermore, future investigations could include the Coloumb blockade and Kondo effect, both of relevance to molecular magnets. A full description of the quantum thermodynamics of single-molecule magnets is also an interesting extension, as quantum thermodynamics is still under investigation for strongly coupled systems and few works have been done in the context molecular magnets.

Even though the main interest has been molecular magnets, parts of the theory is general, and it would be interesting to see if some results apply to neighboring fields. The importance of time-dependent parameters and nonadiabatic effects in the spin equation of motion could be relevant in atomistic spin dynamics and provide insight to the field of quantum dynamics. Lastly, experimental verification, especially of the phase-induced switching proposed in the thesis, would be really exciting.

10. Svensk sammanfattning

Magneter och magnetiska material är något vi känner till i vardagen som objekt av metallisk karaktär, exempelvis järn. Dessa makroskopiska objekt utgörs av en mängd atomer som kollektivt bestämmer deras magnetiska karaktär. Experiment har gjort det möjligt att realisera magneter av enstaka molekyler, objekt på nanometerskala, där enstaka atomer, av exempelvis övergångsmetaller, utgör det magnetiska momentet. Då det endast handlar om ett fåtal atomer och elektroner behöver molekylerna beskrivas med kvantfysikaliska metoder. I denna avhandling studerar vi teorin för molekylära magneter och deras egenskaper under extern elekrisk styrning.

Vi använder oss av icke-jämvikts Greenfunktioner för att studera en molekylär magnet som består av ett enskilt magnetiskt spinnmoment. Greenfunktionerna skapar en fältteoretisk bild över elektronerna i molekylen och deras koppling till det magnetiska spinnmomentet. Vi härleder, utöver detta, en effektiv rörelseekvation för det moleklyära spinnmomentet som tar hänsyn till minneseffekter vid applicering av en spänningspuls. Denna effektiva modell behandlar kopplingen mellan elektronerna som överförs genom molekylen och molekylens magnetiska frihetsgrader. De effektiva fälten som agerar på det molekylära spinnmomentet kan delas upp i ett effektivt magnetfält, ett isotropt Heisenberg bidrag och de anisotropa Ising och Dzyaloshinskii-Moriya bidragen. Med hjälp av denna modell kan vi studera vad som händer när vi applicerar externa elektriska pulser på den magnetiska molekylen.

Vi studerar det transienta svaret hos en magnetiska molekyl med ett enskilt molekylärt spinnmoment vid en steg-liknande spänningspuls. Fokus ligger på hur laddnings-, spinn- och värmeströmmarna beter sig i systemet. Vi analyserar effekten av olika begynnelsevillkor, de interna fälten i den magnetiska molekylen, samt kopplar effekterna till dynamiken hos det molekylära spinnmomentet. Vidare studerar vi olika approximationer i rörelseekvationen för det molekylära spinnmomentet. Vi visar på vikten av att ha tidsberoende parametrar och parametrar som beror av spinnets historik. Utifrån vår studie kan vi få fram olika regimer där de olika approximationerna är giltiga. Hur spinnmomentet i en magnetisk molekyl reagerar på en spänningspuls beror också på längden av den applicerade pulsen. Genom att applicera pulser av olika längd kan vi styra spinnmomentets riktning. Detta beror på fasen hos den applicerade spänningspulsen och vi får ett fasinducerad växlande av det molekylära spinnet.

I avhandlingen studeras också elektrisk kontroll av två magnetiska molekyler i serie. Genom att applicera en spänning går det att styra växelverkan

mellan de två molekylerna. Vi visar på att det finns tre olika regimer för olika spänningar vilka styr spinnkonfigurationen och laddningsströmmarna genom molekylerna. I ett annat arbete studerar vi vad för effekter vibrationer har på den elektroniskt överförda anisotropin i ett system bestående av ett enskilt molekylärt spinnmoment. Vi visar att det går att förändra styrkan på anisotropin med en applicerad elektrisk spänning eller temperaturgradient. Dessutom visar vi att för starkare koppling till vibrationerna går det att låsa anisotropin i ett tillstånd.

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